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16. Summary/Notes

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MESOSPHERIC OZONE FROM MEASUREMENTS OF GROUND BASED SODIUM SOUNDERS

by

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ABSTRACT

Mesospheric sodium has been monitored from the ground by simultaneous observations of the neutral sodium densities and the sodium glow intensity. The first parameter is measured by laser radar and the second by a tilting filter photometer. Based on the Na photochemistry the ratio intensity/abundance is proportional to the ozone density close to the height of peak sodium emission (89 km). Using a two year set of sodium data, taken at São José dos Campos (23^{o}S, 46^{o}W) a number of features of the ozone density variations are determined. The average nocturnal behavior is one of constant ozone density, and a strong peak in ozone concentration is observed in autumn. The results also imply that the reaction rate for $Na + O_3 \rightarrow NaO + O_2$ must be larger than the usually quoted value of 6.5×10^{-12} cm^3 s^{-1}.

1. INTRODUCTION

Although the density of atmospheric sodium is many orders of magnitudes less than the densities of the major atmospheric constituents, it is possible to measure sodium concentrations, making use of its large resonance backscattering cross-section. Using this resonance scattering technique, the atmospheric sodium layer, situated between about 75-105 km, has been monitored by the laser radar technique (Sandford and Gibson, 1970; Kirchhoff and Clemesha, 1973) revealing several features of its morphology (Simonich et al., 1979).

Sodium densities have been measured at São José dos Campos (23^{O}S, 46^{O}W) since 1972, using the above technique. In mid 1976, a tilting filter photometer was installed at the same location, for the measurement of the sodium nightglow, primarily for the simultaneous measurements of the neutral and excited sodium atom population (Clemesha et al., 1978). More detailed descriptions on equipment and calibration can be found in Simonich et al., (1979) and Kirchhoff et al., (1979).

Based on the generally accepted photochemistry of the atmospheric sodium layer, it will be shown in the next section, that the ratio between the sodium nightglow intensity and the neutral sodium atom abundance (i.e., the height integral of density) is proportional in a first approximation to the ozone density at about 89 km. The objective of this paper is to explore this relationship and to deduce nocturnal and seasonal variations of the ozone.

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.

Usually the data are taken at intervals of about 10 minutes. For the present analysis, a sequence of nights was chosen from June 1976 to April 1978. Among these, 77 nights had data over a period of more than five hours each. The photometer was usually operated on every clear moonless night, over the entire period, but the laser radar data are not always available for the whole night, since it requires on site operator assistance. The nightly averages of different nights may therefore, not correspond to exactly the same averaging period. The measurements are believed to be correct to an accuracy of about 15%.

2. SODIUM PHOTOCHEMISTRY

The basic reactions for the sodium photochemistry are believed to be

$$Na + O_3 \rightarrow NaO + O_2, \quad k_1 = 6.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$$

and

$$NaO + O \rightarrow Na^* + O_2, \quad k_2 = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

where the reaction rates k_1 and k_2 are from Hunten (1967). These rates have not been measured in the laboratory, and actually may be incorrect (Kolb and Elgin, 1976; Clemesha et at., 1978; Kirchhoff et al., 1979). Several authors have claimed that the transition from free sodium to sodium oxide explains the position of the peak of the sodium layer, but invariably some of their assumptions have been grossly in error and, therefore, the reactions themselves may be incorrect or incomplete.

Keeping the above restrictions in mind, the present study will make use of the above basic photochemistry in interpreting the ratio between the sodium nightglow and sodium abundance, which will simply be called Ratio

$$\text{Ratio} = \frac{\text{sodium nightglow intensity}}{\text{sodium abundance}}$$

where the numerator and the denominator are both measured quantities. Using the previously defined reactions and assuming photochemical equilibrium, and using brackets to indicate densities,

$$\int [Na][O_3] k_1 \, dz = \int (Na^*) dz$$

where (Na*) indicates the production of excited sodium atoms.

The integration will be transformed into a summation in steps of 2 km, corresponding to the height resolution of the laser radar data. It is centered at the peak of the sodium emission, at about 89 km (Clemesha et al. 1978) extending 5 km to each side. Since the temperature dependence of k_2 is unknown, the reaction rate will be assumed constant. By introducing

$$[\bar{O}_3] = \frac{\Sigma [Na][O_3]}{\Sigma [Na]}$$

the integral may be written

$$[\bar{O}_3] k_1 \, \Sigma [Na] = \Sigma (Na^*)$$

where $\Sigma[Na]$ and $\Sigma(Na^*)$ are respectively the sodium abundance (AB, measured by the laser radar), and the sodium emission intensity neglecting quenching ($I(D_1 + D_2)$, measured by the photometer). Thus

$$[\bar{O}_3] k_1 \, AB = I(D_1 + D_2) = 1.5 \, I(D_2)$$

and

$$\text{Ratio} = [\bar{O}_3] \cdot k_1 \cdot 10^3$$

In Figure 1 are shown several density models. The curves labeled 1 show the envelopes of measured or calculated ozone densities reported by different authors. Curves A, B and C are model ozone density profiles and curve 2 is in average sodium density profile measured at our location. The sodium emission layer, taken as a slab of 10 km thickness is also shown, centered at 89 km.

The average ozone density $\bar{O}_3$, defined previously, is the density of an equivalent ozone slab layer. In practice, the value of $\bar{O}_3$ corresponds closely to the density of the middle of the ozone density profile over the layer. Thus, the difference between $\Sigma[Na][\bar{O}_3]$ and

$[\overline{O}_3]\ \Sigma[Na]$, for models B and C in Figure 1, corresponds to less than 13%. Thus one may reasonably refer to $\overline{O}_3$ as the average ozone density at 89 km.

3. RESULTS

The nocturnal variation is shown in Figure 2, where the average hourly values of Ratio are plotted with the corresponding standard deviations from the mean. All points have been normalized to the overall nocturnal average. Variations from one hour to the next are less than 10% in this average of all data.

The seasonal variation is shown in Figure 3, where the monthly averages are shown as well as the respective standard deviations.

4. DISCUSSION

It has been shown that, if the basic sodium photochemistry assumed is correct, the parameter Ratio is proportional to the ozone density at 89 km. The parameter Ratio in Figure 2, is almost constant throughout the night, which is in agreement with model calculations (e.g. Shimazaki and Laird, 1972).

A rather strong seasonal variation of Ratio, shown in Figure 3, is also expected for O_3 from model calculations, but Shimazaki and Laird (1972) show maximum densities in summer. At our latitude, however, there are reasons to believe that the ozone should go through a maximum in autumn and perhaps a secondary maximum in spring, as will be shown next.

Measurements of the atomic oxygen 5577 Å line and the OH(8,3) band intensities at our latitude by Takahashi et al., (1977) show autumn and late spring peaks for the seasonal variation of the atomic oxygen measurements, with a ratio of 3 between the autumn maximum and the winter minimum. The OH intensity data only show a small increase in autumn, the ratio as above being only of the order of 1.4. Together these results imply, based on the ozone photochemistry, a maximum ozone density occurring also in autumn. It can be concluded therefore, that the photochemical cycle for sodium discussed earlier is consistent, and that the parameter Ratio actually represents a variation of ozone.

The parameter Ratio varies between approximately 10 and 50. If we use the quoted value for k_1, then the calculated ozone is between 1.5×10^9 and 7.5×10^9 cm^{-3} at 89 km. The average value of the ozone density at the height of interest, given in the literature, is about 10^8 cm^{-3} (see Figure 1). It seems unlikely that this value, despite the uncertainties, is in error by a factor as large as 15 to 35. It appears more reasonable to use a larger value for k_1 as proposed by Kolb and Elgin (1976). With k_1 larger by a factor of 50, which would reproduce calculated sodium glow intensities in agrement with measured values (Kirchhoff et al., 1979), the calculated ozone density from Ratio would be within 3×10^7 and 1.5×10^8 cm^{-3}, which obviously are much closer to the average value of 10^8 cm^{-3}.

5. <u>CONCLUSIONS</u>

In view of the lack of experimental data on mesospheric ozone, even approximate values integrated over a 10 km height range, are of considerable interest. The method described in this paper offers a ground-based technique for making such measurements.

The absolute value of an average ozone density, for the height of 89 km, depends on the value of the reaction rate k_1. The relative variations of ozone do not. The interpretation of Ratio being proportional to ozone, depends on the correctness of the photochemical cycle of the atmospheric sodium, given previously. There is no evidence against the cycle itself, but it appears that the reaction rate k_1 must be considerably larger than 6.5×10^{-12} cm^3 s^{-1}. As mentioned already, this has been proposed also by Kolb and Elgin (1976), based on the kinetics of the sodium reactions.

The average ozone density of a layer of thickness 10 km, centered at 89 km, weighted by the sodium density, is then proportional to the parameter Ratio and its variation during the night and over the seasons has been deduced. For the average of the data analysed, the ozone density at about 89 km is practically constant during the night. A strong seasonal variation is seen, with a strong maximum during fall and a secondary, weaker peak during spring.

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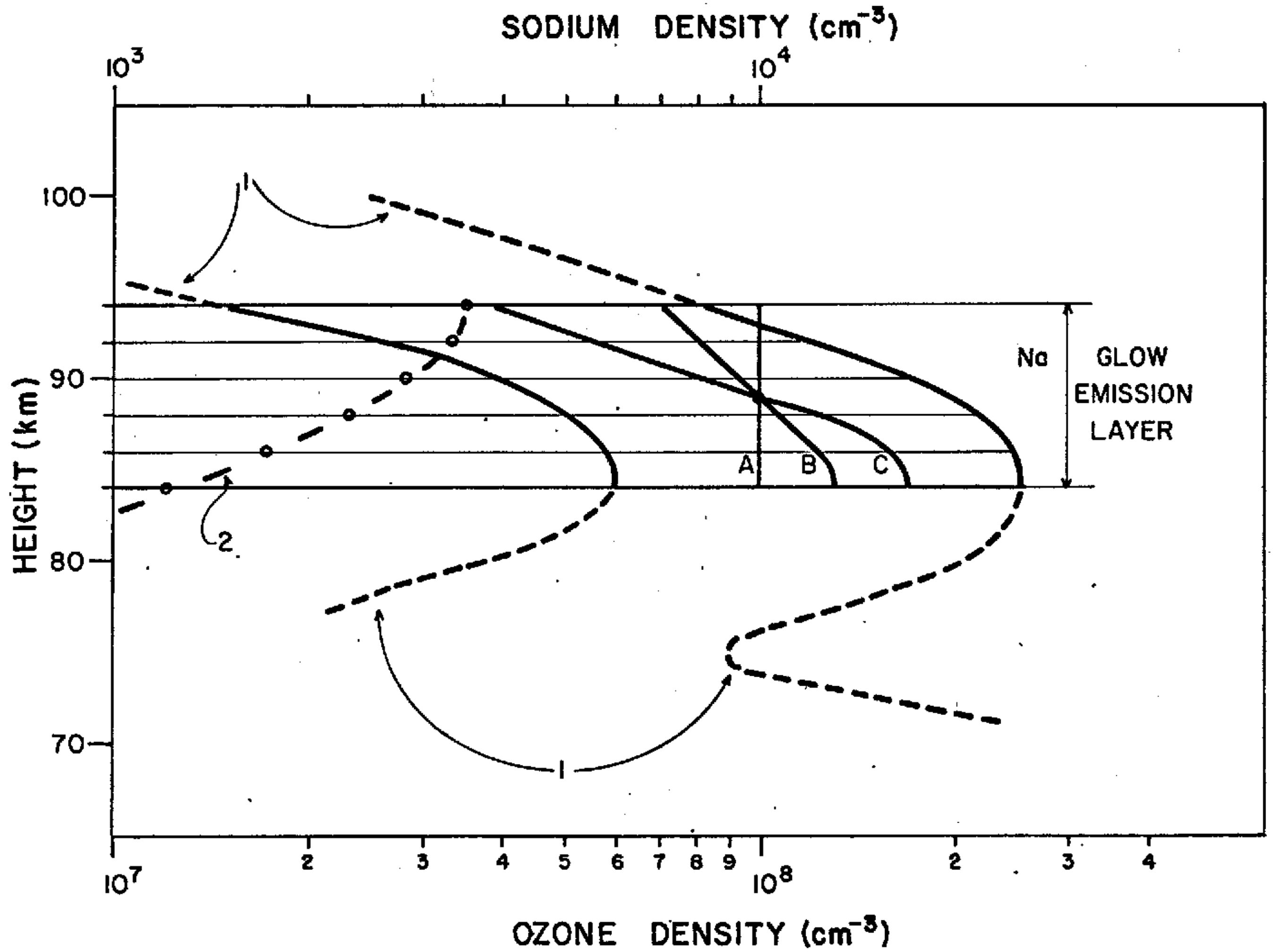
FIGURE CAPTIONS

Figure 1 - Ozone and sodium density profiles. 1- Envelopes of ozone density values quoted in the literature; A,B and C, model ozone density profiles; 2- Sodium average density variation with height from measurements.

Figure 2 - Nocturnal variation of Ratio, shown by hourly average values normalized to the nocturnal average. Bars are the standard deviations from the mean.

Figure 3 - Seasonal variation of Ratio shown by monthly averages. Vertical bars are the standard deviations from the mean.



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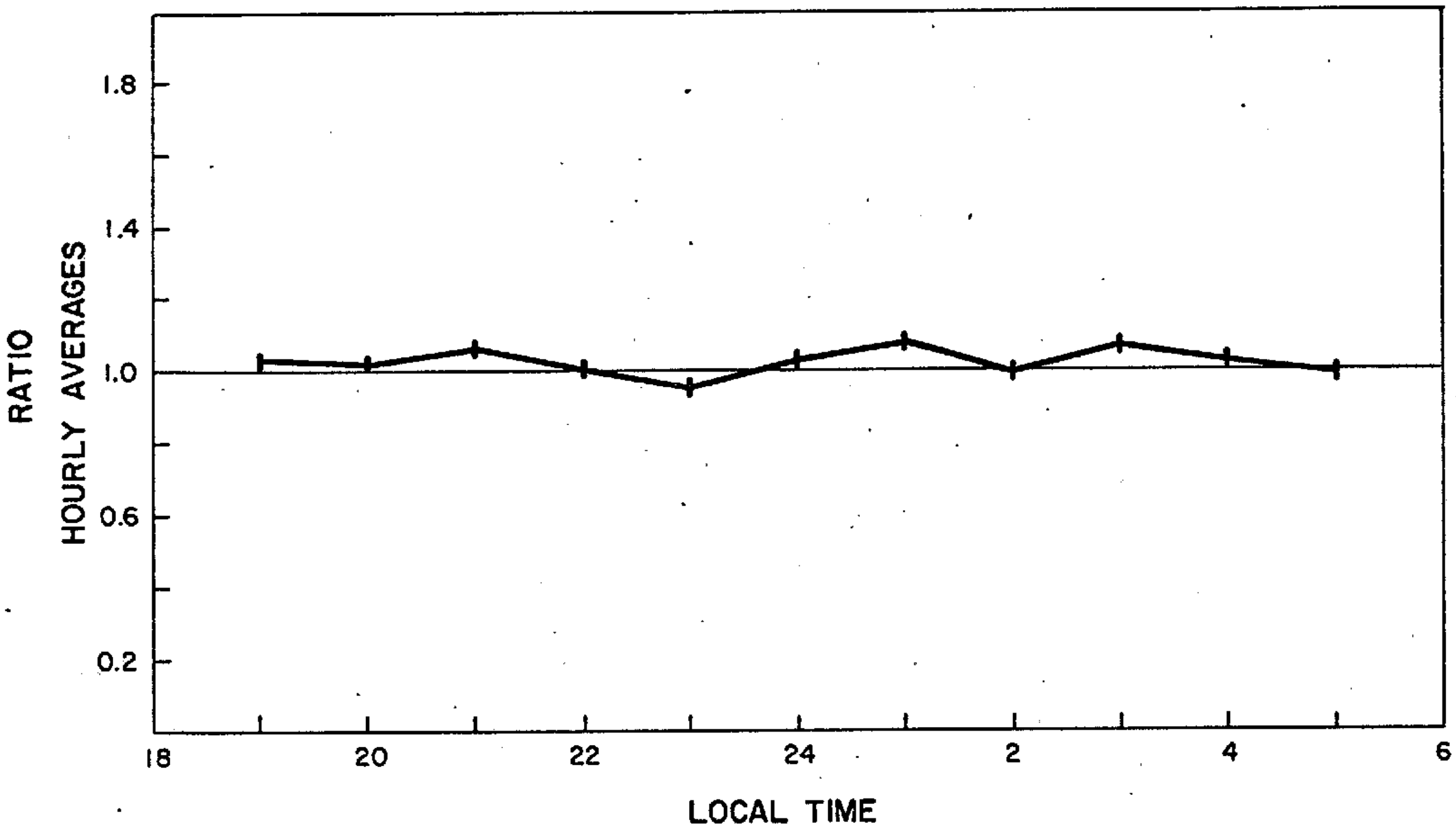
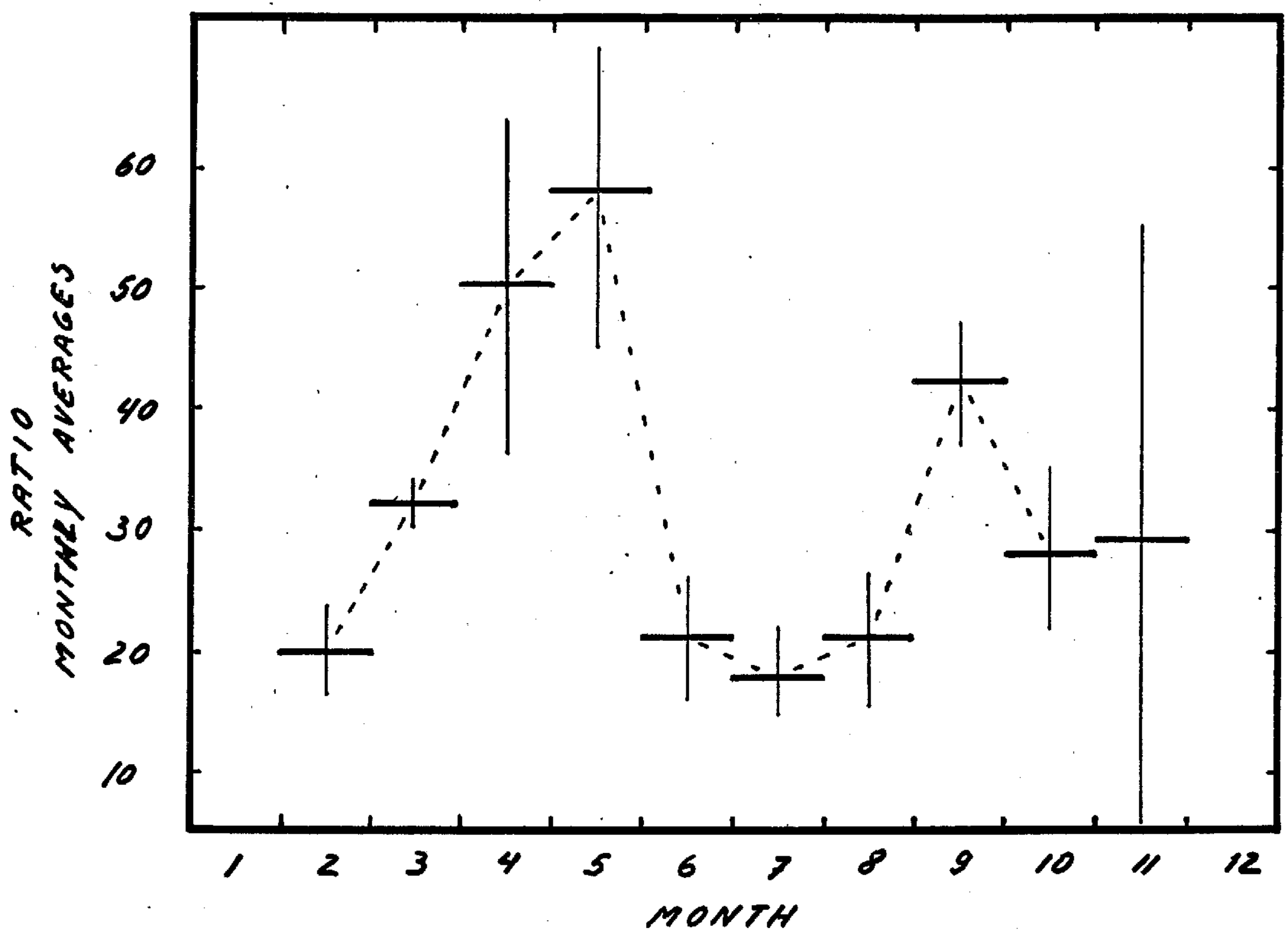


Fig. 2.- Nocturnal variation of Ratio, shown by hourly average values normalized to the nocturnal average. Bars are the standard deviations from the mean.



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