Global ozone budget and exchange between stratosphere and troposphere

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ABSTRACT

A survey of existing data reveals that tropospheric ozone is fairly uniformly distributed within the hemispheres, but that the hemispheres are well separated. Within the northern hemisphere representative data of tropospheric ozone exhibit a uniform seasonal variation the phase of which is delayed by about 2 months with respect to the injection into the troposphere. It is suggested that this delay is controlled by the rate of destruction of ozone within the troposphere. On the basis of this concept and additional reasonable assumptions it is possible to give a quantitative analysis of the ozone budget and of the seasonal variation of the exchange between stratosphere and troposphere. Calculated values of the global rate of ozone destruction, of the average vertical ozone flux and of the average stratospheric residence time of ozone are consistent with observations. Comparison of ozone data with data of fission products and of beryllium-7 enables a refinement of the analysis and allows further conclusions about the annual variation of the exchange between stratosphere and troposphere.

Introduction

The question of the ozone budget has received little attention. A few estimates of the vertical ozone flux by Dütsch and Lettau (see LETTAU, 1951) and by PAETZOLD (1955) resulted in the values listed in Table 1. The last value by V. REGENER (1957) is the only one which was *measured* directly. Regener recorded the vertical profiles of ozone at 4 points within 12 meters above the ground, during the Great Plains Turbulence Field Program, 1953 in Nebraska (see LETTAU & DAVIDSON, 1957). By combination with simultaneous data of the wind profile and the shearing stress at the earth's surface, the ozone flux on two days in August was found to vary in the indicated range. This measured value is of the same order of magnitude as the value by Dütsch at 0° latitude and as Paetzold's average value. However, Regener's value refers to one place and to two days only and it is not known how representative this single value is with respect to average conditions on a global scale.

In this study the attempt is made to give a quantitative analysis of the ozone budget on a global scale. The study was stimulated by the realization that tropospheric ozone is a much more regular phenomenon than hitherto assumed. If we avoid ozone concentration data, which are influenced by ozone destruction at the earth's surface or in polluted air near the ground, it becomes apparent that the troposphere, at least within the northern hemisphere can be treated as a rather well mixed ozone reservoir. This implies that the rate of horizontal mixing must be larger than the average rate of ozone destruction within the troposphere. Representative values of tropospheric ozone and its seasonal variation together with some assumptions about the mechanism of ozone destruction in the troposphere and about the seasonal variation of the rate of injection of stratospheric ozone into the troposphere result in a quantitative model of the ozone budget and the injection rate. The calculated values are compared with observations on ozone, fission products and beryllium-7 and quantitative data for a variety of important parameters are obtained which are consistent with these observations.

Distribution and variation of tropospheric ozone

We will begin our discussion of tropospheric ozone with Table 2 which contains a listing of most of the representative series of ozone

TABLE 1. *Data in the literature on the density of the vertical flux of atmospheric ozone.*

Author	Type of data	Flux density in 10^9 mol./cm² sec	Flux density in 10^{-9}g. O_3/m² sec
Dütsch	0° latitude	70	56
(see Lettau, 1951)	45° latitude	3	2.4
	90° latitude	0.4	0.32
	All values are estimates		
Lettau (1951)	Average value, estimated	4	3.2
Paetzold (1955)	Average value estimated	25–50	20–40
Regener (1957)	Measured value during two nights near the ground	90–250	72–200
Kroening & Ney (1962)	Estimate from vertical profiles near the earth's surface	60	48

measurements at the earth's surface and within the troposphere. Usually the data obtained at or near the earth's surface are strongly affected by ozone destruction at or near the ground. Average concentrations of ozone near the ground are thus of little value for general considerations because they more or less reflect the microclimatological conditions of the sampling site. It is imperative to obtain values which are representative for the troposphere. The daily maximum values of ozone usually occur around noon, when vertical mixing is strongest and when the influence of the ground is widely eliminated. It can be expected that these values are approximately representative for ozone in the undisturbed troposphere in areas which are free of air pollution. In polluted air ozone destruction occurs not only at the earth's surface but to a considerable degree also within the air or ozone is formed by photochemical reactions among pollutants (Los Angeles smog).

The *upper limits* of the range of ozone concentrations listed in Table 1 represent in some cases individual daily values, in other cases monthly average values of daily maxima and are thus not strictly comparable. Nevertheless these upper limits are rather uniform and show that representative ozone concentrations within the troposphere do not vary too much with time and space. The same is indicated by the *average values*. In most cases these average values represent the average daily maximum values, but in some cases the selection of maximum values was not possible to the desired extent. Despite these shortcomings the average values also reveal the important fact that representative ozone concentrations vary only within a rather narrow range for a large variety of places and throughout the year.

The usual range of representative average values is between 30 and 60 $\mu g/m^3$. Values higher than 90 $\mu g/m^3$ are already rare except for polluted atmospheres like Los Angeles, where 1000 $\mu g/m^3$ and more can be reached. To a small extent anthropogenic ozone sources can also be expected for other places with suitable conditions as for instance in Albuquerque. In reducing atmospheres, as for instance in the planetary ground layer over Central Europe (Lindenberg, Dresden-Wahnsdorf and perhaps to some degree at the Fichtelberg) the maximum values are usually lower than in the layers aloft as will be discussed further in a later section. We are convinced that the agreement of data would be better if the ground influence (surface and pollution) could be positively eliminated and if the data were separated according to season.

This suggestion is strongly supported by Fig. 1. Fig. 1*a* gives a comparison of three sets of rather representative data for tropospheric ozone for entirely different locations within the northern hemisphere. Arosa, at a latitude of 47° N is located at 1860 meters in a high valley in the alps. GÖTZ & VOLZ (1951) selected the *daily maximum concentrations* as the most representative ones and we calculated from these data the monthly average values in Fig. 1*a*. Their original diagram is reproduced in Fig. 2. Another set of data was obtained at

TABLE 2. *Compilation of representative ozone concentration near the ground and at higher levels within the troposphere.*

Observer	Location, time and results	Altitude (Meters)	Ozone concentration $\mu g/m^3$	
			Range approximate	Average approximate
Götz & Volz (1951)	Arosa, Switzerland, 1950–51, high valley, daily maxima value.	1860 m above sea level	19–90 daily maximum values Fig. 1	50
Ehmert (1952)	Weissenau, Bodensee, Germany, 1952	20 m above ground	0–90 all values	35[a]
Kay (1953)	Farnborough, England, 1952–53	0–12000 m above ground	26–50 a few aircraft soundings	38[b]
Regener (1954)	Mt. Capillo and Albuquerque, New Mexico, USA, 1951–52	3100 and 1600 m above sea level	3–120 all data	36[a]
Regener (1954)	O'Neil, Nebraska, USA, 1953	12 m above ground	0–90 all data	35[a]
Teichert (1955)	Lindenberg Observ., Germany, 1953–54	80 m above ground	0–50 all data	30[a]
Brewer (1955)	Tromso, Norway, 1954	0–10000 m above ground	60–70 a few aircraft soundings	65
Teichert & Warmbt (1956)	Fichtelberg, Central Germany, 1954–55	1215 m above sea level	20–67 monthly average values of hourly observations	40
	Brocken, Central Germany, 1955	1152 m above sea level	26–52 monthly average values	40
	Kaltennordheim, Central Germany, 1955	494 m above sea level	15–25 monthly average values	20[a]
	Wahnsdorf, near Dresden East Germany, 1954–55	257 m above level	2–26 monthly average values of hourly observations	12[a]
Price & Pales (1959, 1961)	Mauna Loa, Hawaii, 1958	3000 m above sea level	20–80 daily maximum values	50
Wexler *et al.* (1960)	Little America Antarctica, 1958	50 m above sea level, near the ground	10–70 all values	50
Ramanathan *et al.* (1961)	Srinagar, North India, 1957–1960	1700 m above sea level	26–59 monthly average values of daily maxima	50
Dave (1961)	Ahmedabad, 1954–55	50 m above sea level, near the ground	24–50 monthly average values of daily maxima	40

[a] Influence of ozone destruction near the ground not eliminated in these average values. To some extent this applies also to other sets of data, except for those which refer to daily maximum values.
[b] Values likely too low due to ozone destruction in the intake tube.

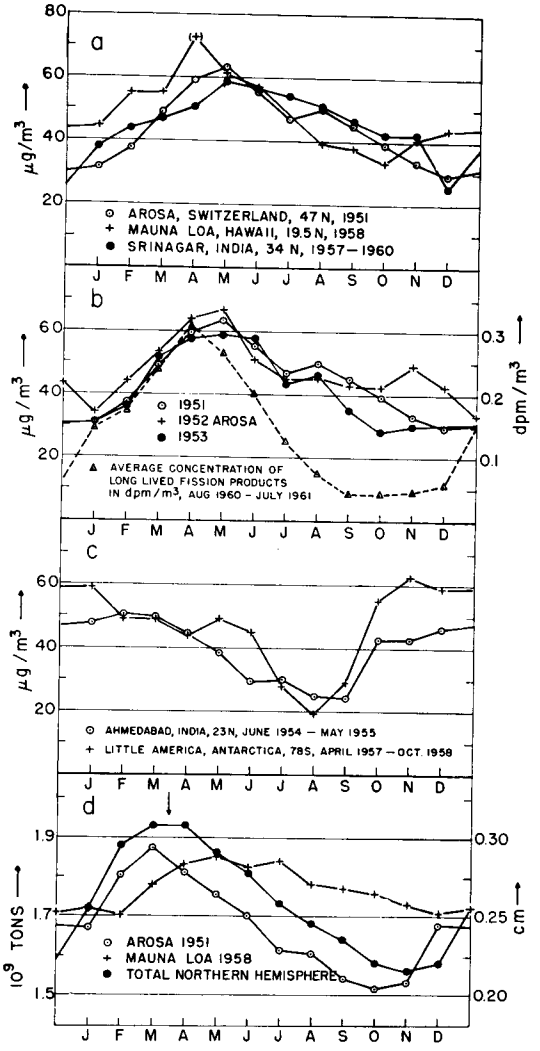

FIG. 1. Annual variation of monthly average values of daily maximum ozone concentration at various places. (*a*) Values for Arosa 1800 m above sea level (GÖTZ & VOLZ, 1951), Mauna Loa 3000 m above sea level (PRICE & PALES, 1959, 1961) and Srinagar 1700 m above sea level (RAMANATHAN, 1961). The value in April at Mauna Loa is based on a few days only. (*b*) Values for three consecutive years in Arosa, 1951 (GÖTZ & VOLZ, 1951) and 1952 and 1953 (VOLZ & PERL, 1961). For comparison the average monthly concentration of long lived fission products in surface air for the northern hemisphere obtained from the 80th Meridian Network data (LOCKHART, 1961). (*c*) Values for Ahmedabad 50 m above sea level (DAVE, 1961) and Little America 50 m above sea level (WEXLER *et al.*, 1960). (*d*) Total ozone for Arosa (GÖTZ & VOLZ, 1951) Mauna Loa (PRICE & PALES, 1959, 1961) and the integrated average value based on data by DÜTSCH (1946) after correction for newer absorbtion data (DÜTSCH, 1959).

the Mauna Loa Observatory, Hawaii, which is ideally located at 20° N in the center of the Pacific at 3000 meters altitude, well above the trade wind inversion. These data were taken during the IGY, 1958, by PRICE & PALES (1959, 1961).[1] Here, the highest daily values occur in the second half of the night, because during the day warm air rises along the slope of the mountain and the ozone concentration decreases by about 20% due to contact with the earth's surface. We selected for the monthly average values in Fig. 1*a* the mean hourly readings between midnight and 6:00 in the morning. The value in April is based on only a few days due to failure of the instrument.

The third series of measurements was obtained in Srinagar, North India, on the foothills of the Himalaya, at 34.5° N and at 1700 meters above sea level.[2] Prof. Ramanathan states that the low value in December is affected by fog and stagnant air and may be too low compared with respect to undisturbed conditions.

The values plotted in Fig. 1*a* are monthly average values. The individual values show of course fluctuations from day to day. We have no daily data from Srinagar, but for the two other stations, Arosa and Mauna Loa, the standard deviations of the daily maximum values are not much different and amount to about 20% as indicated by Table 3.

All three sets of data in Fig. 1*a* agree surprisingly well, if the differences in longitude and latitude are taken into account. This indicates that generally tropospheric ozone in the northern hemisphere is indeed fairly well mixed. Superimposed on this general level are those short term and local fluctuations which are caused either by destruction of ozone near the ground or by a somewhat different history or "ozone age" of the different air masses. The rather uniform distribution of tropospheric ozone implies that the average life time of tropospheric ozone must be longer than the average time required by large scale horizontal

[1] We are very grateful to Mr. Pales and Mr. Price for supplying us with the original data for use in this study. Their main results were presented at the Symposium on ozone, Oxford, 1959. It should be mentioned that Mr. Pales and Mr. Price have some reservations with regard to the reliability of these observations.

[2] We are very grateful to Prof. Ramanathan and his associates for supplying us with the monthly average values of the hourly readings for use in this study. The data are not yet published.

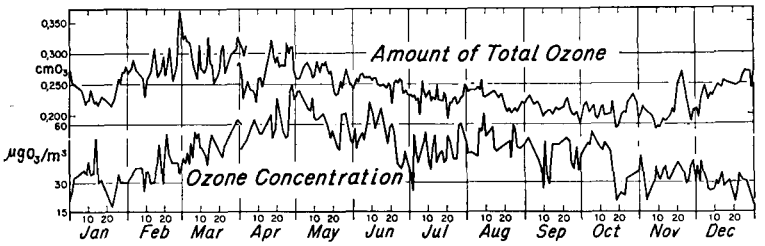

FIG. 2. Total ozone and daily maxima of surface ozone in Arosa, 1950/51 (GÖTZ & VOLZ, 1951).

TABLE 3. *Standard deviations of daily maximum surface ozone concentrations.*

	Winter	Summer
Arosa	0.23	0.22
Mauna Loa	0.18	0.26

mixing (mixing time) to smooth out latitudinal or longitudinal variations of the stratospheric injection or the tropospheric destruction near the ground. The agreement between Mauna Loa and the continental sites indicates also that the average destruction rate over oceans cannot be too different from that over continents.

Another interesting feature of tropospheric ozone shown by Fig. 1*a* is the seasonal variation with about the same phase and amplitude throughout the northern hemisphere. This variation is repeated more or less each year as indicated by Fig. 1*b*, where 3 consecutive years for Arosa are plotted.[1] The yearly variation is not quite symmetrical. The maximum in spring is better defined and sharper than the broad minimum in winter. The phase of the annual variation, which will be of some importance for our theoretical considerations later is thus best determined by the spring maximum. But the annual variation is regular enough to be fairly well approximated by a simple sin-function, a fact which will again be of importance for our analysis.

The three stations in Fig. 1*a* are all located at 1.7 km and higher above sea level, i.e. above the normal planetary boundary layer. The station most representative for undisturbed conditions of the troposphere is certainly Mauna Loa in the centre of the Pacific and generally more than 1 km above the trade wind inversion, which represents in this area the upper limit of the planetary boundary layer. Except for a slight decrease of the ozone concentration during noon time when the observatory is affected by heated air which rises along the slope the data are free from the local influence of the earth's surface.

In Arosa and Srinagar conditions are less favorable because in these places the influence from the ground is more pronounced although still less than in stations at level ground. The daily variations are larger than in Mauna Loa but the selection of daily maxima values around noon apparently eliminates the local ground influence at these places quite well, as indicated by the agreement with Mauna Loa.

It can be expected that for stations on level ground the surface influence will further in-

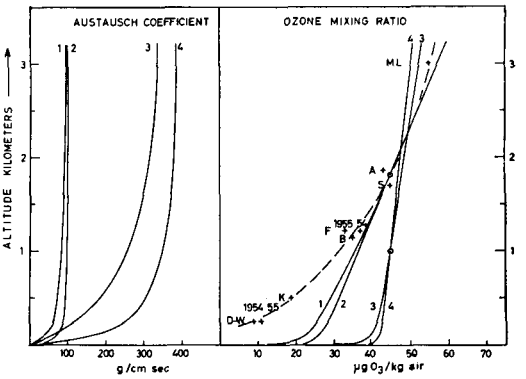

FIG. 3. *Left:* Vertical profiles of the Austausch coefficient used for the calculations of the ozone profiles at right. *Right:* Calculated vertical distributions of ozone for conditions explained in the text. Also plotted are the yearly average values of the daily maximum ozone surface mixing ratios for the following stations: ML = Mauna Loa; A = Arosa; S = Srinagar; F = Fichtelberg; B = Brocken; K = Kaltennordheim/Rhön; D–W = Dresden–Wahnsdorf. The dashed curve indicates the trend of the Central European data.

[1] We are grateful to Dr. Volz and Miss Perl for supplying us with the original data of 1952 and 1953 for use in this study.

crease at least in middle and high latitudes in winter because of the higher probability of horizontally and vertically extended surface inversion layers. However, the amplitude and the annual variation of the concentrations in Ahmedabad and Little America Station agree well with those from the mountain stations (see Fig. 1) indicating that the selection of daily maximum values for these two stations results in fairly representative values for the troposphere. This implies that even for such stations the ozone depleted surface layer is usually not very thick so that increased or convective turbulence can eliminate it. Simple numerical considerations point in the same direction. In Fig. 3 we calculated a few examples of ozone profiles under the assumption that the vertical ozone flux is independant of altitude and that ozone destruction occurs only at the earth's surface. The concentration data were converted to mixing ratios ozone/air, because only the mixing ratio is a conservative property. The ozone flux was taken to be 1.0×10^{-7} g O_3/m^2 sec according to Regener's values and in rough agreement with our calculations later.

If F is the vertical ozone flux, m the ozone mixing ratio and A the Austausch coefficient we have

$$F = A \cdot \frac{dm}{dz}.$$

For A we can assume the following models: Near the surface with a roughness r, A can be expressed by

$$A = \alpha(z + r).$$

For altitudes above the planetary ground layer, i.e. above about 1 km, A_0 can be assumed constant as a first approximation. These features can be combined in the convenient analytical expression

$$A = \frac{A_0 \alpha (z + r)}{A_0 + \alpha (z + r)}.$$

The parameter r is of very little importance for the numerical results and can be taken to be 10 cm. To cover approximately the range of conditions to be expected we assumed four combinations of the parameters α and A_0:

1. α = 0.0073 g/cm² sec for low surface winds.
   A_0 = 100 g/cm sec for low turbulence in the free atmosphere.
2. α = 0.029 g/cm² sec for about 5 m/sec wind at 5 m above ground.
   A_0 = 100 g/cm sec.
3. α = 0.0073 g/cm² sec.
   A_0 = 400 g/cm sec for high turbulence in the free atmosphere.
4. α = 0.029 g/cm² sec.
   A_0 = 400 g/cm sec.

The vertical distribution of m is

$$m = \frac{F}{A_0} \cdot z + \frac{F}{\alpha} \ln \left(\frac{z}{r} + 1 \right) + \text{const.}$$

The integration constant was adjusted in such a way that the most representative tropospheric values of Mauna Loa, Arosa and Srinagar are best approximated, i.e. it was adjusted to a mixing ratio of 45 μg/kg air in 1.8 and 1.0 km respectively.

Fig. 3 shows the profiles of A and those of m for all four combinations. It is apparent that a rapid decrease of m occurs only near the ground and that A_0 controls the ozone distribution over most of the troposphere. The few reliable ozone soundings in the troposphere indicate that an increase of m by a factor of two within the troposphere from 1 km to 10 km is probably a good approximation of average conditions. This would be intermediate between case 1 and 2 (for which this factor is 3.0) and case 3 and 4 (for which this factor is 1.6). Average Austausch values of the free Atmosphere between 100 and 400 are likely if convection is involved as it is the case under normal conditions.

Although these calculations are not conclusive they seem to indicate that under normal conditions the ozone depleted surface layer is rather shallow. Under such conditions the daily maximum of convective turbulence around noon should be sufficient to almost eliminate this layer. These considerations should be independent of the altitude above sea level.

However, the assumption that ozone destruction occurs exclusively at the surface is likely to be correct for unpolluted air only. There is indication that in polluted areas, as e.g. in Central Europe, ozone is also destroyed *within* the air. Fig. 4 compares the Arosa values from Fig. 1*a* with corresponding values from Fichtelberg and Wansdorf (Teichert & Warmbt, 1956; see also Table 2). Fichtelberg is a peak elevation in medium altitude mountain ranges

and Wahnsdorf near Dresden is located on almost level ground. The data for Fichtelberg and Wahnsdorf represent average values at 12:00 and 18:00 respectively which are closest to the daily maxima in these places. In contrast to the data from Ahmedabad and Little America Station the concentrations in both stations, particularly in Wahnsdorf are markedly lower than in Arosa, not only during winter but also in summer. This excludes the possibility that the effect is primarily due to a higher frequency of stable surface inversion layers. The effect is even better demonstrated in Fig. 3, where we plotted the annual average maximum values for all stations given by Teichert and Warmbt (1956) in their studies. The dashed curve connects the observed values as a visual aid and does, of course, not represent a vertical profile. It shows how the altitude above sea level of the observation affects the average maximum ozone concentration in Central Europe. The systematic trend makes it unlikely that local geographical or microclimatological conditions are the controlling factor. Rather, all these features point to large scale chemical destruction of ozone within the planetary boundary layer, i.e. below 1.5 km, over Central Europe.

This is supported by the observation (TEICHERT & WARMBT, 1956) that in Wahnsdorf the lowest concentrations occurred with SSE winds which carry pollution from the nearby city of Dresden. In addition to this the maximum concentration in Wahnsdorf occurs at about 18:00. This delay against other stations may also be due to considerable destruction within the air.

The rather uniform distribution of tropospheric ozone above the planetary boundary layer encourages an attempt to treat the troposphere as a well mixed ozone reservoir and to give a quantitative analysis of the cycle and budget of atmospheric ozone. Such analysis is of interest for considerations of global radioactive fallout, particularly because the type of data available for both constituents, ozone and fission products, differ fundamentally so that they supplement each other in a favorable way. For ozone the total stratospheric burden can easily and accurately be determined because it is practically equivalent to total ozone and such data are now available on a global basis. For fission products this quantity is most difficult to obtain and least accurately known. The rate of deposition at the earth's surface, i.e. the vertical flux, on the other hand can be obtained for fission products by world wide rain water analysis but is difficult to measure for ozone (see Table 1).

Our quantitative analysis will be based on the fact that tropospheric ozone in the northern hemisphere and its seasonal variation can be approximated by an expression of the form

$$\theta = a_1 + a_2 \sin[\omega(t - a_3)] \text{ [tons]} \qquad (1)$$

where t is the time in years, a_1, a_2 and a_3 are constants and ω is numerically equal to 2π but has the dimension of t^{-1}.

It is apparent from Table 2, and Figs. 1, 2 and 3 that 50 $\mu g/m^3$ can be accepted as a fairly representative average value for low tropospheric ozone concentrations. In order to obtain the total tropospheric ozone content, it is necessary to have some information about the vertical distribution of ozone within the troposphere. Reliable ozone soundings in the troposphere are rare and only those obtained with chemical methods are accurate enough. Recent data by the new chemical ozone sonde by V. REGENER (1960) indicate a fairly *constant mixing ratio* (HERING, 1961). Older data by Ehmert, Kay and Brewer (see JUNGE, 1958), although less accurate, point to a more constant volume concentration with altitude. Since the general ozone flux is downwards, one should expect on the average some increase of the mixing ratio with altitude. We try to cover this range of possibilities by calculating a_1, i.e. the annual average for θ for three cases, assuming a fixed concentration of 50 $\mu g/m^3$ at an altitude of 1 km and an average tropopause height of 12 km:

(1) The mixing ratio is constant with altitude:

$$a_{1a} = 0.95 \times 10^8 \text{ tons } O_3.$$

(2) The mixing ratio increases from 1 km to 12 km by a factor of two:

$$a_{1b} = 1.30 \times 10^8 \text{ tons } O_3.$$

(3) The concentration of 50 $\mu g/m^3$ is constant with altitude (i.e. the mixing ratio increases by a factor of about 4)

$$a_{1c} = 1.50 \times 10^8 \text{ tons } O_3.$$

We think that a_{1b} is the best approximation.

The amplitude of the yearly variation of ozone is about ± 15 $\mu g/m^3$ (Fig. 1*a*). This results in the following a_2 values for the same three cases as above:

$$a_{2a} = 0.28 \times 10^8 \text{ tons } O_3$$

$$a_{2b} = 0.39 \times 10^8 \text{ tons } O_3$$

$$a_{2c} = 0.45 \times 10^8 \text{ tons } O_3$$

The constant a_3 will be determined later.

The total *stratospheric* ozone burden was calculated from a diagram by DÜTSCH (1946) which gives the latitude dependence of total ozone for each month. These values were integrated over the northern hemisphere and plotted in Fig. 1*d*. The *average* burden of total ozone in the northern hemisphere is about 1.75×10^9 tons. Figs. 1 and 2 show that the phase of the surface ozone is somewhat delayed against that of stratospheric (total) ozone. The maximum of stratospheric ozone is at the beginning of April and the maximum of the surface ozone is around the middle of May in Arosa and at the end of April at Mauna Loa. It is difficult to obtain a reliable value for this time delay which seems to be of the order of one to two months. This time delay can be interpreted as the result of a limited life time of tropospheric ozone and is of great importance for our considerations.

The only set of representative data for surface ozone from the southern hemisphere, which was available to us was from Little America Station, Antarctica (WEXLER *et al.*, 1960). Here the daily average values are practically equivalent to the average maximum values, because the daily variation is very small. Despite the extreme climatological conditions the range of concentrations is in agreement with the representative ozone values from the northern hemisphere (Table 2 and Fig. 1), indicating that the overall destruction rate at the earth's surface and the rate of injection into the troposphere must be close to those of the northern hemisphere, unless one assumes the unlikely case that both deviate in the same manner. This implies that the destruction rate at the ocean surface cannot be much different from the destruction rate over land (because of the different land/ocean distribution in both hemispheres) and that the additional ozone destruction by air pollution in the northern hemisphere is of little importance on a global scale.

However, the phase difference between the Little America values and those of the northern hemisphere is not 6 months as to be expected and the shape of the curve is also different, the minimum being more pronounced than the maximum. This is likely due to differences between the hemispheres of the cycle of the exchange process stratosphere-troposphere and will not be discussed here further. The primary reason why we plotted the values in Fig. 1*c* is a comparison with the data from Ahmedabad. Ahmedabad is located in West India at 23° N and we expected to find here the same variation as in other parts of the northern hemisphere. However, the trend of the curve is quite different and rather matches the annual variation in Antarctica, particularly between May and November. In summertime this part of India is under the realm of the Monsoon which carries air masses from the southern hemisphere across the equator into India. It is therefore not surprising to find this agreement with data from the southern hemisphere. It is a very interesting fact and implies that mixing across the meteorological equator is fairly slow and that the air masses over India retain their identity within the monsoon circulation rather well as indicated by the comparison of Srinagar (34° N) and Ahmedabad (23° N). We like to mention here that data on the yearly variation of carbon dioxide and on the global distribution of tritiated methane also point to rather slow mixing across the equator with an exchange rate of about 0.3 $year^{-1}$ (JUNGE, 1962). On the basis of these results it can be expected that systematic investigations of the annual variation of ozone and carbon dioxide across the equator at various latitudes can contribute significantly to our understanding of the tropical circulation.

Theoretical considerations

In the previous section we demonstrated that the northern hemisphere (and the southern most likely just as well) can be treated as a well mixed ozone reservoir. The annual variation of the ozone content of this reservoir can be approximated by a simple sin-function which shows a certain time delay as compared with the ozone source in the stratosphere. These facts enable a simple analysis of the ozone

[1] We are grateful to Dr. Dave for supplying us with the original data for use in this study. The data are not published.

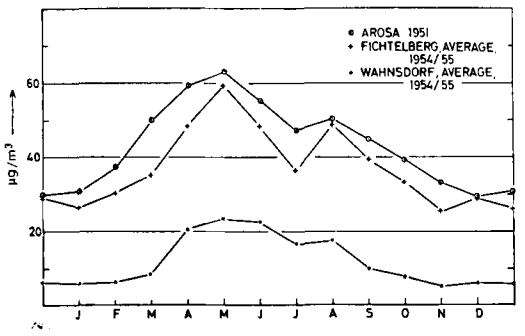

FIG. 4. Annual variation of monthly average values of surface ozone concentrations at Fichtelberg 1215 m above sea level and Dresden–Wahnsdorf 257 m above sea level in comparison with the Arosa data 1951 in Fig. 1*a*. The data of Fichtelberg are the monthly average values for 12:00 and the data of Wahnsdorf are for 18:00. (TEICHERT & WARMBT, 1956).

budget if a few additional assumptions are made. Ozone destruction occurs primarily at or near the ground, if we disregard polluted air masses. The ozone destruction is either controlled by the concentration of ozone which is in contact with the reducing surface or by the eddy diffusion flux above the ground, in case the chemical destruction is a fast process. In both cases, however, on the average over time and space the rate of ozone destruction D will be approximately proportional to the ozone concentration and thus proportional to the total tropospheric ozone content θ, i.e.

$$D = -c_0\theta \text{ (tons/year)} \tag{2}$$

can be considered a rather good approximation. The expression (1) for θ and the assumption (2) for D require that the rate of injection of stratospheric ozone into the troposphere has the form

$$I = c_1 + c_2 \sin(\omega t) \text{ (tons/year)}. \tag{3}$$

Here $t = 0$ is not identical to the beginning of the calendar year and any phase difference between I and θ is taken care of by the constant a_3. Combination of (2) and (3) gives

$$d\theta/dt = I + D = c_1 + c_2 \sin(\omega t) - c_0\theta \tag{4}$$

with the solution

$$\theta = c_1/c_0 + (c_2/\omega)[(c_0/\omega)^2 + 1]^{-1/2} \times \sin[\omega t - \text{arc sin}(\{c_0/\omega\}^2 + 1)^{-1/2}]. \tag{5}$$

Comparison of (5) and (1) yields

$$a_1 = c_1/c_0,$$

$$a_2 = c_2/\omega \sqrt{\left(\frac{c_0}{\omega}\right)^2 + 1},$$

$$a_3 = \frac{1}{\omega} \text{ are sin}\left(1 \Big/ \sqrt{\left(\frac{c_0}{\omega}\right)^2 + 1}\right).$$

This enables us to calculate c_0, c_1 and c_2. Since a_3 is the most uncertain value, we plotted in Fig. 5 c_0 as a function of a_3. The delay time a_3 between I and θ can be taken from the observations, if we assume that I is in phase with the total ozone burden of the stratosphere. There is a justification for this in the fact that the ozone concentration in the low stratosphere of middle and northern latitudes which is responsible for the total ozone maximum in spring is in fact the controlling factor for the injection rate. The higher this concentration, the larger the ozone gradients at and above the tropopause and also across the tropopause gap and consequently the larger the ozone flux. However, this assumption can only be considered a very rough approximation. Indeed a comparison with fission product data, which will be discussed later points to actual delay times which are somewhat longer than those indicated by Figs. 1*a* and 1*d*. The value of a_3 thus remains the most uncertain among the parameters taken from observations. To cover the range of possible a_3 values we calculated Table 4, which gives c_0, c_1 and c_2 for various combinations of values for a_1, a_2 and a_3.

For a range of a_3 from 0.5 to 2.5 months, line 2–4 gives the corresponding values for c_0 and for the life-time τ_t in months, which would vary from 0.6 to 5.90. In line 5–10 the constants c_1 and c_2 are calculated for the three possibilities of a_1 and a_2 and line 11 to 16 gives the average stratospheric life time of ozone τ_s if the total stratospheric burden is 1.75×10^9 tons. The last lines give the vertical ozone flux computed from c_1 in line 5–7 for comparison with the data in Table 1.

The calculations in Table 4 indicate the importance of the parameter a_3. If we assume the injection rate to be in phase with total ozone a comparison of Figs. 1*a*, 1*b* and 1*d* indicates values between 1 to 2 months. This results in

TABLE 4. *Various calculated parameters of the ozone budget.*

Delay Time a_3 months	0.5	1.0	1.5	2.0	2.25	2.5	
c_0 in month^{-1}	1.8	0.9	0.5	0.3	0.23	0.17	
c_0 in year^{-1}	21.6	10.8	6.0	3.6	2.75	2.05	
Average tropospheric residence time $\tau_t = c_0^{-1}$ in month	0.6	1.1	2.0	3.3	4.35	5.90	
c_1 in tons/year for $a_{1a} : c_{1a}$	20.5	10.3	5.7	3.4	2.6	1.95	$\times 10^8$
c_1 in tons/year for $a_{1b} : c_{1b}$	28.1	14.1	7.8	4.7	3.6	2.67	$\times 10^8$
c_1 in tons/year for $a_{1c} : c_{1c}$	32.4	16.2	9.0	5.4	4.1	3.08	$\times 10^8$
c_2 in tons/year for $a_{2a} : c_{2a}$	6.30	3.50	2.42	2.03	1.94	1.86	$\times 10^8$
c_2 in tons/year for $a_{2b} : c_{2b}$	8.80	4.86	3.38	2.82	2.70	2.60	$\times 10^8$
c_2 in tons/year for $a_{2c} : c_{2c}$	10.15	5.62	3.90	3.25	3.10	2.98	$\times 10^8$
$c_{1a,b,c}$ in percent of average total stratospheric burden 1.75×10^9 tons	117	60	31	19	15	11	
	162	83	43	27	21	15	
	190	95	51	31	23	18	
Average stratospheric residence time τ_s in years	0.9	1.7	3.2	5.2	6.7	9.1	
	0.6	1.2	2.3	3.7	4.7	6.7	
	0.5	1.1	2.0	3.2	4.3	5.5	
Vertical flux F in the troposphere in g/m^2 sec	2.6	1.3	0.7	0.43	0.33	0.24	$\times 10^{-7}$
	3.5	1.8	1.0	0.58	0.45	0.34	$\times 10^{-7}$
	4.0	2.0	1.1	0.68	0.51	0.38	$\times 10^{-7}$

$$1.1 \leq \tau_t \leq 3.3 \text{ months},$$

$$1.1 \leq \tau_s \leq 5.2 \text{ years},$$

and $$1.3 \leq F \leq 0.68 \times 10^{-7} \text{ g/m}^2 \text{ sec}.$$

The values which can be compared most readily with observations are those of F. Table 1 indicates that the calculated range is close to that observed by Regener. But this agreement is not very significant because it is not known how representative for average conditions Regener's local value may be. The other data in Table 1 are estimates and differ widely.

A direct comparison of τ_s with observed stratospheric residence times of fission products is difficult, because above 25 to 30 km ozone is in photochemical equilibrium and is therefore not a conservative property of the air. Another difficulty is the different spatial distribution of both constituents within the stratosphere. Activity from fairly recent tests in 1959 showed residence times between one and two years but these values refer primarily to layers below 20 km and most of the stratospheric ozone is concentrated at higher levels. MARTELL (1959) pointed out that it is very likely that fission products in higher layers have residence times of 5 years and more. This is also indicated by the global fallout rate during 1960/61, prior to the recent resumption of atomic tests but almost 3 years after the last tests series in October 1958, which showed a small systematic decrease per year consistent with residence times longer than two years. Due to the depletion of the lower stratosphere long lived activity during this interval is likely to come from layers similar to those of ozone or higher. We feel therefore that the residence time of a constituent with the same stratospheric distribution as ozone may be close to 5 years.

At the present time the ozone data do not allow to narrow the limits for τ_t, τ_s and F further. But a comparison with data on the annual variation of fission products and Be^7 in tropospheric air proved useful in this respect. Both artificial stratospheric radioactivity and cosmic ray produced Be^7 become attached to tropospheric aerosols in a similar manner and the average life time of these tropospheric aerosols is fairly well known to be about 1 month. For artificial radioactivity and for Be^7 we thus know c_0 and can compute a_3.

In Fig. 1*b* we plotted the gross fission product concentration in surface air averaged for the northern hemisphere. The data selected here were obtained by LOCKHART *et al.* (1961) along the 80th meridian from September 1960 to August 1961, i.e. just prior to the resumption of nuclear tests in September 1961. The values of August 1960 and August 1961 match very

closely, indicating that the fraction removed during this interval was small and that a semi-steady state with respect to the stratospheric distribution of long lived activity in the stratosphere was reached. The values in Fig. 1*b* are plotted in a scale which permits comparison with the ozone data. We see that the maximum in spring is about one month earlier than for ozone and that the amplitude is considerably larger. If we approximate this annual variation again by a sin-function we can apply the same analysis as for ozone. For simplicity we use here the average concentration of fission products in air itself instead of the total tropospheric burden. We have

$$c_0 = 12 \text{ year}^{-1},$$
$$a_1 = 0.175 \text{ dpm/m}^3,$$
$$a_2 = 0.125 \text{ dpm/m}^3.$$

This corresponds to a maximum $a_1 + a_2 = 0.30$ dpm/m³ and a minimum $a_1 - a_2 = 0.05$ dpm/m³ in agreement with Fig. 1*b*. Calculation yields:

$a_3 = 0.9$ month (Fig. 5),

$c_1 = a_1 \cdot c_0 = 2.1$ dpm/m³ year,

$$c_2 = a_2 \cdot \omega \sqrt{\left(\frac{c_0}{\omega}\right)^2 + 1} = 1.70 \text{ dpm/m}^3 \text{ year},$$

and

$$I = 2.1 + 1.7 \sin(\omega \cdot t), \text{ with}$$

$$I_{max} = 3.8 \text{ and } I_{min} = 0.4 \text{ dpm/m}^3 \text{ year}.$$

If we assume the phase of the injection rate for ozone to be the same as for fission products we can now determine a_3 for ozone by adding 0.9 month to the phase difference between ozone and fission products which, according to Fig. 1*b*, is about one month. This gives for ozone $a_3 = 2$ months.

The beryllium-7 data offer another possibility for comparison. Be^7 is continuously produced in the atmosphere by cosmic radiation at a constant rate. The vertical distribution of the production rate, which is fairly well known from calculations (LAL *et al.*, 1958) shows a broad maximum at 16 km in middle and higher latitudes, i.e. at a somewhat lower height than ozone. In the tropics the major fraction is produced in the upper troposphere. The significant difference between the vertical distribution of Be^7 and that of ozone and artificial

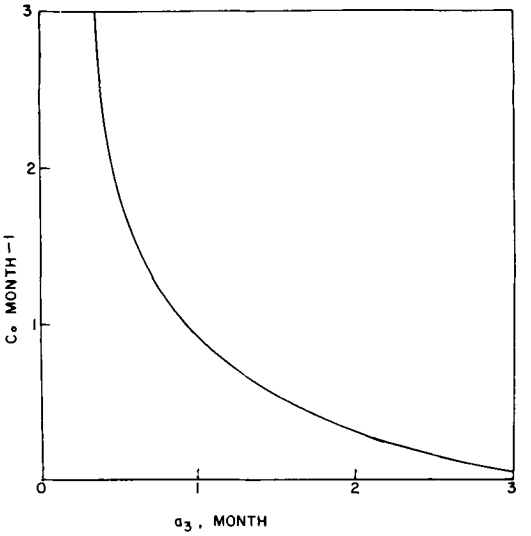

FIG. 5. Relationship between c_0 and a_3.

radioactivity is thus an upper tropospheric source in low latitudes and a stratospheric source area lower than that of ozone and fission products.

Several studies by Indian authors (e.g. LAL, RAMA & ZUTSHI, 1960) showed that the average rate of deposition of Be^7 in low latitude rains agrees with the tropospheric fraction of the production rate in these latitudes and with a residence time in the troposphere of about 35 days. This is a confirmation of the calculated production rates and of the fact that the exchange stratosphere-troposphere is slow compared with the half life of Be^7, 53 days. Recent measurements of the Be^7 concentration in the stratosphere (DASA 539*b*, 1961) are also in fairly good agreement with computed equilibrium concentrations, except near the tropopause where depletion becomes obvious. These profiles demonstrate, that by far most of the stratospheric beryllium reservoir is located north and south of 30° latitude.

Data on tropospheric Be^7 concentrations in middle and northern latitudes are plotted in Fig. 6 together with the fission product curve taken from Fig. 1*b*. Apparently the Be^7 data scatter more widely than those for fission products but the maxima seem to be in phase. The amplitude of Be^7 in England is a little larger and in Sweden and particularly in Chicago smaller than the amplitude of the fission products. It looks as if in general the amplitude

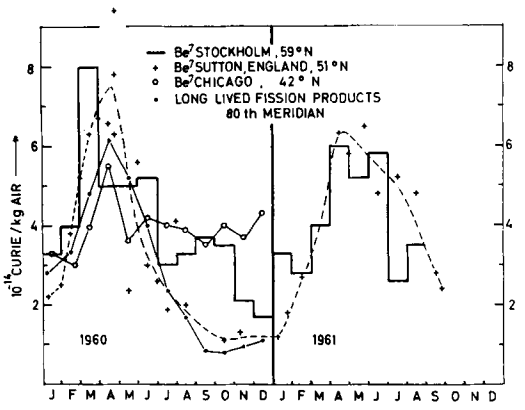

FIG. 6. Annual variation of the beryllium-7 concentration in surface air for Stockholm (LINDBLOM, 1962), Sutton (PARKER, 1962) and Chicago (GUSTAFSON *et al.*, 1961). For comparison the annual variation of long lived fission products from Fig. 1*b* in arbitrary units.

of Be^7 is somewhat but not much smaller than the amplitude of fission products and that it decreases with latitude (Chicago). This trend should be expected on the basis of the distribution of the beryllium production rate discussed above and implies that the rate of horizontal mixing in the troposphere is not sufficient to eliminate the latitudinal differences of the annual variation, i.e. it implies that the average tropospheric mixing time is not much shorter than the life time of aerosols.

Fig. 6 indicates that within the limits of accuracy the phase of the injection rate for Be^7 and for fission products is the same. Since fission products arrive from higher and beryllium from lower levels of the stratosphere than ozone this supports our conclusion that a_3 for ozone should be close to 2 months. The amplitude of the Be^7 concentrations seems to show that the amplitude of the injection into the troposphere in middle and northern latitudes is rather large and not very dependent on the height of origin within the stratosphere. This implies that the exchange between stratosphere and troposphere in these latitudes is controlled by large scale and high reacting processes, rather than by small and medium scale turbulent processes. These latter processes are unlikely to have such a pronounced annual variation. The Be^7 data are not representative enough to compute c_1 and c_2.

It should be pointed out that the annual variation of fission products and beryllium in the troposphere cannot be due to an inverse variation of the removal rate in the troposphere. In both cases rain is the most important removal process, but observations show clearly that both the concentration in rain and the deposition rate by rain are in phase with the concentration in air (for Be^7 see PARKER, 1962, and LINDBLOM, 1962; for fission products this is demonstrated for many locations).

We can summarize our discussion on the ozone budget and the stratospheric-tropospheric exchange as follows:

1. A comparison of the annual variation of tropospheric concentration of ozone, fission products and Be^7 indicates that the time delay a_3 with respect to the injection rate into the troposphere can be interpreted as being due to the rate of destruction or removal in the troposphere. This time delay is close to one month for aerosols and close to two months for ozone.

2. An a_3 value of two months for ozone gives the following figures for the ozone budget (see Table 4) if we also assume the values a_{1b} and a_{2b} as the most likely ones:

$$\tau_t = 3.3 \text{ months},$$
$$\tau_s = 3.7 \text{ years},$$
$$F = 0.60 \times 10^{-7} \text{ g/m}^2 \text{ sec},$$
$$I = 4.7 + 2.8 \sin(\omega \cdot t) \text{ tons/year},$$
$$I_{max} = 7.5 \text{ and } I_{min} = 1.9 \text{ tons/year},$$
$$I_{max}/I_{min} = 4.0.$$

3. These values seem to be at the same time a reasonable compromise between the various observational facts:

(*a*) The latitude variation of the Be^7 concentration in the troposphere (and also that of fission products, as we shall see later) indicates that the tropospheric mixing time is of the same order as the aerosol life time, i.e. about one month. In view of its rather uniform distribution, the life time of ozone can hardly be shorter than 3 months.

(*b*) A stratospheric residence time of 3.7 years of a constituent with a distribution similar to ozone seems to be quite acceptable in view of the results from fission products.

(*c*) The agreement of F with Regener's value is still satisfactory, although a larger discrepancy would not be disturbing.

(*d*) We feel that the true values of a_3, τ_t and τ_s for ozone might be even a little larger (e.g. $a_3 = 2.25$, $\tau_t = 4.4$ month, $\tau_s = 4.7$ years) rather than smaller, but not much, because otherwise τ_s seems to become too large.

A few words about the seasonal variation of the injection rate may be appropriate. If we accept the constants a_{1b} and a_{2b} as the most likely values in Table 4 we have for ozone

$$I_{max}/I_{min} = 4.0$$

and for fission products

$$I_{max}/_{min} = 9.5.$$

If Σ denotes the total stratospheric ozone burden (Fig. 1*d*) we can define an "instantaneous" stratospheric residence time of ozone by

$$\tau_i = \Sigma/I.$$

For the maximum and minimum of I in spring and fall we obtain the following values.

	Spring	Fall
I	7.5×10^8	1.9×10^8 tons/year
Σ	2.0×10^9	1.5×10^9 tons
τ_i	2.6	8.0 years

The ozone which is primarily removed in spring, is the amount Σ_l located in the lower stratosphere, which is approximately given by the difference of Σ between spring and fall

$$\Sigma_l = (2.0 - 1.5) \times 10^9 = 0.5 \times 10^9 \text{ tons.}$$

If this ozone is injected at the spring rate, an approximate residence time τ_l for this low stratospheric ozone is given by

$$\tau_l = 0.5 \times 10^9/0.75 \times 10^9 = 0.66 \text{ years.}$$

This is in agreement with the finding of MARTELL & DREVINSKY (1960) that debris injected into the low northern stratosphere in early winter has indeed an "instantaneous" residence time of this magnitude. It should be kept in mind, however, that the concept of an "instantaneous" life time or even the concept of an average life time of a certain area of the stratosphere is somewhat doubtful and can only describe conditions semi-quantitatively. Also, the calculation of our stratospheric ozone amount Σ_l is rather crude. These estimates shall only show that the conclusions from our model are generally consistent with a variety of observations.

We saw that tropospheric ozone has obviously very little variation with latitude. Nothing is known about a latitude dependence of the injection rate I, but whatever it may be, a tropospheric life time of about 3 to 4 months and perhaps a fairly uniform destruction rate at the surface of the earth will result in a rather uniform tropospheric ozone distribution. Condensed fission products have a tropospheric life time of about one month and it is, therefore, of interest to compare tropospheric ozone and fission product distribution. LOCKHART *et al.*, (e.g., 1959) provided extensive material on Sr^{90} and gross fission product concentration in air near the ground along the 80th meridian. Their data indicate a consistent variation with latitude, a maximum around 30° N and a minimum around 65° N. The ratio maximum to minimum is about 2:1. So far as we can see this is different from ozone and reflects the fact that the residence time of aerosols of about 4 weeks is of the same magnitude as the horizontal mixing time in the troposphere, a fact which was already indicated by the beryllium data.

The consistent maximum at 30° and the minimum at 65° can be due either to a variation of the injection rate with latitude or to a variation of the removal rate of aerosols, or to a combination of both.

In our previous discussion we sometimes referred to a mixing time within the troposphere. In this closing paragraph we will make an estimate of the rate at which large scale horizontal mixing within the hemisphere eliminates differences in horizontal distribution. We consider a simple model in which the latitudinal distribution of the concentration of a constituent is given by

$$K = K_1 \sin K_2 x$$

and in which the shrinking of the latitude circles with latitude is neglected. Here x varies from zero to d, where d is the distance from the equator to the pole and $K_2 = \nu\pi/d$. The variation from equator to pole consists of one maximum at 45° for $\nu = 1$ and two maxima for $\nu = 2$. If $E(\text{cm}^2/\text{sec})$ is the large scale eddy diffusion coefficient we have

$$\frac{\partial K}{\partial t} = E\frac{\partial^2 K}{\partial x^2} = -EK_1K_2^2 \sin K_2 x$$

or

$$\frac{\partial \ln(K)}{\partial t} = -EK_2^2.$$

The mixing time can be defined as the time τ_m in which the concentration differences are reduced to $1/e$

$$\tau_m = 1/EK_2^2 = d^2/Er^2\pi^2.$$

According to LETTAU (1951), E values range from 2×10^{10} to 2×10^{11} cm²/sec within the west wind belt. Since we are here interested in an average value for all latitudes, including the subtropics where latitudinal mixing is less pronounced we assume $E = 2 \times 10^{10}$ cm²/sec. This yields for $d = 1 \times 10^9$ cm

and $\nu = 1$, $\tau_m = 60$ days,

and for $\nu = 2$, $\tau_m = 15$ days.

These estimates of the effects of horizontal mixing can, of course, give nothing more than the order of magnitude of the mixing time to be expected. The calculated values seem to be in the right range of a few weeks, considering the fact that the subtropics represent a considerable fraction of the earth's surface.

Conclusions

Tropospheric ozone is a much more regular phenomenon than hitherto thought, at least in the northern hemisphere. With respect to ozone the troposphere can be considered a well mixed reservoir with a simple annual variation the phase of which is delayed against that of the stratospheric ozone variation. The analysis for the ozone budget which is presented here on the basis of these facts and a few assumptions and simplifications can only be regarded as a first approximation. However, it yields results which are in reasonable agreement with observations on ozone, fission products and beryllium-7. These results suggests that tropospheric ozone may be a very powerful tool for studying the exchange mechanism between stratosphere and troposphere and there seems to be enough justification for making an effort to establish a meridional network of representative surface ozone recording stations and to run it over several years continuously. This would provide better data for a_3 and may also show small systematic differences of the delay time, which by refined mathematical treatment can provide information on the injection rate as a function of latitude and perhaps longitude.

Recent data (BROECKER, MCMURRAY, MÜNNICH, OLSSON, VOGEL, 1962) seem to indicate that injections of bomb produced C^{14} from the stratosphere into the troposphere take place preferentially in polar regions so that a decrease in amplitude and an increase in phase difference results if the material spreads southward within the troposphere. With characteristic large scale mixing coefficients in the troposphere of the order of 10^{10} cm²/sec a time lag between the phase of injection and tropospheric concentration may therefore partly be due to differences in phase within the troposphere between northern and middle latitudes. Unfortunately no data on tropospheric ozone north of Arosa were available to the author to check this question for ozone. Vertical profiles of ozone show that the ozone leaks into the troposphere at all latitudes including the tropopause gap. The data in Fig. 1*c*, though not conclusive do not indicate a systematic phase difference within the southern hemisphere and the same is true for the latitude range from 19° N to 47°N (Fig. 1*a*). In Fig. 1*a* there is an indication that the spring maximum is a little earlier in Hawaii than in Arosa. Such a difference would be expected if the tropopause gap is the main way of exchange. However, the present data do not allow further conclusions.

With better data, the real annual variation of θ can be represented by Fourier series and a better expression for I can be obtained. Differences in the Northern and Southern hemispheres could give information on differences of the large scale hemispherical circulation pattern, particularly of the winter polar, stratospheric vortex and its breakdown in spring. Such differences should be expected on the basis of other meteorological observations.

Finally, a systematic study of the seasonal variation of ozone across the thermal equator should provide better and useful information on the interesting and important subject of the blocking action of the equatorial circulation for large scale exchange between the hemispheres, as indicated by ozone, carbon dioxide and tritiated methane data (JUNGE, 1962). Surface ozone, thus, seems to be another field of air chemistry which should receive more attention in future work.

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