The ozone distribution over the equator and its dependence on vertical motions

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(Manuscript received December 9, 1964)

ABSTRACT

The vertical distribution of ozone over the equator is computed for two vertical velocity profiles. The results are in fair agreement with observations from stations close to the equator. The level of maximum ozone concentration is well reproduced by the model; below this level the computed values are somewhat lower than the observed ones.

It is well known that the vertical distribution of atmospheric ozone deviates considerably from the vertical distribution computed theoretically on the assumption of photochemical equilibrium. It is further generally accepted that below about 25 km the failure of the theoretical model lies in the assumption of a static atmosphere. It has been shown by PRABHAKARA (1963) that most of the difference between observed and computed vertical distributions may be eliminated by assuming a model for the motion of the atmosphere which is in accordance with our present knowledge. The present note is a part of a paper presented at the International Atmospheric Ozone Symposium in Albuquerque, 1964, and concerns only the vertical distribution of ozone in the tropics.

As usual for the lower levels we shall consider the reactions

$O + O_2 + M \rightarrow O_3 + M$	$k_2 = 2.8 \times 10^{-34}$ cm^6 sec^{-1}
$O + O_3 \rightarrow 2O_2$	$k_3 = 8 \times 10^{-12} \cdot e^{-3.26/RT}$ cm^3 sec^{-1}
$O_2 + h\nu \rightarrow 2O$	$J_2 = 5.71 \times 10^{-6}$ sec^{-1} for zero optical depth
$O_3 + h\nu \rightarrow O + O_2$	$J_3 = 9.85 \times 10^{-3}$ sec^{-1} for zero optical depth

If the concentrations of O, O_2, O_3 and M are denoted by x, y, z and m, time variations in the ozone content may be expressed by

$$\frac{dz}{dt} = k_2 mxy - J_3 z - k_3 xz. \tag{1}$$

A similar expression may be given for dx/dt. It is, however, easy to show that atomic oxygen may, for all practical purposes, be regarded as being in photochemical equilibrium with the existing concentrations of O_2 and O_3. Consequently

$$x = \frac{2J_2 y + J_3 z}{k_2 my + k_3 z} \tag{2}$$

which may be substituted into (1):

$$\frac{dz}{dt} = \frac{2J_2 y k_2 my - 2k_3 z(J_2 y + J_3 z)}{k_2 my + k_3 z}. \tag{3}$$

The night-time variations of ozone are extremely small at the levels we are considering; during daytime we have $J_3 z \gg J_2 y$ and $k_2 my \gg k_3 z$. Equation (3) may therefore be approximated by

$$\frac{dz}{dt} = 2J_2 y - \frac{2J_3 k_3}{k_2 my} z^2. \tag{4}$$

In the course of the day J_2 and J_3 will vary with the sun's elevation. Relative to the variation of the ozone content, these variations are very rapid and for the integration of (4) we may let J_2 and J_3 be represented by their mean values during the day. Furthermore, since the pressure (and consequently y and m) varies during the integration it is convenient to introduce the relative ozone concentration $\zeta = z/m$. With these substitutions and the simplifications mentioned, (4) may be integrated to give

$$\frac{\zeta - \zeta_e}{\zeta + \zeta_e} = \frac{\zeta_0 - \zeta_e}{\zeta_0 + \zeta_e} \cdot \exp(-t/\tau), \tag{5}$$

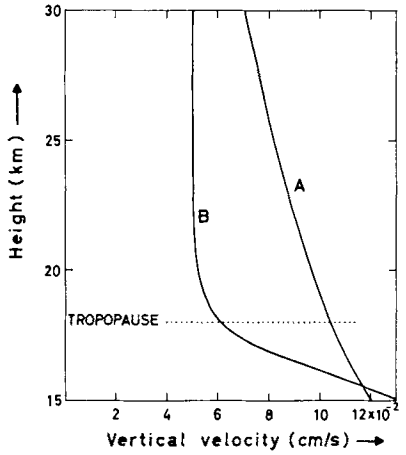

FIG. 1. Vertical velocity profiles used in the computations. Profile A is in accordance with MURGATROYD and SINGLETON's data, profile B is arbitrarily chosen. It is seen from Fig. 2 that profile B gives the best agreement with observations; still better agreement would be obtained with vertical velocities a little lower than those indicated by the curve B.

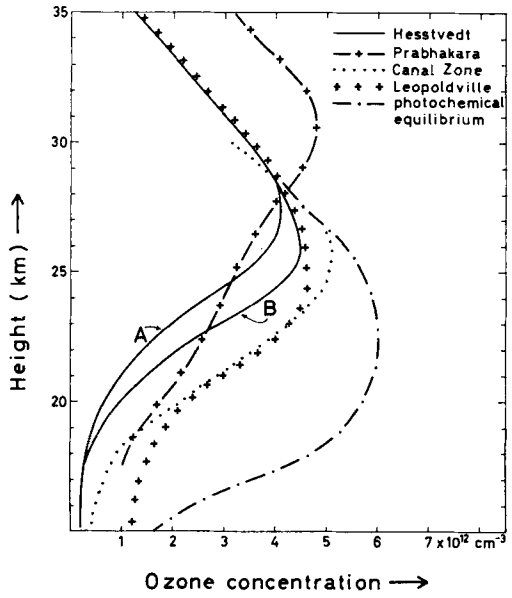

FIG. 2. Observed (Canal zone and Leopoldville) and theoretically computed vertical distributions of ozone at the equator.

where index e is used to denote the photochemical equilibrium value and the index 0 denotes the conditions at $t = 0$. τ is the lifetime of ozone. In expression (5), ζ_e and τ may be represented by their mean values in the interval of integration. For ζ_e and τ the following expressions are easily obtained

$$\zeta_e = y \sqrt{\frac{J_2 k_2}{J_3 k_3 m}} \tag{6}$$

and

$$\tau = \tfrac{1}{2} \sqrt{\frac{k_2 m}{J_2 J_3 k_3}}. \tag{7}$$

In the present work the values of J_2 and J_3 recently computed by DÜTSCH (private communication) were adopted. The k_2-value listed above is due to ELIAS, OGRYZLO and SCHIFF and the k_3-value was calculated by CAMPBELL and NUDELMAN on the basis of experiments by LEIGHTON, URBACH, WOJTOWICZ and ZAZLOWSKY. (For references to determinations of k_2 and k_3, see SCHIFF, 1964, and BARTH, 1964.) Expression (5) was used to compute the vertical distribution of ozone in an air column with a prescribed vertical velocity profile. The computations were started at a height of 15 km where the ozone concentration was assumed to be 10^{11} cm^{-3}. Furthermore stationary conditions were assumed. Two velocity profiles, shown in Fig. 1, were selected, one in accordance with the circulation model of MURGATROYD and SINGLETON (1961) and one, arbitrarily chosen, with a lower constant ascent in the stratosphere and a higher velocity in the troposphere.

The results of such computations are shown by the solid curves in Fig. 2. The level of maximum ozone concentrations was found to be 26 and 27 km for the two cases. For comparison mean observed values for the Canal Zone (10° N) and Leopoldville are plotted. Good agreement between theoretical and observed values is obtained down to the peak concentration level. This makes us believe that the value selected for k_2/k_3 is a realistic one. Below the peak concentration level the computations gave lower values than the observations. A comparison of the distribution curves in Fig. 2 shows that better agreement would have been obtained by using smaller values for the vertical velocity. (When comparing the curves A and B to the ozone distribution for Leopoldville we must remember the important fact that we selected the value 10^{11} cm^{-3} for the concentration at 15 km; the corresponding value observed at Leopoldville is one order of magnitude higher.) However, the disagreement does not

necessarily mean that the computations are unrealistic. The strongest ascent takes place within a very narrow belt of about 5 degrees' width. The average ozone profiles may also comprise cases when the station was outside this belt.

In his computation of the vertical and meridional distribution of ozone PRABHAKARA separated the air-mass into the advection caused by the mean motion and the turbulent transport. However, the disagreement between his vertical ozone distribution (shown in Fig. 2) and the observations is not so much caused by the selected values for the mean velocity and the diffusion coefficients but rather by his choice of value for k_2/k_3.

A comparison between observed values, values obtained for ascending air and the photochemical equilibrium values shows that the introduction of the air motion is an important step forward in theoretical studies of atmospheric ozone.

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