A Worldwide Anomaly in the Concentration of Ozone above 40 km

S. RANGARAJAN

Institute of Tropical Meteorology, Poona, India

10 September 1968 and 11 February 1969

1. Introduction

The concentrations of ozone in the earth's atmosphere at altitudes higher than about 30 km are believed to be governed mainly by conditions of photochemical equilibrium. Observational evidence for such an assumption is available from the patterns of seasonal changes of ozone at heights of about 30–35 km as deduced from Umkehr data or from direct ozone soundings. Thus, by evaluating the Umkehr data of Arossa, Switzerland, Dütsch (1960) found that there is an annual wave at these heights with a maximum value in spring/summer and a minimum in winter. A similar analysis by Dütsch (1964) using extensive data confirmed this. Direct measurements by the Brewer type of chemical ozonesondes flown at Boulder, Colo., have yielded nearly the same type of annual variation of ozone in the upper stratosphere up to the highest level reached by the balloons, i.e., 30 km (Dütsch, 1966). Using optical ozonesondes Paetzold (1959) had also found earlier that the total ozone above 30 km at Weissenau, Germany, attained a maximum in summer and a minimum in winter. All investigations on the annual variations made so far appear to be confined to altitudes $\lesssim 35$ km.

2. Seasonal patterns of ozone variation above 40 km

To study the situation at still higher levels in the stratosphere, Umkehr data must be used since even under best conditions ozonesondes seldom reach heights above 30–35 km. Despite the lower resolution obtainable with the Umkehr technique, the relative changes in time for the same levels in the stratosphere can be determined with sufficient accuracy. Relative changes in space cannot, however, be estimated with the same accuracy because variations in the instrumental constants as well as in the haziness of the atmosphere could possibly lead to small systematic differences from one location to the other. With the recent development of the computer method by Mateer and Dütsch (1964) for uniform and objective evaluations, the Umkehr method has become even more useful and reliable. After a careful study of the information content of Umkehr observations Mateer (1965) has concluded that the method is particularly reliable for higher levels. The Umkehr data published by the Meteorological Service of Canada in cooperation with the World Meteorological Organization formed the basic material for a study made by the author on ozone concentrations at the highest possible levels. An additional source of data became available with the publication (Dütsch, 1964) of results of Umkehr evaluations for several stations for the period prior to 1964.

This study, aimed primarily at examining the possible effects of solar activity on the ozone in the upper stratosphere, has revealed a rather unexpected pattern for the annual variation of ozone in the uppermost layer that is centered near 45 km. The concentration at this level is seen to attain a *maximum in winter* and a *minimum in summer*, thus leading to an annual wave almost completely out of phase with the familiar one occurring at the lower levels. The region from 35–40 km appears to be a transition layer separating the two regimes. Figs. 1–3 depict the monthly mean partial

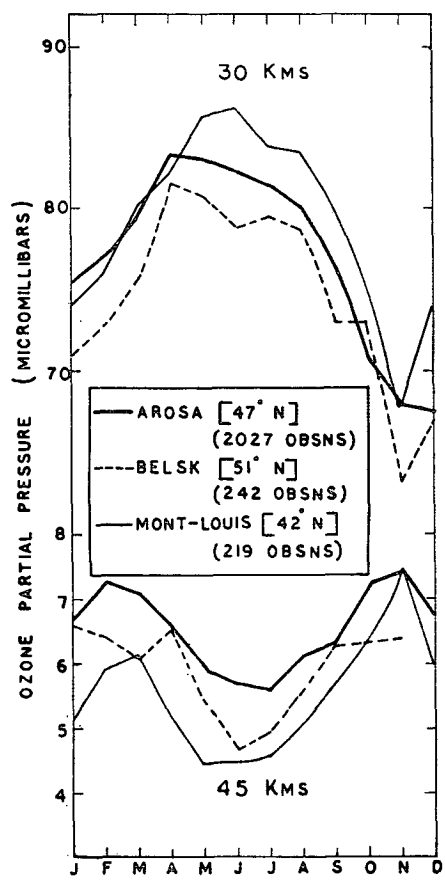

FIG. 1. Seasonal changes in the mean ozone concentration at 30 and 45 km for three stations in Europe.

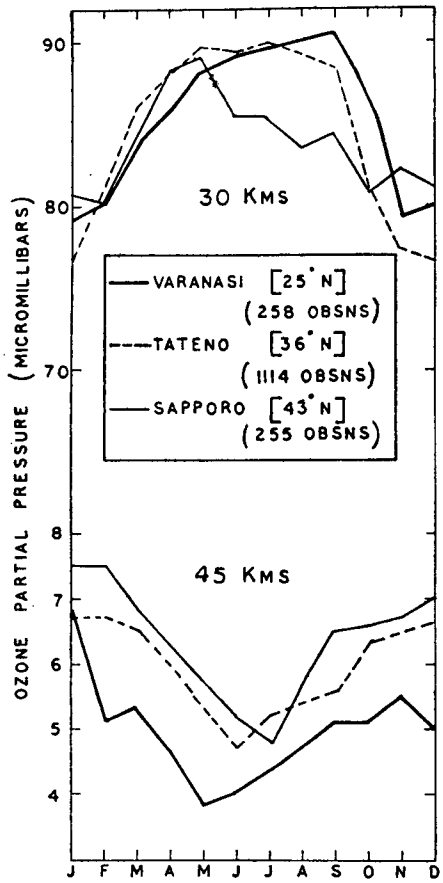

FIG. 2. Same as Fig. 1 except for three stations in Asia.

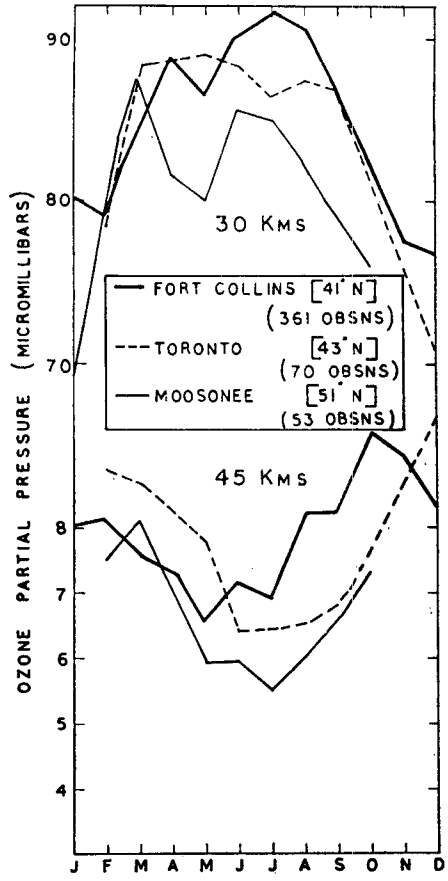

FIG. 3. Same as Fig. 1 except for three stations in North America.

pressures of ozone at 30 and 45 km for nine stations in the Northern Hemisphere, three each in Europe, North America and Asia. The period and number of observations for the various stations are not uniform, however, as can be seen from Table 1 which gives for each of the stations the latitude, data coverage and some statistical information on the annual variation of ozone concentration at 45 km. While the data from Toronto and Moosonee are especially limited, they were still useful in illustrating the near similarity of the annual variation at widely located stations. In the case of Arosa and Mont-Louis, a secondary maximum is observable in November. It may be mentioned in this connection that the Umkehr method determines for the ninth and last layer the total amount of ozone above the 2-mb level, it being arbitrarily assumed in all seasons that 65% of this amount is contained in the layer extending between the 2 to 1 mb level which is centered around 45 km. The assumption, however, does not invalidate the general conclusions that are based on the relative changes from one month to another for the same location.

The similarity of the curves in Figs. 1–3 show that in the Northern Hemisphere, in general, the annual wave of ozone variation at 45 km is nearly out of phase with that at 30 km.

While long-period changes in solar activity could possibly influence ozone concentrations at levels above 35 km, no corrections for such an affect were made due to the lack of available information. It may be pointed out that in the case of Arosa and Tateno the data covered periods of high and low solar activity and no significant correlation was obtained between the ozone concentration at the highest level and any of the indices of solar activity.

As far as the Southern Hemisphere is concerned, the analysis had to be extremely limited on account of the paucity of stations that record Umkehr observations. Some data for the IGY/IGC period are available for two or three stations in the Southern Hemisphere but these do not cover all the months of the year. The beginning of regular Umkehr observations at Pretoria, South Africa, during 1964 has now considerably enriched the observational material for this part of the Southern Hemisphere. Based on 569 sets of Umkehr observations for this station, seasonal variation of ozone concentration at 30 and 45 km are shown in Fig. 4. The only other station having at least some data for

TABLE 1. Summary of Umkehr observations.

Station	Period of data coverage	Total number of Umkehr observations	Statistics relating to the ozone concentrations at 45 km: Absolute annual range (μ mb)	Variation with respect to annual mean (%)	Relative standard deviation of individual values around respective monthly mean (%) Lowest	Highest
Europe						
Arosa (47N)	1956–65	2027	1.7	27	11	28
Mont-Louis (42N)	1963–66	219	3.0	55	11	18
Belsk (51N)	1963–66	242	1.9	31	13	25
Asia						
Tateno (36N)	1957–66	1114	2.0	33	11	28
Sapporo (43N)	1958–66	255	2.7	42	19	30
Varanasi (25N)	1963–66	258	3.1	46	20	30
North America						
Fort Collins (41N)	1960–63	361	2.9	37	9	20
Toronto* (45N)	1959–62	70	3.9	50	10	16
Moosonee* (51N)	1957–61	53	2.6	40	7	24
Southern Hemisphere						
Pretoria (25S)	1964–67	569	1.4	30	16	25
Aspendale**	1957–59	35	4.4	60	—	—

* Data not available for 2 or 3 months.
** Data very meager.

the greater part of the year is Aspendale, Australia, and the annual variation at this station based on only 35 observations covering the IGY/IGC period is also shown in Fig. 4. Although only based on data of two stations the results for the Southern Hemisphere are seen to corroborate fully the general conclusions drawn for the Northern Hemisphere if due consideration is given to the seasonal differences in the two hemispheres.

3. Possible causes for the anomaly

The anomalous behavior of the ozone changes at 45 km characterized by a *winter maximum* and a *summer minimum* is thus seen to be nearly worldwide in extent and certainly calls for an explanation. At 45 km, the characteristic restoration time (time required for a reduction of a departure from photochemical equilibrium concentration to $1/e$ of its initial value) is of the order of a few hours only according to the classical photochemical theory (e.g., Dütsch, 1961) even if widely different values for the solar radiation intensities and the rate coefficients are chosen. With such a short restoration time, it appears unlikely that organized air motions in the upper stratosphere could counteract the photochemical production and lead to a complete reversal of the phase of the annual oscillation between 35 and 45 km. We must therefore, determine whether there are any factors which could possibly affect the photochemical equilibrium concentration of ozone in a preferential manner between summer and winter at the high levels of the stratosphere.

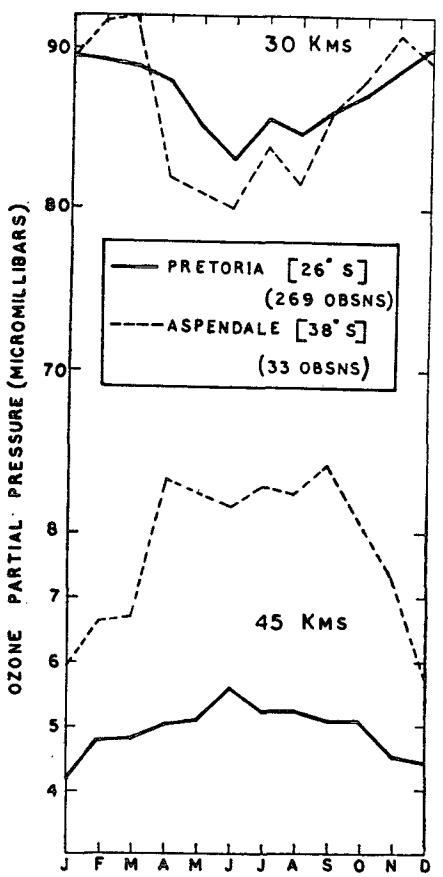

FIG. 4. Same as Fig. 1 except for two stations in the Southern Hemisphere.

According to classical theory the equilibrium concentration of ozone is given by the expression $[O_2]^{\frac{3}{2}}\cdot(\varphi_1/2\varphi_2)^{\frac{1}{2}}[(f_1/f_2)ks]^{\frac{1}{2}}$ where $[O_2]$ is the oxygen molecule concentration, φ_1 and φ_2 the quantum yields for oxygen and ozone photodissociation, respectively, f_1 and f_2 the number of light quanta absorbed per second by each oxygen molecule and ozone molecule, respectively, k the ratio of the rate coefficients for the ozone-forming and ozone-destroying reactions by collision process, and s a correction factor to take into account the relative inefficiency of the nitrogen molecule in three-body collisions (Dütsch, 1961). Of these factors, only f_1 and f_2 and the temperature-dependant constant k need be considered in discussing the annual variation in the equilibrium ozone amounts at any fixed location for any one particular level. For levels $\lesssim 35$ km, the seasonal changes in the solar zenith angle will exercise a predominating influence through changes in f_1 and f_2. This would account for the summer maximum, generally observed at all locations. At levels >40 km, however, the importance of the solar zenith angle decreases, while that of the temperature dependant ratio k increases. It is possible that the higher temperature during summer could lead to a decrease in the value of k and thus to a decrease in the equilibrium ozone concentration. To investigate on the annual range of temperature near the 45-km level, studies were made of the Weekly Synoptic Analyses for 1967 prepared by the Upper Air Branch of the U. S. Weather Bureau utilizing the rocket meteorological data of the IQSY period. It was found at the 2-mb level (42 km) that the annual range of mean temperatures is about 2–5C at 30N, increasing to 15–20C at 50N. While no such information is available at present for other areas of the earth, it may be assumed that the same order of temperature ranges will prevail between summer and winter. If seasonal changes in air temperatures were to be the predominating factor in determining photochemical equilibrium amounts of ozone at 45 km, we should expect a marked latitudinal influence on the annual range of ozone concentration. At high latitudes where the annual range of temperature is larger, the range of ozone variation ought to be appreciably larger. On the contrary, as shown by Table 1, when expressed as a percentage of the annual mean value at the respective locations the observed ranges are found to be of the same general magnitude at all the stations between latitudes 25 and 51N.

It is thus seen from a preliminary examination that classical photochemical theory may not be able to account fully for the reversal of the annual variation of ozone above 40 km. During the past two or three years, the inadequacy of the classical photochemical theory of ozone has been brought out by Hunt (1966a,b), Hesstvedt (1968) and Brewer and Wilson (1968). The role of water vapor in reducing the equilibrium concentrations of ozone has been stressed by the above investigators. What is not available at the present time are observational data on the concentrations of water vapor in the upper stratosphere in the different seasons. There are, however, indication that the water vapor concentration in the summer stratosphere is likely to be higher than in the winter stratosphere. Thus, Hesstvedt (1963) has presented a tentative model for the distribution of water vapor in the stratosphere and mesosphere in order to account for the observed increase of the H_2O mixing ratio with height in the stratosphere and also to explain the formation of noctilucent clouds at high latitudes in summer. This model is based on all available evidence for the existence of vertical meridional circulations in the stratosphere and mesosphere, visualizes 1) a continuous upward transport of H_2O from the troposphere into the stratosphere of the low latitudes in all seasons, 2) an upward transport in the summer stratosphere between 30 and 50 km, and 3) a downward transport over the same heights in the winter stratosphere. While the calculated concentrations of water vapor associated with the air motions are not known, it would appear that the circulation scheme of Hesstvedt is consistent with an H_2O concentration in the upper stratosphere which is higher in summer than in winter. The seasonal variation in H_2O concentration might also be responsible, at least in part, for the reduced ozone amounts at 45 km during summer. This question appears to merit further consideration. So far as the observational aspect is concerned, it appears worthwhile to extend the Umkehr observations to a larger network of stations, especially at those locations where clear skies may be expected for a significant number of days during each month of the year.

REFERENCES

Brewer, A. W., and A. W. Wilson, 1968: The regions of formation of atmosphere ozone. *Quart. J. Roy. Meteor. Soc.*, **94**, 249–265.

Dütsch, H. U., 1960: Vertical ozone distribution from Umkehr observations. *Arch Meteor. Geophys. Biolim.*, **11A**, 240–251.

——, 1961: *Current Problems of the Photochemical Theory of Atmospheric Ozone: Chemical Reactions in the Lower and Upper Atmosphere.* New York, Interscience Publishers 167–179.

——, 1964: Worldwide ozone distribution at different levels and its variation with season from Umkehr observations. Tech. Rept., NCAR, Boulder, Colo. 34 pp.

——, 1966: Two years of regular ozone soundings over Boulder, Colorado. Tech. Rept. TN-10, NCAR, Boulder, Colo., 43 pp.

Hesstvedt, E., 1963: On the water vapour content in the high atmosphere. *Geofys. Publikasjoner*, **25**, No. 3, 1–18.

——, 1968: On the photochemistry of ozone in the ozone layer. *Geopfys. Publikasjoner*, **27**, No. 5, 1–16.

Hunt, B. G., 1966a: The need for a modified photochemical theory of the ozonesphere. *J. Atmos. Sci.*, **23**, 88–95.

——, 1966b: Photochemistry of ozone in a moist atmosphere. *J. Geophys. Res.*, **71**, 1385–1398.

Mateer, C. L., 1965: On the information content of Umkehr observations. *J. Atmos. Sci.*, **22**, 370–381.

——, and H. U. Dütsch, 1964: Uniform evaluation of Umkehr observations from the world ozone network, Part I. Tech. Rept., NCAR, Boulder, Colo., 105 pp.

Paetzold, H. K., 1959: Vertical atmospheric ozone distributions. *Ozone Chemistry and Technology*, American Chemical Society, 209–220.

Staff, Upper Air Branch, NMC, ESSA, 1967: Weekly synoptic analyses, 5, 2, and 0.4 mb surfaces for 1964. ESSA Tech. Rept. WB-2, Silver Spring, Md.