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16.Summary/Notes

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ABSTRACT

Sodium nightglow measurements made at São José dos Campos (23.2°S), with a tilting filter photometer, over a period of two years show that on the average the intensities reach a minimum close to local midnight. Between midnight and dawn the intensity remains fairly constant or increases slightly. The most consistent feature is the pre-midnight decrease in intensity. Seasonal variations show peak intensities at the equinoxes, with the stronger one occurring in autumn. In a few cases, the nocturnal variation does not follow the average trend, showing rather strong peaks in intensity which have been related to dynamic effects. Based on the photochemistry described, the sodium oxide is estimated to vary with season in a similar fashion to mesospheric ozone. The generally accepted rate coefficients for the sodium photochemistry cannot explain the measured intensities. In order to produce results that are consistent with the measurements, model calculations require a coefficient larger by a factor of about 10 for the reaction $Na + O_3 \rightarrow NaO + O_2$, *and for* $NaO + O \rightarrow Na^* + O_2$ *a rate smaller by a factor of* 10^3.

1. INTRODUCTION

Measurements of the sodium nightglow have been made routinely at São Josẽ dos Campos, São Paulo, Brazil, (23.2^{o}S, 45,9^{o}W) since early 1976. The photometer is operated close to a laser radar station which measures the neutral sodium densities (Kirchhoff and Clemesha, 1973), primarily to study the simultaneous variations of the sodium atoms in the neutral and excited states (Clemesha et al., 1978). Obviously, this puts our station in a privileged situation to study the photochemistry of sodium. Since several interesting claracteristics distinguish our nightglow data from measurements at other stations, this, and the general lack of measurements in the southern hemisphere, seem to justify the presentation of only the nightglow data in some detail. This paper, therefore, describes only the sodium intensity data, but, using also accumulated information on the neutral sodium densities, a case is built to show that the generally accepted sodium photochemistry is inadequate.

Sodium nightglow intensities have been measured using a tilting filter photometer. A 10 Å bandwidth interference filter was used for all observations before 1977, thus including both sodium D_1 and D_2 line intensities in the measurements. After that, a 3 Å bandwidth interference filter has been used in conjunction with a curved slit aperture in the photometer optics, allowing the separation of the D lines, and much better signal-to-noise ratios. The photometer is calibrated by comparison with a radioactive krypton-excited phosphor light source.

The Q branch contamination of the OH (8,2) band emission is corrected by also measuring the intensity of the R branch at about 5868 Å. For the OH rotational temperature range of 160-200^{o}K, measured at our location by Takahashi et al. (1974), the R/Q ratio varies in the range 0.86 - 1.05. Allowing for the filter transmission this gives an effective range of 0.7 - 0.9, for the 10 Å bandwidth filter, and 0.8 - 1.0 for the 3 Å filter. Since the amplitude of the R branch is typically of the order of 10% of the sodium emission, the error introduced by assuming equal R and Q intensities is less than 3%. In practice, therefore, the R branch intensity is taken as the baseline for the D line measurements.

2. NOCTURNAL VARIATIONS

Nocturnal variations of the sodium nightglow intensity are shown in Figure 1. The great majority of our measurements show variations during the night with the general shape of curve 2 in Figure 1 (data of July 29, 1976). Variations with the shape of curve 1 of Figure 1 (data of October 10, 1977) are less frequent. A consistent feature of all the data is the pre-midnight decrease in intensity, with the minimum occurring around midnight. Between midnight and dawn the intensity either increases or remains fairly constant. Decreasing intensities during this period are very rare.

The average nocturnal variation is shown in curve 3 of Figure 1, for winter (June, July, August) 1976-77. For the computation of this curve, hourly values were interpolated for each night of observation and hourly averages were then calculated for a given period. The error bars shown are the standard deviations from the mean.

Average nocturnal variations for other periods have the same trend as above, as shown in Figure 2. Curves 1, 2 and 3 represent respectively the average nocturnal variations for winter, summer and equinox.

3. SEASONAL VARIATIONS

Seasonal variations are shown in Figure 3, which displays the nocturnal averages for the measurements during 1976 and 1977. Both D lines were measured during 1976 and therefore the intensities shown for this period are higher than those during 1977, when only the D_2 line was monitored.

Strong maxima at the equinoxes are observed, with peaks that are about a factor of 3 larger than the minima during summer and winter. Larger night-to-night variations appear to be present in the 1976 data, which also show a larger number of nights classified as disturbed (section 4).

The seasonal variation observed at our location (23.2^{o}S) is similar to the variations observed at other low latitude stations. Figure 4 compares our measurements (curve 1) with those at Davao (7.1^{O}N), and Haleakala (20.7^{O}N) shown in curves 2 and 3 of Figure 4, respectively. A phase shift of 6 months must be kept in mind when comparing north and sourthern measurements.

The peak that occurs during the autumnal equinox seems to be more pronounced than the spring one. This is consistent with previously published southern hemisphere results (Ciner and Smith, 1973) although those data were not properly corrected for the OH contamination. This is also true for northern hemisphere results. At higher latitudes, however, it appears that the spring maximum vanishes altogether (Smith and Steiger, 1968; Fukuyama, 1976).

4. DISTURBED DATA

On a few nights rather strong deviations from the average monthly nocturnal variation have been observed. While the average behavior is one of either a decreasing or fairly constant intensity, these days show strong peaks in intensity.

Three of the strongest perturbations of this kind, observed during the winter of 1976, are shown in Figure 5, where the winter average is also shown for comparison (curve 1).

Curve 2 of Figure 5 shows the nocturnal variation of the sodium nightglow measured on August 23, 1976, normalized to the night's average of 177.0 Rayleighs. In curve 3 the variation of June 27, 1976 is shown, normalized to 113 R, and curve 4 shows the variation of July 25, 1976, normalized to 82.7 R, where the dashed portion indicates a data gap.

5. CALCULATIONS

Several reactions have been proposed to explain the photochemical cycle of atmospheric sodium. The corresponding rate coefficients are based on the rates of the analogous hydrogen reactions and are, thus, rather uncertain. Using recent models for the various atmospheric constituents involved, it appears, however, that the following reactions are dominant

$$Na + O_3 \longrightarrow NaO + O_2 \qquad (1)$$

$$K_3 = 6.5 \times 10^{-12}\ cm^3\ s^{-1}$$

$$NaO + O \longrightarrow Na^* + O_2 \qquad (2)$$

$$K_1 = 4 \times 10^{-11}\ cm^3\ s^{-1}$$

The rate coefficients shown, were estimated by Hunten (1967), applying collision frequency corrections to the rates of the analogous hydrogen reactions. Ever since, these reaction rates have been used in the literature, with the belief that they are roughly correct.

As it stands, however, the above scheme is inconsistent with the experimental evidence. At any height, neglecting transport, neutral sodium is converted to sodium oxide, and vice-versa. Thus, the total sodium, neutral plus oxide, must be constant at a given height. It turns out, however, that with the above rates, the sodium oxide densities at the height of the sodium layer, are at least an order of magnitude less than the sodium densities, which implies that photochemistry must have a negligible effect on the latter.

Furthermore, it has been shown (Clemesha et al., 1978) that although the above reactions provide the correct width and height for the nightglow, its intensity is about a factor of 50 too small compared with measurements.

If it is assumed, then, that the reactions are correct, the rates must be adjusted. To increase the calculated glow intensity, K_3 must be increased by a factor of about 10. If it is also assumed that the total sodium is well mixed with the rest of the atmosphere, K_1 must be decreased by a factor of 10^3, to get the peak sodium densities at the correct height.

The adjusted reaction rates are therefore

$$K_3 = 5.16 \times 10^{-9} \exp\left(\frac{-875}{T}\right) \text{cm}^3 \text{ s}^{-1} \tag{3}$$

$$K_1 = 3 \times 10^{-10} \exp\left(\frac{-1790}{T}\right) \text{cm}^3 \text{ s}^{-1} \tag{4}$$

where the temperature dependences (Megie, 1976) are based on the activation energies of reactions (1) and (2).

The nocturnal time evolution of initial density profiles has been calculated by integrating the continuity equation, using the method described by Richtmeyer (1957), and more recently used by Shimazaki and Laird (1972). The basic reactions for the atmospheric model, as well as their reaction rates , are the same as those used by Megie (1976) who studied the diurnal variations of neutral sodium densities using the above method. Megie did not, however, calculate the sodium nightglow intensities, and, thus, apparently, did not notice the inconsistency mentioned above. Initial density profiles were taken from Shimazaki and Laird (1972), as well as their temperature and diffusion coefficients. Sodium density profiles are from Simonich et al. (1978).

The calculated nocturnal variation of the sodium intensities is shown in curve 4 of Figure 1. Input data are for winter conditions. It can be seen that the variation is consistent with the measurements, during the first half of the night only.

On the basis of the photochemistry described, it is possible to estimate the seasonal variations of the sodium oxide and ozone. The seasonal nightglow variation at our location is that of Figure 3, the neutral sodium densities are maximum in winter and twice as large as those in summer (Simonich et al., 1978), whereas the 05577 line peaks during equinox, at about twice the value during summer (Takahashi et al., 1977).

Both the concentrations of the various constituents and the rate coefficients may vary with season, the variation of the latter being due to seasonal temperature variations. Using square brackets to denote density, and using n to indicate the ratio between the value of a given variable at any season and its value in summer, we get from reactions (1) and (2)

$$n(Na^*) = n\,[NaO] \cdot n\,[O] \cdot nK_1 \tag{5}$$

or

$$n(Na^*) = n\,[Na] \cdot n\,[O_3] \cdot nK_3 \tag{6}$$

where (Na*) is the production rate of excited sodium atmos per cm^3 per second.

Based on (5) and (6) above, we can thus estimate the density variations from season to season, as shown in Table 1. For example, the NaO densities decrease to half the summer densities in the autumnal equinox.

6. DISCUSSION AND CONCLUSIONS

Comparisons of data from different locations show significant differences in the nocturnal intensity variations. Saxena (1970) reports variations by factors of 1 - 3 for northern latitudes of 29.5°, 32.7° and 49.9°, while our monthly averages show variations from the nocturnal average of some 10 per cent. There is also no consistent minimum in intensity close to midnight in the variations reported by Saxena. The most consistent feature at 19.5°N seems to be a post-midnight increase in intensity, while at 32.7°N there is a steady increase throughout the night during January, February and March.

Decreasing intensity variations during the early part of the night are also observed at 33°S (Wiens and Weill, 1973), with the exception of the August - September - October average, which shows an almost steady increase through the night. However, the minimum intensity is reached earlier, at about 22 hs. At 15°N, the same authors report decreasing intensities during winter and spring, while a minimum is observed at about 22 hs during autumn and summer.

Some features of the nocturnal variation, as for example the after midnight increase in intensity cannot be explained by photochemistry (Curve 4 in Figure 1). It has been shown by Takahashi et al. (1977), for the nocturnal variation of the OH (8,3) band, that this increase could be due to the semi-diurnal solar tide. (See also Petitdidier and Teitelbaum, 1977). A downward wave propagation on measured sodium densities, has in fact been observed at our latitude (Clemesha et al., 1978) and it is thus very likely that the nocturnal variation is strongly influenced by tidal density and temperature variations.

The seasonal variation is similar to that at other latitudes. As previously reported (Wiens and Weill, 1973; Civer and

Smith, 1973) there is a six month time lag between north and southern hemisphere variations, with the spring equinox peak almost vanishing at high latitudes.

Using the measured seasonal variations of some of the chemical constituents involved in the sodium photochemistry, it appears that the sodium oxide is decreased in winter to about 15% of its summer densities (Table 1). The corresponding seasonal variation of ozone, calculated in the same manner, involves a decrease by a factor of 5 from summer to winter, which is consistent with the results of Shimazaki and Laird (1972).

More work is needed for the interpretation of the disturbed data of section 4. It is interesting to note, however, that on those occasions, as well as during the normal period, the sodium intensity variations correlate extremely well with the variations of sodium density measured by laser radar, and also with the OH (8,3) band intensities. On one of the disturbed nights, the data of July 25, 1976, the downward propagation of a wave can be easily identified in the neutral sodium simultaneous density measurements (Clemesha, et al., 1978). The peak of this wave arrives at 88 km, the calculated height of the peak sodium emission, at the time when the sodium intensities suddenly increase, close to 2:30 hs, at about which time there is also a sudden increase in the OH intensity, showing again the strong influence of dynamic effects.

Forty years of research in atmospheric sodium have not yet solved the problems of the basic photochemistry. It is now obvious, however, with the assumptions of the previous section, that the reaction rates in (1) and (2), which have been used in the literature for the past decade, are incorrect. They do not provide an adequate Na/NaO ratio, and the calculated nightglow is too low. Whether reactions (1) and (2) are dominant in the photochemical cycle, and whether the required values for the rate coefficients, suggested in (3) and (4) are correct, remains to be seen. The adopted value for K_3 is larger than the reaction rate for the analogous hydrogen reaction, which might be difficult to justify in terms of Kinetic Chemistry. These coefficients do, however, provide results in the calculations that are more consistent with the measurements, than those in (1) and (2).

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TABLE CAPTION

Table 1. Calculated seasonal variations, referred to summer. a - From measurements; b - Calculated from equation (5) or (6); c - Estimated.

FIGURE CAPTIONS

Figure 1. Nocturnal variations of the sodium nightglow. 1 - Measurements of October 10, 1977, normalized to the nocturnal average at 65.0 Rayleighs. 2 - Measurements of July 29, 1976, normalized to the nocturnal average of 110.9 Rayleighs. 3 - Average winter (June, July, August) 1976-77 variation. 4 - Calculated nocturnal intensity variation for winter conditions.

Figure 2. Average nocturnal variations for the different seasons. 1 - Winter; 2 - summer; 3 - equinox ; data for 1976 - 77.

Figure 3. Seasonal variations of the nocturnal average sodium nightglow intensities. Both D lines were measured in 1976, but only D_2 during 1977.

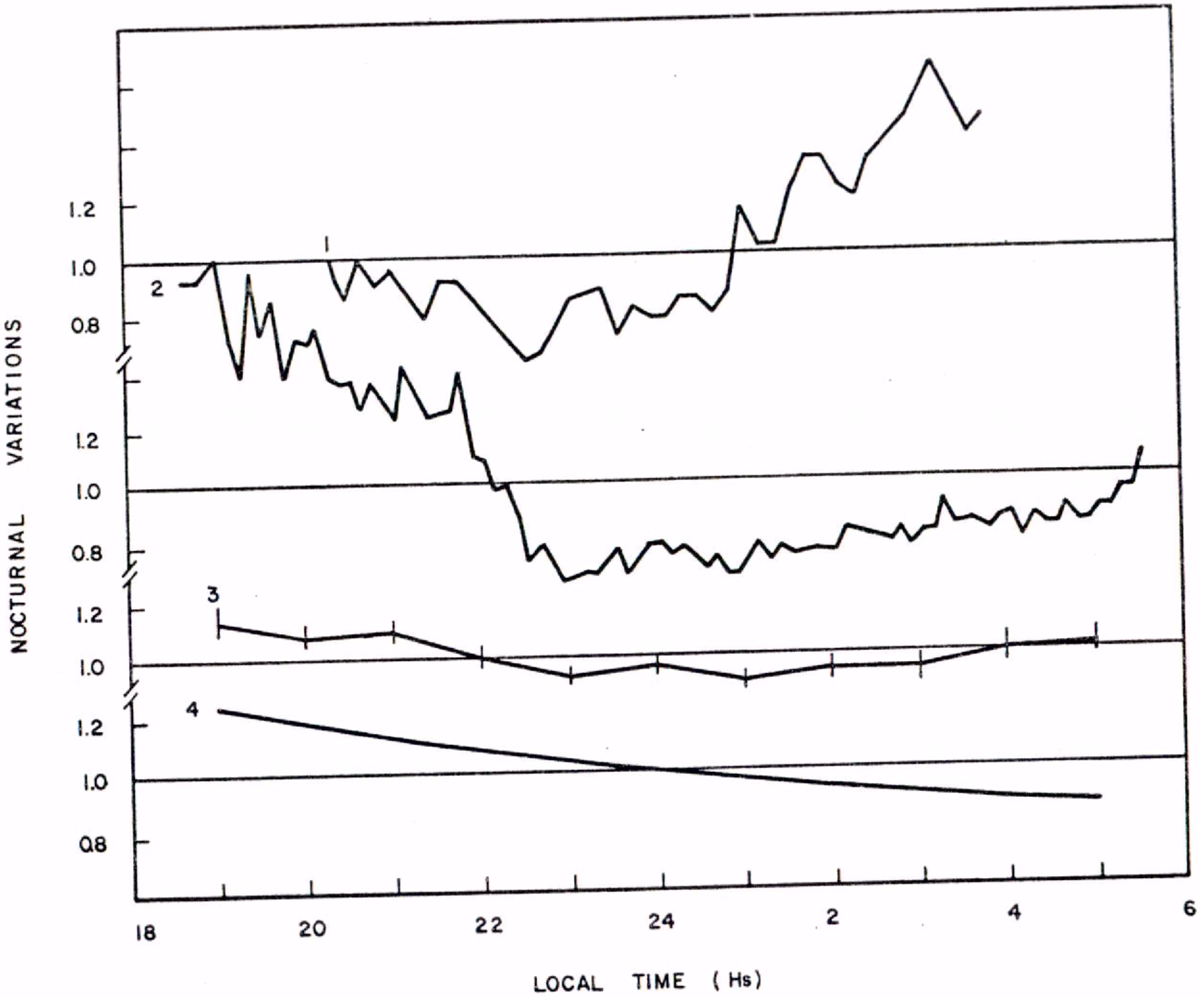
Figure 4. Comparison of seasonal variations at low latitudes. 1 - Results from previous figure, latitude 23.2°S; 2 - Results for Davao, latitude 7.1°N; 3 - Results for Haleakala, 20.7°N (Curves 2 and 3 from Fukuyama, 1977).

Figure 5. Disturbed data. 1 - Winter 1976-77 average from figure 1, shown for comparison. 2 - Nocturnal variation of August 23, 1976, normalized to the nocturnal average of 177.0 Rayleighs. 3 - Nocturnal variation of June 27, 1976, normalized to 113.0 Rayleighs. 4 - Nocturnal variations of July 25, 1976, normalized to the nocturnal average of 82.7 Rayleighs.

TABLE 1

CALCULATED SEASONAL VARIATIONS, REFERRED TO SUMMER. a - FROM MEASUREMENTS; b - CALCULATED FROM EQUATION (5) OR (6); c - ESTIMATED

	SUMMER	EQUINOX	WINTER	EQUINOX
a	Na*	2 (Na*)	Na*	2 (Na*)
a	Na	1.5 Na	2 Na	1.5 Na
a	O	1.26 O	O	1.26 O
b	O_3	0.89 O_3	0.22 O_3	0.89 O_3
c	K_1	3.3 K_1	6.6 K_1	3.3 K_1
c	K_3	1.5 K_3	2.3 K_3	1.5 K_3
b	NaO	0.5 NaO	0.15 NaO	0.5 NaO
c	T	1.13 T	1.25 T	1.13 T



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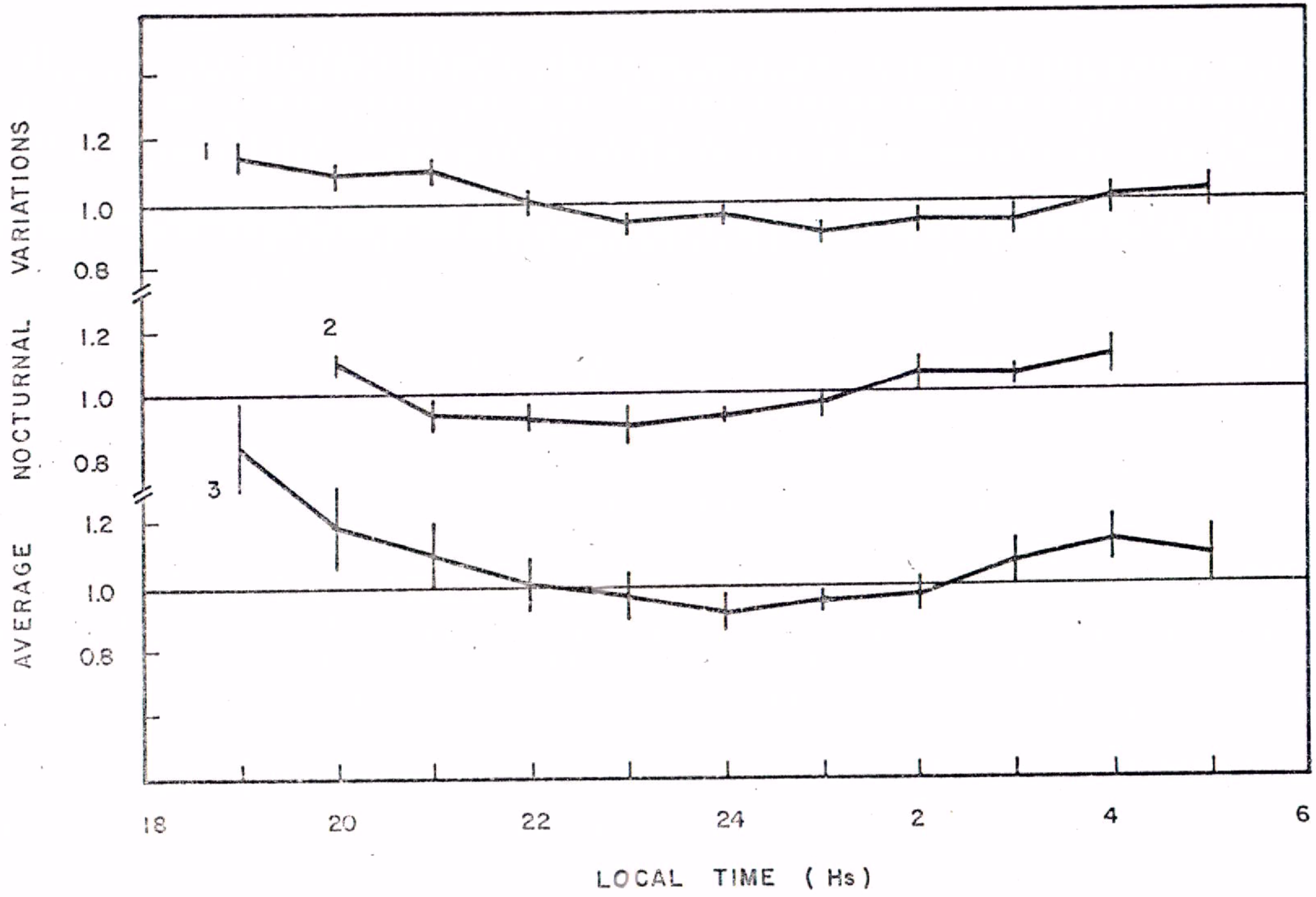

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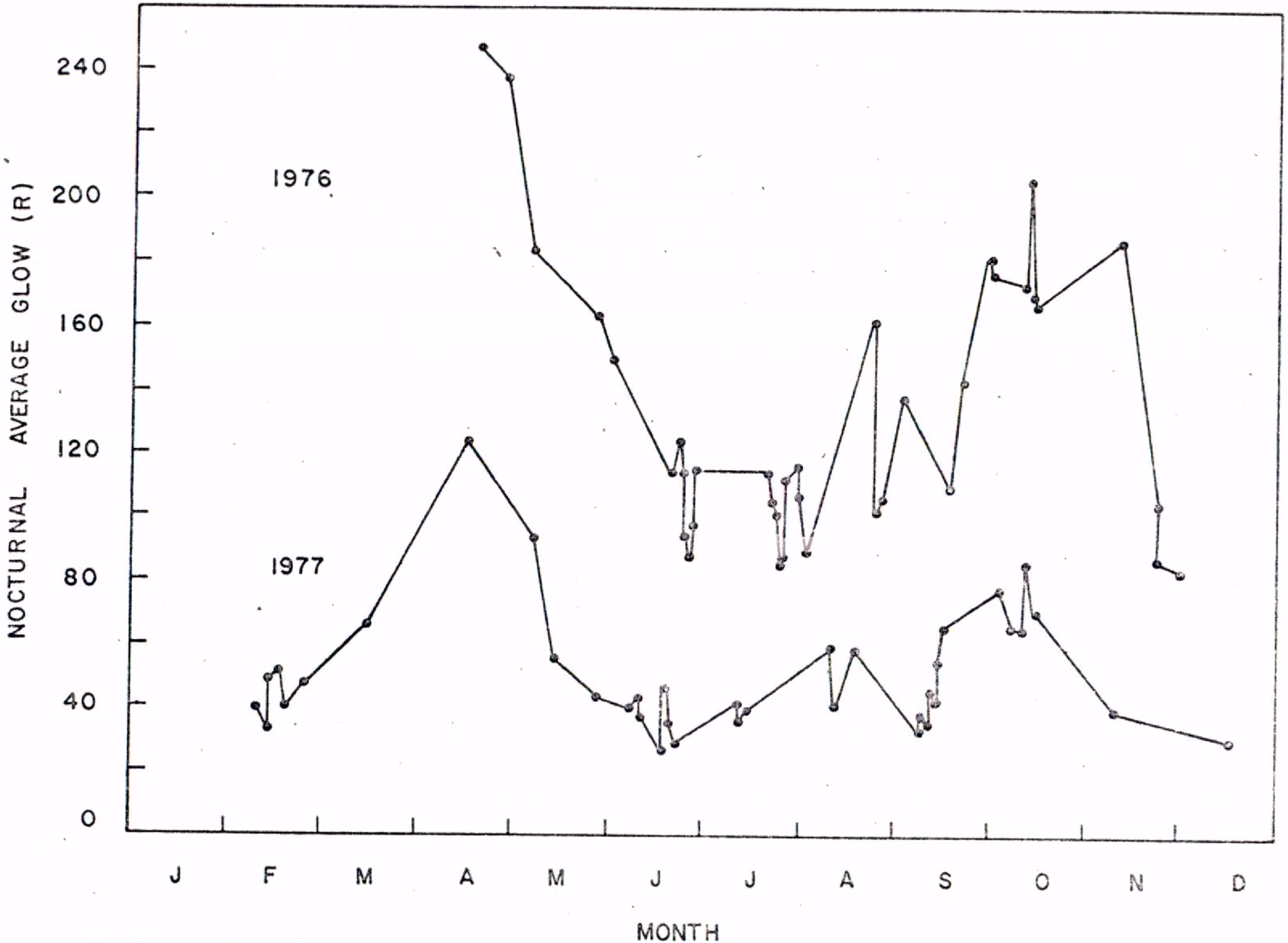

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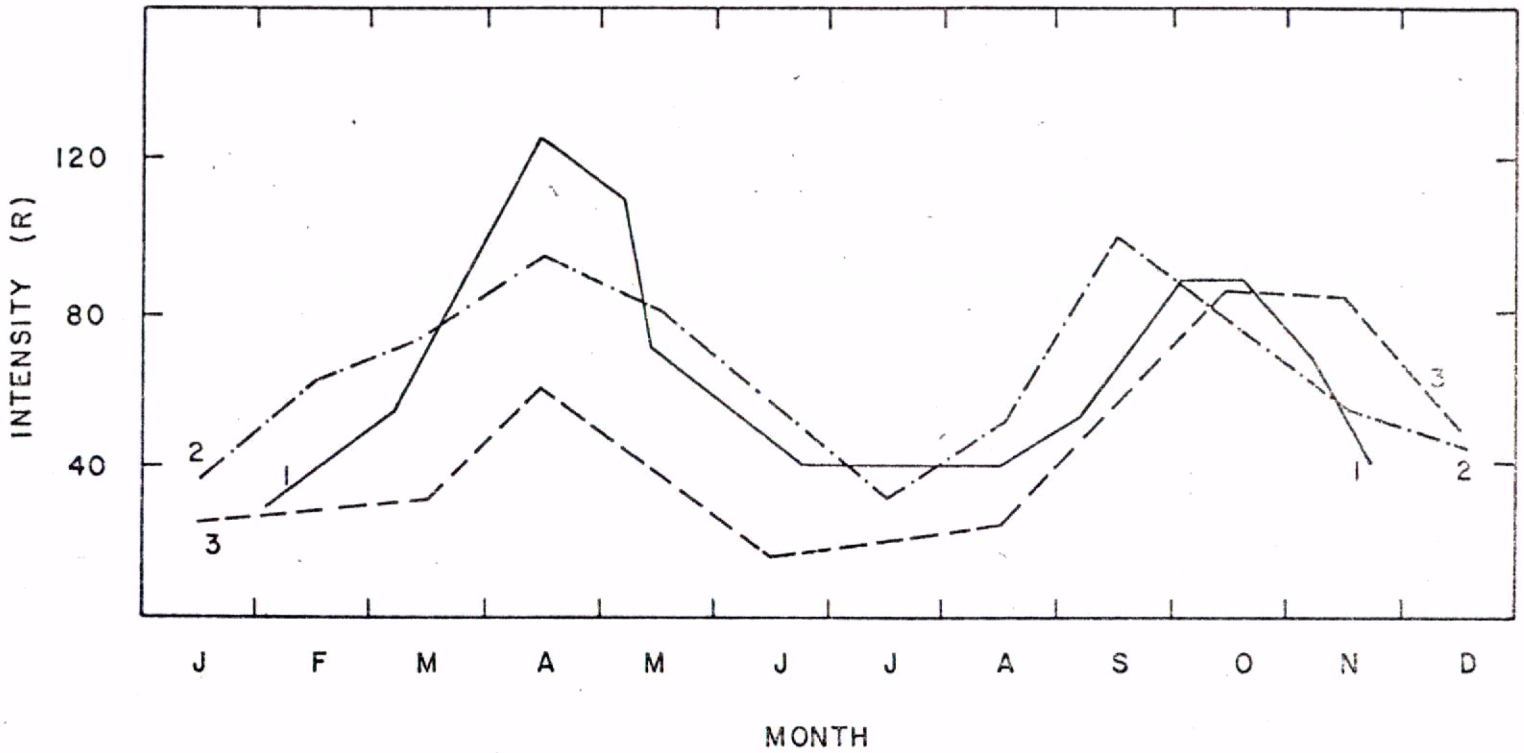

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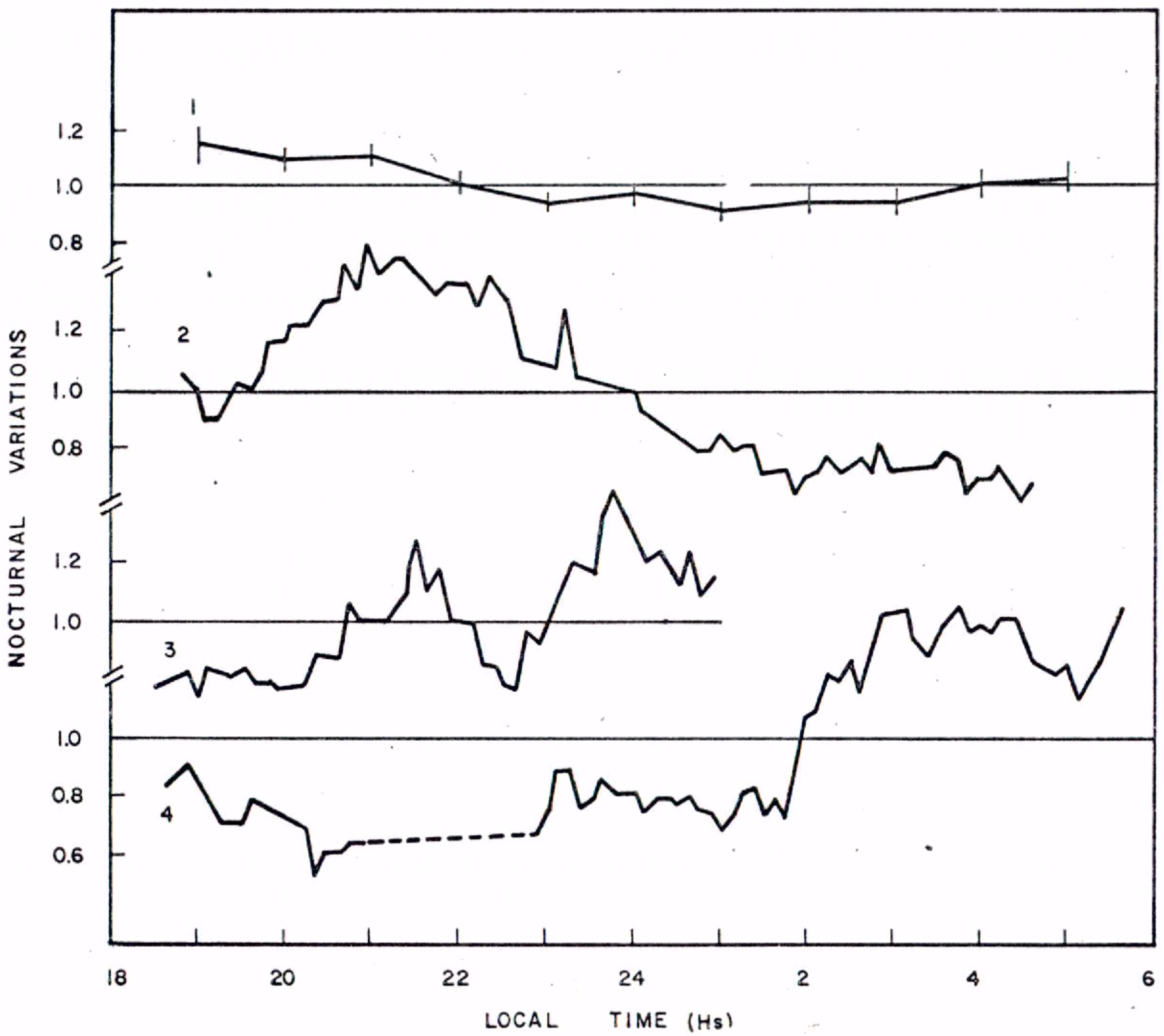

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