Some aspects of the seasonal variation of carbon dioxide and ozone

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ABSTRACT

An attempt is made to estimate the seasonal source function, Q, of CO_2 on the basis of data for the biosphere, provided by Lieth, and for other sources. The variation of soil respiration appears to be the most uncertain factor. The resulting CO_2 variations in the atmosphere are calculated for horizontal exchange coefficients, K, which vary with latitude. Comparison with observations given by Bolin & Keeling shows that the results are not very sensitive with respect to the assumed variations of Q and of K with latitude. Previous results on the O_3 budget are used to calculate seasonal variations of tropospheric O_3 for stratospheric injection rates, and K values which vary with latitude. It is concluded that tropospheric O_3 may be a useful tracer for the study of the global exchange mechanisms between stratosphere and troposphere, and of related problems.

1. Introduction

Global seasonal variations of CO_2 and O_3 in the troposphere offer opportunities for quantitative studies of the budget of these constituents and of large-scale exchange processes. Bolin & Keeling (1963) analyzed seasonal CO_2 variations based on data covering latitudes from pole to pole. Assuming the horizontal eddy exchange coefficient K to be constant, they determined the seasonal and latitudinal distribution of the CO_2 source function. They could show that for $K = 3 \times 10^{10}$ cm^2 sec^{-1} this source function gives seasonal CO_2 variations which are in good agreement with the observations. The source function appeared to be in qualitative agreement with the expected behavior of the biosphere but no attempt was made for a quantitative comparison with independent data. In addition, the assumption of a constant K across the equator is perhaps a rough approximation and the question arises to what degree this may affect the results. In this paper we will look further into some of these questions.

In 1962 one of the present authors made a study of the global O_3 budget. On the basis of a few available representative data on the seasonal variation of tropospheric O_3 and the time delay between peak concentrations in the stratosphere and the troposphere, a quantitative expression for the injection rate of O_3 from the stratosphere into the troposphere was obtained. At that time, however, no attempt was made to study the question of the latitudinal distribution of this injection. The O_3 model developed provides an opportunity to investigate the effect of various injection mechanisms on the tropospheric O_3 variations. If it can be shown that the latitude dependence of the seasonal O_3 variation is sufficiently sensitive to the latitude of injection, tropospheric O_3 may be a useful natural tracer to study stratospheric-tropospheric exchange processes.

The present CO_2 and O_3 studies are both based on similar theoretical considerations and numerical programs. For CO_2, we estimated the latitudinal distribution of the source function from biological and other data, and calculated the resulting CO_2 distribution for different models of K including some which show a pronounced decrease at the equator. For O_3, we assumed various models for the latitude dependence of the injection into the troposphere and computed again the tropospheric O_3 distributions. Here interest was focused on whether the resulting distributions are sufficiently different that more and better tropospheric O_3 data may provide information on the injection mechanism.

2. Seasonal component of the CO_2 source function

The seasonal variation ($Q(\mu, t)$ of the CO_2 source function, with $\mu = \sin \varphi$, φ = latitude and t = time, is influenced by:

Table 1. *Net production of carbon in plants according to Gessner (1959) and Müller (1960)*

Form of vegetation	Net production per year in 10^{15} g
Boreal coniferous forest	1.5
Deciduos forest	1.5
Tropical and subtropical forest	10.3
Transition forest	1.4
Grassland	1.6
Agricultural areas	4.2
Deserts	0.5
Total	21.0

(*a*) The biosphere over land.
(*b*) Human activities.
(*c*) Temperature variations of the ocean surface.
(*d*) The biosphere of the ocean surface waters.

We will attempt to estimate these contributions. (*a*) About 75 per cent of the CO_2 assimilated by plants is converted to organic material and 25 per cent is released again to the atmosphere by respiration. On the average, the net uptake of CO_2 by plants is compensated by the decay of organic matter on and in the soil. The release of CO_2 from the soil is to a large degree due to bacterial action and depends on the type, structure and condition of the soil. The net uptake of CO_2 by plants is restricted to the growing season, which is the warm period in northern latitudes and the rainy period in subtropical areas. At the equator there is no seasonal variation of growth and decay, and the CO_2 budget will be balanced throughout the year.

The net uptake of carbon from the atmosphere can be determined from the yearly production of plant material. Table 1 gives figures by Gessner (1959) and Muller (1960).

For our considerations it is important to know how the net uptake is distributed with latitude. Lieth (1965) attempted to plot the C uptake on a world map by making use of all available literature. He considers these maps as a first approach, and emphasizes that details are still uncertain. We replotted these maps on others of equal area and integrated the values for each 10° latitude belt. Table 2 gives the result. As to be expected, most of the C is exchanged in the tropics. The difference between the hemispheres is apparent. The total uptake according to Table 2 is 38.4×10^{15} g C. This is higher by a factor of 1.83 than the value in Table 1, and reflects the quality of the data presently available.

For our present purpose, these figures have to be converted to ppm in the atmosphere. One gram C gives 3.67 g CO_2. The surface area of the earth for a 10° latitude belt is $2\pi R^2 \cos\varphi \, d\varphi$, with $d\varphi = 0.175$ and $R = 6.366 \times 10^8$ cm. If we assume uniform mixing up to the troposphere, and no penetration into the stratosphere, the air masses, m, involved are:

for $\varphi > 30°$ and a tropopause height of 10 km $m_1 = 755$ g cm^{-2},
for $\varphi < 30°$ and a tropopause height of 16 km $m_2 = 927$ g cm^{-2}.

With $\varrho_{air} = 1.29$ and $\varrho_{CO_2} = 1.98$ the densities of air and CO_2 at STP respectively, the resulting mixing ratio is

$$[CO_2] = \frac{3.67 \times C \times \varrho_{air} \times 10^{-6}}{2\pi R^2 \cos\varphi \times d\varphi \times m_i \, \varrho_{CO_2}} \text{ (ppm year}^{-1}\text{)}.$$

Fig. 1*A*, curve 1, gives Lieth's figures in ppm year^{-1} as a function of latitude. If net uptake and the release from the soil are balanced within each latitude belt, as should be expected, and if there were no seasons, $Q(\mu, t) = 0$. A seasonal difference between uptake and release is primarily due to the more pronounced variation of net uptake as compared with soil release. For $\varphi >$ about 30° the growing season is determined by higher temperatures; for $\varphi < 30°$ rainfall is the controlling factor. For $\varphi > 30°$ we can

Table 2. *Total carbon uptake by plants over land for 10° latitude belts in 10^{15} g year^{-1}, Lieth (1965)*

Latitude ...	5°	15°	25°	35°	45°	55°	65°	75°	85°
Northern Hemisphere	6.4	3.9	3.2	2.5	2.8	2.5	1.3	0.0	0.0
Southern Hemisphere	7.2	4.9	2.4	1.1	0.2	0.0	0.0	0.0	0.0

Table 3. *Climatological factor f*

$\mu = \sin\varphi$ ...	0.0	0.1	0.2	0.3	0.4	0.5	0.6
Norhern Hemisphere	0.00	0.00	0.16	0.48	0.58	0.80	1.00
Southern Hemisphere	0.00	0.00	0.15	0.43	0.58	0.78	1.00

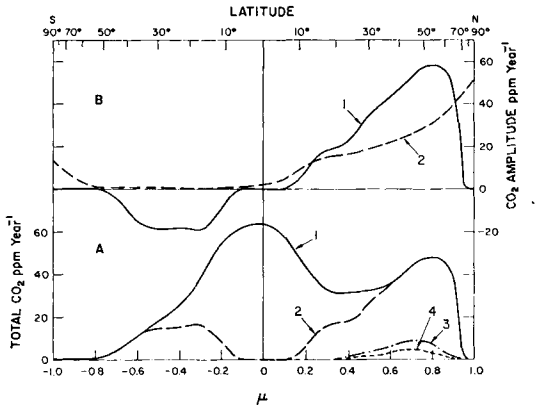

Fig. 1. (*A*) Curves: *1*, Total uptake by plants from Table 2 converted to ppm CO_2 year^{-1}; *2*, same as curve 1 after application of factor *f*; *3*, total anthropogenic source function according to Bolin & Keeling (1963); *4*, estimated upper limit of the seasonal component of curve 3. Curves 1 and 2 should be reduced by a factor 0.72. (*B*) Curves: *1*, Amplitude of the seasonal component of the CO_2 source function assuming a 39 per cent soil respiration during summer; *2*, computed amplitudes of CO_2 by Bolin & Keeling (1963). Curve 1 is correct.

expect that the total amount of C given in Table 2 or Fig. 1*A* is removed from the atmosphere during the summer. For $\varphi < 30°$ summer and winter will only differ by a fraction, *f*, of this amount, with *f* becoming zero at the equator. Since rain is the important factor in these latitudes we tried to estimate *f* by

$$f = \frac{N_S - N_W}{N_S + N_W},$$

where N_S and N_W is the average representative number of rainy months in summer and winter for each 5° latitude belt, respectively. These values for N_S and N_W were determined with the help of the atlas by Walter & Lieth (1960). Table 3 gives the result. At the equator $f = 0$, as to be expected, and for $\varphi > 30°$ $f = 1$. We know that this procedure can only give a rough approximation. But with the biological data presently at hand it is hardly possible to arrive at much more reliable figures. After application of *f* to curve 1, we obtain curve 2, Fig. 1*A*.

In our calculations (see Section 4) it will be assumed that the source function for each latitude has the form

$$Q(\mu, t) = a(\mu) \times \cos 2\pi t,$$

with $0 \leqslant t \leqslant 1$ for the year. The figures of $a(\mu)$ are therefore obtained from curve 2, Fig. 1*A* by multiplication with π. However, these $a(\mu)$ values do not include the relase of CO_2 from the soil. The seasonal variation of this release is not known, but it can be expected to be somewhat higher during the warm season. If ε is the fraction of CO_2 released during summertime, the actual uptake of CO_2 during the warm season is $(1-\varepsilon)$ CO_2 and the same amount is released from the soil during the winter. The actual values of the amplitude thus become

$$a(\mu) = [CO_2] \times f(1-\varepsilon)\pi.$$

In Fig. 1*B*, curve 1, $a(\mu)$ is plotted for $\varepsilon = 0.39$ for reasons to be discussed on page 429. The values of $a(\mu)$ assume, of course, opposite sign in the two hemispheres.

(*b*) The anthropogenic contribution to the seasonal source function is not easy to estimate because of inadequate statistical data. Only for the U.S. were we able to obtain sufficient data on household fuel consumption, i.e., for cooking and heating, to estimate its contribution to total fuel consumption. The fraction of all three fuel types—coal, oil and gas—used for domestic purposes is about 30 per cent. Heating, which is the major contribution to the seasonal variation of the anthropogenic source function, is a fraction of this, perhaps 50 per cent. The fraction of total fuel used for domestic purposes is most likely higher in countries which are less industrialized. For lack of data we think that on a worldwide basis the fraction

may be 50 per cent, with possibly 25 per cent used for heating alone, i.e. causing the seasonal variation of the anthropogenic source.

The total anthropogenic output at the present time is 1.6 ppm year^{-1}, averaged for the whole atmosphere. Bolin & Keeling assumed the source to be located exclusively in the northern hemisphere and calculated an approximate latitudinal distribution which is reproduced in Fig. 1*A*, curve 3 (after reduction by a factor of 0.67, to adjust the value of the integral under the curve from 2.4 ppm in their Fig. 22, to the correct value of 1.6 ppm). Twenty-five per cent of this would be our estimate of the variable component. But we have to consider the fact that the variable component will be confined to the troposphere in contrast to the long-term increase of CO_2 which penetrates into the upper atmosphere. For this reason, and to be on the safe side, we took 50 per cent of curve 3. This curve, 4, represents our estimated upper limit of the variable anthropogenic component of the source function. It amounts to about 15 per cent of the total uptake by plants in the same latitude regions, and to about 30 per cent of the amplitude given in Fig. 1*B*, curve 1. It can therefore apparently not be neglected, but considering the uncertainties in the biological data we did not include the anthropogenic contribution in Fig. 1*B*, curve 1. Because the heating occurs during the cold season, this component tends to increase the natural variation.

(*c*) Another contribution to the seasonal variation can come from temperature changes of the ocean surface waters. Kanvisher (1960) has shown that a ± 1°C change in temperature of 15°C ocean water results in a change of ± 0.17 cm^3 CO_2 per liter of ocean water for atmospheric mixing ratios of 315 ppm. To compare the effect on atmospheric CO_2 with the previous sources we chose the latitude belt between 30 and 40°, since for this belt the annual temperature change has a maximum with an average amplitude of ± 4°C. Assuming 40 meters to be the average thickness of the layer involved in the annual temperature variation, the total amount of CO_2 released or taken up amounts to $\pm 0.6 \times 10^{15}$ g CO_2. The uptake by vegetation of the same latitude belt is, 9.2×10^{15} g CO_2 according to Table 2. Considering that the exchange time between atmosphere and ocean is about 5 years, the calculated CO_2 exchange of the ocean water will in reality be much smaller. We can conclude, therefore, that the seasonal temperature changes of the ocean surface waters do not contribute to $Q(\mu, t)$.

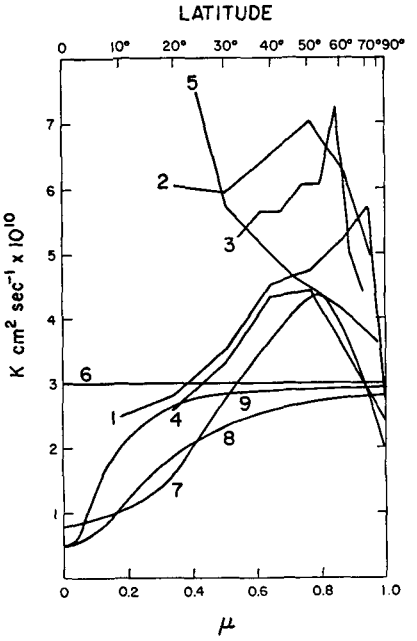

Fig. 2. Comparison of average K values as a function of latitude. Curves: *1*, Lettau (1939), Northern Hemisphere; *2*, Wagner (1938), Northern Hemisphere; *3*, Möller (1950*a*), North Atlantic; *4*, Möller (1950*b*), Northern Hemisphere; *5*, Defant & Defant (1958), Northern Hemisphere; *6*, Bolin & Keeling (1963), global average; *7*, values based on global wind data by Flohn (1961); *8*, *9*, model distributions of K used in the calculations for comparison with curve 6.

(*d*) The change in biological activity in ocean waters and associated exchanges of CO_2 with the atmosphere are hard to assess on a global basis due to lack of data. The production data given by Lieth in his map cannot be considered reliable, and seasonal variation remain unknown. Again, the low exchange rate between ocean and atmosphere has to be taken into account. On the basis of the information available, this contribution appears to be negligible.

3. Meridional eddy diffusion coefficient

Bolin & Keeling used in their analysis a constant eddy diffusion coefficient for the whole troposphere, given by $K = 3 \times 10^{10}$ cm^2 sec^{-1}. In the subsequent discussion we will compare this value with other information.

Lettau (1933, 1939) calculated the horizontal austausch coefficient $A = \varrho K$(g cm^{-1} sec^{-1}), ϱ = air density, on the basis of the mixing length concept, using surface weather maps to determine the meridional geostrophic wind components. His values thus refer to the lower troposphere and do not include the effects of surface friction. He computed A for the whole northern hemisphere and the winter, 1910, from which we derived average values for different latitudes, Fig. 2, curve 1. The data were converted to K values for better comparison by applying a density $\varrho = 10^{-3}$ g cm^{-3} which is representative for the lower troposphere. The values can be considered a first approximation only, because they are based on rather old data of one winter, and are not representative for the whole troposphere.

Wagner (1938) also used the mixing length concept, but in a somewhat different manner. He determined the meridional transports by taking the differences between the relative pressure minima and maxima for each latitude. These pressure differences represent the geostrophic wind components for the lower tropospheric layers. The mixing length is estimated from the average distance between the extremes of the surface pressure. His values are based on March 1931 only, and are given by curve 2. They are less representative than those of Lettau because of the shorter time period. Both sets of data are based on the mixing length concept, whose application to large scale horizontal exchange may be somewhat dubious.

Möller (1950*a*, *b*) modified the mixing length concept by a coefficient α (sec^{-1}) which characterizes the speed at which an air parcel assumes the properties of the surroundings. He arrives at the expression $K = \bar{v}^2/\bar{\alpha}$ where $\bar{v}^2$ is the mean square of the meridional wind component and $\bar{\alpha}$ an average value. If $\bar{\alpha}$ is constant with time and space, this concept provides a possibility to calculate K from v data. Möller showed that for a period of 13 years α is rather constant throughout the year at 500 above ground in central Europe. Assuming that the same value can be applied to the whole northern hemisphere, he calculated A values from surface wind data over the North Atlantic and also for the northern hemisphere during January. Conversion by $\varrho = 10^{-3}$ g cm^{-3} to K, and averaging for latitude belts results in curves 3 and 4. The assumption of $\bar{\alpha}$ being constant with latitude was never proven and the data again have to be considered with caution.

We applied the same concept with the same $\bar{\alpha}$ value for a height-latitude cross section of meridional wind components published by Flohn (1961). Curve 7 gives these figures, which are representative for the whole depth of the troposphere and for a whole year.

Curves 1 through 4, and curve 7, although obtained by quite different and approximate methods as well as for different periods and areas, agree reasonably well with regard to the general level and the general tendency to decrease toward the equator. A possible exception is curve 2. This seems to indicate that the assumption of a constant K is only a rough approximation. One set of data, curve 5, obtained by A and F. Defant (1958), shows a different trend, however. These authors attempted to calculate K by considering the global heat budget and its variation with latitude. Because of the uncertainty of some of the parameters involved, the values cannot be considered very reliable. It should be kept in mind, however, that this method is the only one which includes the net effect of the Hadley circulation on latitudinal exchange, and this may partly account for the difference. The Hadley circulation will tend to enhance the exchange between the equator and $\varphi < 30°$. For transport of water vapor and momentum (see e.g., Palmén & Alaka, 1952) we know that the organized circulation near the equator can exceed the turbulent fluxes considerably. But it should be noted that both water vapor and momentum have their sources in the shallow trade wind currents. These atmospheric constituents are therefore much more affected by the Hadley circulation than those which are rather uniformly mixed vertically.

At present we have no way of assessing the influence of the Hadley cell on tropospheric transport for such constituents as CO_2 and O_3. The latitudinal variation of the net values of K in the tropical zone may vary between curve 7 and the constant value of curve 6. In order to study the effect of any restriction of the horizontal exchange in the equatorial region, we calculated the seasonal variations for CO_2 and O_3 for K_6, K_7 and also for assumed model distributions like K_8 and K_9. These latter K values show a decrease at the equator by a factor of 6.

4. Computation of CO_2 variations

If $q = q(\mu, t)$ is the variation of the CO_2 mixing ratio with latitude and time around the annual average value $q(\mu)$, $Q = Q(\mu, t)$ source function, R the earth's radius, and $K = K(\mu)$ the horizontal eddy diffusion coefficient, the equation for horizontal diffusion in polar coordinates is (Bolin & Keeling, 1963)

$$\frac{\partial q}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial \mu}\left[K(\mu)\,(1-\mu^2)\,\frac{\partial q}{\partial \mu}\right] + Q. \qquad (1)$$

Bolin & Keeling assumed K to be constant and expanded for each latitude the observed q values with regard to t in Fourier series and with regard to μ in Legendre Polynomials. From these data they computed the source function $Q(\mu, t)$. On the basis of CO_2 budget considerations and of comparisons between observed and calculated q distributions, they derived an average K value of 3×10^{10} cm^2 sec^{-1}.

In our calculations we tried to determine $Q(\mu, t)$ directly from biological, climatological and other data, with the intent to obtain $q(t, \mu)$ for the general case of a variable $K(\mu)$. To keep the calculations within reasonable bounds, we assumed for the time variation of $Q(t, \mu)$ trigonometric functions with the same phase at all latitudes. For the present purpose this approximation is justified since we are primarily concerned with a comparison between the varous models for K. Even with this simplifying assumption the case for a variable $K(\mu)$ can only be solved by numerical computations. For this purpose we replaced q and Q by

$$z(\mu, t) = [\phi_1(\mu) + i\,\phi_2(\mu)]\,e^{i\,2\pi t} \qquad (2)$$

and

$$Z(\mu, t) = [\psi_1(\mu) + i\,\psi_2(\mu)]\,e^{i\,2\pi t}, \qquad (3)$$

with the amplitudes being expanded in Legendre Polynomials

$$z(\mu, t) = \sum_{n=0}^{N} k_n P_n(\mu)\,e^{i\,2\pi t}, \qquad (4)$$

$$Z(\mu, t = \sum_{n=0}^{N} K_n P_n(\mu)\,e^{i\,2\pi t}, \qquad (5)$$

and with

$$k_n = q_n + ip_n \quad \text{and} \quad K_n = Q_n + iR_n. \qquad (6)$$

Inserting (4) (5) in (1) gives

$$\sum_{n=0}^{N}\{K(\mu^2-1)\,P_n'' + [K'(\mu^2-1) + 2\,\mu K]\,P_n' + i\,2\pi R^2 P_n\}\,k_n = R^2\sum_{n=0}^{N} K_n P_n. \qquad (7)$$

Using the relation

$$(1-\mu^2)\,P_n'' - 2\,\mu P_n' + n(n+1)\,P_n = 0 \qquad (8)$$

results in

$$\sum_{n=0}^{N}[K'(\mu^2-1)\,P_n' + (i\,2\pi R^2 + n(n+1)\,K)\,P_n]\,K_n = R^2\sum_{n=0}^{N} K_n P_n. \qquad (9)$$

N is the number of terms in the expansion of Q and also gives the upper limit of the expansion in (7). With the aid of the recursion formula

$$(\mu^2-1)\,P_n' = n(\mu P_n - P_{n-1}), \qquad (10)$$

we obtain

$$\sum_{n=0}^{N}[K'n(\mu P_n - P_{n-1}) + n(n+1)\,KP_n + i\,2\pi R^2 P_n]\,K_n = R^2\sum_{n=0}^{N} K_n P_n. \qquad (11)$$

A comparison of coefficients in (11) is only possible if the terms

$$F_n(\mu) = K'(\mu)\,n(\mu P_n - P_{n-1}) + n(n+1)\,K(\mu)\,P_n$$

and

$$G_n(\mu) = 2\,\pi R^2 P_n(\mu)$$

are again expanded in Legendre Polynomials

$$F_n(\mu) = \sum_{m=0}^{N} D_{mn} P_m(\mu), \qquad (12)$$

$$G(\mu) = \sum_{m=0}^{N} C_{mn}\,P_m(\mu)\,2\,\pi R^2. \qquad (13)$$

Here

$$C_{mn} = 1 \text{ for } m = n \quad \text{and} \quad C_{mn} = 0 \text{ for } m \neq n.$$

The coefficients D are given by

$$D_{mn} = (m + \tfrac{1}{2})\int_{-1}^{+1} F_n(\mu)\,P_m(\mu)\,d\mu. \qquad (14)$$

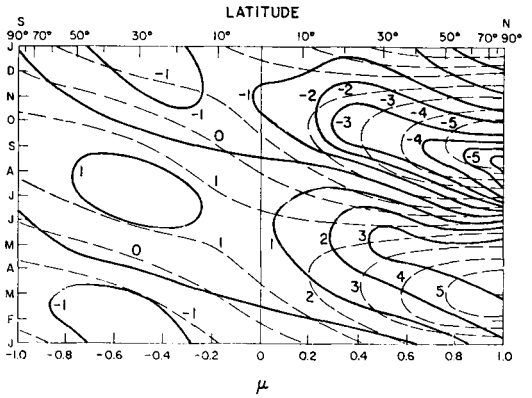

Fig. 3. Isopleths of the seasonal variation of CO_2 in ppm. Solid lines: Observed values according to Bolin & Keeling. Dashed lines: Calculated $q(\mu, t)$ values for $K = 3 \times 10^{10}$ cm^2 sec^{-1}.

If these expansions are inserted into (11) comparison of the coefficients and separation of the real and imaginary part results in

$$\sum_{n=0}^{N} \left(\frac{D_{on}}{R^2} q_n - 2\pi C_{on} p_n \right) = Q_0 \qquad (15)$$

$$\sum_{n=0}^{N} \left(\frac{D_{Nn}}{R^2} q_n - 2\pi C_{Nn} p_n \right) = Q_N$$

and

$$\sum_{n=0}^{N} \left(2\pi C_{on} p_n + \frac{D_{on}}{R^2} p_n \right) = R_0$$

$$\sum_{n=0}^{N} \left(2\pi C_{Nn} p_n + \frac{D_{Nn}}{R^2} p_n \right) = R_N$$

The real part of the solution of (1) considering (2) and (3) gives

$$q(\mu, t) = \sum_{n=0}^{N} (q_n \cos 2\pi t - p_n \sin 2\pi t) P_n(\mu), \qquad (16)$$

with q and p to be determined by (15).

In order to perform the numerical calculations, $Q(\mu, t)$ and $F_u(\mu)$ have to be expanded in Legendre Polynomial. For functions like $F_u(\mu)$ which vary considerably in the interval $-1 \leqslant \mu \leqslant +1$ it is necessary to approximate using 4th order parabolas. It can be shown that expansion to $n = m = 16$ gives reasonable approximations for the eddy diffusion coefficient K_7, K_8 and K_9 Fig. 2.

5. Results of CO_2 computations

As mentioned in Section 2, the seasonal variations of soil respiration, i.e. the value of ε, is the most uncertain parameter for determining the amplitude of $Q(\mu, t)$ from curve 2, Fig. 1*A*. We found in our calculation that the amplitudes given by curve 1, Fig. 1*B*, give $q(\mu, t)$ distributions which agree reasonably well with the observations. Curve 1, Fig. 1*B* was obtained from curve 2, Fig. 1*A* by assuming $\varepsilon = 0.39$ for all latitudes. Fig. 3 gives a comparison in isopleths of Bolin & Keeling's observations with our computations of q, using the amplitudes of curve 1, Fig. 1*B*, together with a constant $K = 3 \times 10^{10}$ cm^2 sec^{-1}. A better comparison for selected latitudes is afforded by Fig. 4.

In this first set of data the calculations were intentionally made for the same constant K used by Bolin & Keeling, in order to allow comparison with their analysis. It can be seen, particularly in Fig. 4, that the magnitude of our calculated amplitudes comes out reasonably well, considering both summer and winter conditions. The deviations from the observed data refer primarily to the phase. They are due to the unrealistic assumption of a simple trigonometric function for the time dependence of $Q(\mu, t)$. The observed data show a pronounced asymmetry between summer and winter, which cannot, of course, be reproduced by our model. The uptake of CO_2 in summer occurs during a shorter period than the release during winter, resulting in higher amplitudes during the warm season. Further southward the agreement both for amplitudes and phase becomes quite good, except near the south pole.

We should discuss this result a little further. The comparison between the observed and the calculated values in Figs. 3 and 4 is somewhat subjective, and slightly smaller amplitudes of our source function may have resulted in even better agreement. But if we accept curve 1, Fig. 1*B* as a good choice the question remains to what degree this confirms curve 2, Fig. 1*A*. In order to convert curve 2, Fig. 1*A* into curve 1, Fig. 1*B*, ε must be 0.39. But we do not know how good curve 2, Fig. 1*A* really is. If for instance this curve is replaced by another which differs by a factor $\delta \gtrless 1$ we are able to compensate this by replacing ε by ε^1 according to

$$a(1-\varepsilon^1)=0.61; \quad \varepsilon^1=\frac{a-0.61}{a}.$$

Since ε^1 has to be $0 \leqslant \varepsilon^1 \leqslant 1$, a cannot be smaller than 0.61. The total uptake figure of Müller & Gessner was lower by a factor of 0.54 than that of Lieth. If we assume this factor to be independent of latitude $a = 0.54$. We see that this is not possible and that the figures of Müller & Gessner are apparently too low. On the other hand it is likely that the decay of organic matter is higher in summer than in winter, i.e. that $\varepsilon > 0.5$. If this is correct $a > 1.22$. This suggests that the correct net uptake may be even somewhat larger than the values of Lieth, but since we know practically nothing about ε it is not possible to draw any further conclusions. We feel, therefore, that comparison with atmospheric CO_2 data supports the data of Lieth but that better data for ε are needed.

It is of interest to compare our source function with that obtained by Bolin & Keeling. Since the latter is expanded in a Fourier series, there is no simple amplitude which can be compared directly with our curve 1, Fig. 1*B*. The best alternative is to determine from their source function data (Fig. 27) by integration the total uptake or release, and to convert this to amplitudes by multiplying with π. The result is given by curve 2, Fig. 1*B*. The increase toward the poles is, of course, unrealistic and is partially due to truncation errors of their series expansions. In middle-north latitudes their data show values about one half of ours, but further south the agreement is better.

They found no sources in the southern hemisphere, but they adjusted their analysis in such a way as to give minimum values south of the equator.

Although Q is not negligible in the southern hemisphere the effect on q is small, as is evident in a comparison between the CO_2 observations, the computations by Bolin & Keeling and our q values in Figs. 3 and 4. Considering the differences between curves 1 and 2, Fig. 1*B*, it is apparent that the resulting q values are not very sensitive to variations in Q. Atmospheric CO_2 observations are therefore hardly suitable to obtain information on the latitude distributions of the seasonal source function.

We calculated q for our source function, curve 1, Fig. 1*B*, and for a variety of $K(\mu)$, including those of curves 7, 8 and 9, Fig. 2. The

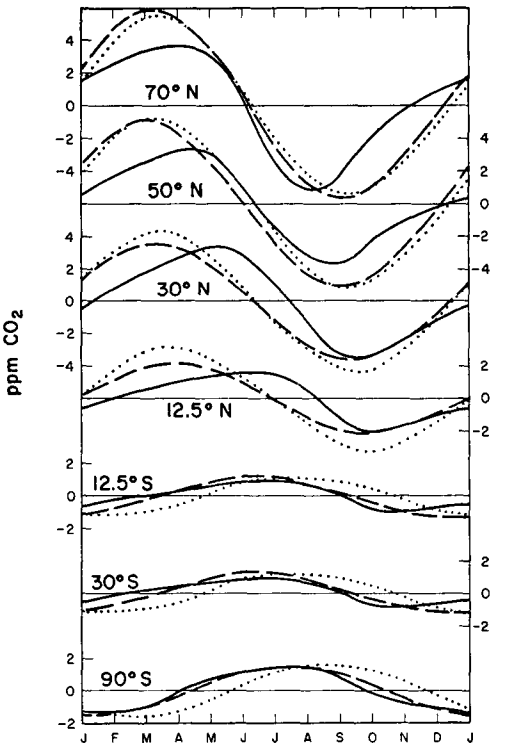

Fig. 4. Same as Fig. 3, but for discrete latitudes to show more detail. Solid lines: Observed values according to Bolin & Keeling. Dashed lines: Calculated $q(\mu, t)$ values for $K = 3 \times 10^{10}$ cm^2 sec^{-1}. Dotted lines: Calculated $q(\mu, t)$ values for K according to curve 7, Fig. 2.

differences among the resulting three sets of q data were so small that we included in Fig. 4 only those for curve 7. But even the differences compared with a constant K are not large. In low latitudes in the northern hemisphere the amplitudes of q for curve 7 are slightly larger with about the same phase; south of the equator there is a phase delay but no change in amplitude. This is what can be expected if the exchange across the equator is restricted.

The insensitivity of q with respect to latitudinal variations of K is an interesting result. It shows that it will hardly be possible to obtain information on variations of K from CO_2 data, unless the number and quality of the data are considerably increased and better knowledge for the source function is available. On the other hand, we see that calculations of global variations of tracers, at least in cases similar to that of the CO_2, can give quite satisfactory results, with the simple assumption of a constant K.

Table 4. *Information on the seasonal variation of O_3 on 4 stations in the Northern Hemisphere*

Name of station	Latitude	Amplitude of O_3 variation $\mu g\ m^{-3}$	Time of spring maximum
Arosa	47°	14	May
Srinagar	34°	10	May
Ahmedabad	23°	14	February–March
Mauna Loa	19°	12	April

6. The seasonal component of the O_3 source function

In a study of the global O_3 budget Junge (1962) arrived at a value for the hemispherical rate of injection of stratospheric O_3 into the troposphere

$$I = c_1(1 + c_2 \sin 2\pi t)\ [g_{O_3}\ \text{year}^{-1}],$$

with $c = 4.7 \times 10^{14}$ g year^{-1}, $c_2 = 0.6$ and $0 \leqslant t \leqslant 1$. $t = 0$ should be chosen so that the maximum of I occurs about the middle of March. This injection is balanced by destruction of O_3 at the earth's surface, at a rate assumed to be proportional to the concentration $q(\mu, t)$ of O_3, i.e. equal to $c_0 \times q(\mu, t)$, with c_0 remaining constant with time and space. On the basis of the data available the most likely value for the tropospheric residence time of O_3, $\tau = c_0^{-1}$ is 3 months, or $c_0 = 3.6$ year^{-1}. This destruction rate results in a delay of the phase of q against that of I by 1 to 2 months, so that the spring maximum of $q(\mu, t)$ in May agrees with observations.

This quantitative model of the tropospheric O_3 budget is certainly only a first approach, but has provided the best figures on tropospheric O_3 obtained so far. It was derived on the basis of only four available representative recordings of lower tropospheric O_3 in the northern hemisphere, and the occurrence of a time difference of 1 to 2 months between the spring maximum of O_3 in the lower stratosphere and the troposphere. Some important information for these stations is given in Table 4. All these stations are located in unpolluted areas, and with the exception of Ahmedabad, all are located on mountains. For evaluation only the daily maximum values were taken, which occur mostly around noon when turbulence reaches a maximum. These values can be considered reasonably representative for the lower troposphere because under these conditions the ozone-depleted layer near the earth's surface is to a large extent, eliminated.

Table 4 derived from Fig. 1, Junge (1962), shows that the amplitudes do not differ much considering the large differences in location of the stations, the different years of observations and the different methods used. This immediately suggests a rather uniform source and sink of O_3, or a sufficiently long residence time, or a combination of these factors. The times of spring maxima are also very much similar, except for Ahmedabad. This station, however, is strongly influenced by air masses from the southern hemisphere during the monsoon season, and can therefore not be considered representative of northern hemisphere conditions.

Warmbt (1964) has recently discussed results from a network of seven stations in Central Europe, where surface O_3 concentrations were measured over several years four times or more a day. Two of the stations are located on mountains at 1200 and 1100 meters above sea level and two stations are located at the coast of the Baltic Sea. The average values of the daily maxima of these four stations agree well with those listed in Table 4 and this confirms our concept. The three other inland stations show lower values and it is likely that they are influenced by air pollution or other local effects.

Another interesting set of data was provided by the North American O_3 network (Hering & Borden, 1965). They gave bimonthly average values for 2 km layers in the troposphere for 10 stations ranging in latitude from Thule to the Canal Zone. Although these data confirm very nicely the uniform distribution of tropospheric O_3, the number of data and their accuracy at the low tropospheric concentrations is not sufficient to derive reliable Q values.

Representative data from the southern

hemisphere are available from Antarctica stations, Little America and Mirny. At both stations the amplitudes are not much different from the values in Table 4, but surprisingly, the phase is delayed only by about 3 months instead of 6, as should be expected if the hemispherical circulation is symmetrical. Also the maxima are broader and the minima sharper than for the stations in Table 4. This must be due to some basic difference in the hemispheric circulation pattern and is itself a very interesting fact. Due to the lack of information for latitudes between Antarctica and Hawaii, it is hard to judge how far this can be assumed for the whole southern hemisphere. For this reason we assumed symmetry of the source function in both hemispheres for our exploratory calculations.

The tropospheric O_3 budget requires a decrease of the O_3 mixing ratio towards the earth's surface to compensate for the destruction.

The data from the North American network (Hering & Borden, 1965) show that the concentration of O_3 in $\mu g\ m^{-3}$ does not change with altitude. This means that the mixing ratio increases with altitude approximately inverse to the air density.

Since tropospheric O_3 data are normally given in ngm^{-3}, we can assume a uniform concentration to simplify our calculations, emphasizing that this assumption has no effect on the results.

If $b(\mu)$ is the latitude dependent amplitude of the seasonally-variable component of the O_3 source function, we have

$$Q(\mu, t) = b(\mu) \sin 2\pi t - c_0 q(\mu, t)$$

with

$$\int_0^1 b(\mu)\, d\mu = 10^{12} c_1 \times c_2 (2\pi R^2 H)^{-1} [\mu g m^{-3}\ \text{year}^{-1}],$$

$H = 10^6$ cm as the average height of the troposphere neglecting higher values at tropical latitudes. In complex form, and expanded in Legendre Polynomials, we have

$$Z(\mu, t) = \sum_{n=0}^{N} (iR_n + c_0 k_n)\, P_n(\mu)\, e^{i2\pi t}$$

with

$$b(\mu = \sum_{n-0}^{N} R_n P_n(\mu)$$

and

$$K_n = q_n + ip_n.$$

By inserting $Z(\mu, t)$ in equation (1) the solution is obtained in a similar way as for CO_2.

The model of the O_3 budget provides no information on the latitudinal variation of the amplitude of the injection rate, i.e. on $b(\mu)$. This dependence of b on μ reflects the stratospheric-tropospheric exchange process which is of considerable importance for meteorology. Up to the present time we know very little about this mechanism, and opinions on this subject differ widely. Danielsen (1964) demonstrated the occurrence of large scale folding processes of the tropopause near jet streams, leading to intrusions of stratospheric air into the troposphere. Although individual cases of this process are now decumented very well by studies of such slow changing atmospheric properties as the potential vorticity or the concentration of radioactive fission products, the question remains as to the fraction of the total hemispherical air exchange between stratosphere and troposphere due to this mechanism.

This process will occur primarily at those latitudes in which the tropical jet stream is most frequent, i.e. between about $\varphi = 30$ and 40°. Observations by Feely (1960) on the distribution of fission products in the lower stratosphere, and by Briggs & Roach (1963), on the distribution of water vapor and ozone in the vicinity of jet streams, support the idea that the latitudes of the tropopause break are important for the exchange. The increase of I in springtime is most likely due both to an intensification of jet stream activity, and to the greater rate at which O_3 is supplied from higher stratospheric layers at lower latitudes to the lower stratosphere at higher latitudes at late winter.

Curve 1, Fig. 5*A* gives a model for $b(\mu)$ based on these considerations. However, several authors have presented data which indicate that the polar tropopause is another region of preferred injection, e.g. Martell & Drevinsky (1960), Lockhart *et al.* (1959, 1960) and Munnich & Vogel (1963). Curve 2, Fig. 5*A* includes this possibility based on a subjective estimate.

A third possibility, e.g. considered by Staley (1962), suggests exchange at all latitudes $\varphi > 30°$. Lifting and lowering of the troposphere due to seasonal temperature changes or due to dynamic effects of pressure systems can result in such effects. Curve 3, Fig. 5*A*, represents a corresponding model for $b(\mu)$. In reality we will probably find a combination of all these processes, as suggested by curve 4.

These models of $b(\mu)$ were used together with

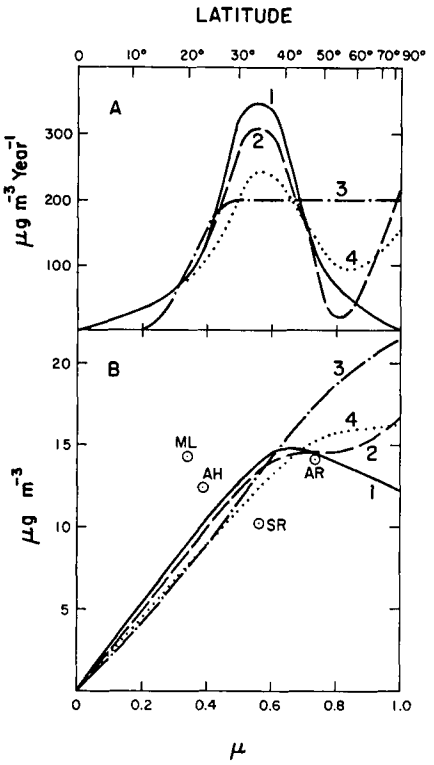

Fig. 5. (*A*) Assumed models of the O_3 amplitudes $b(\mu)$ based on various concepts about the exchange mechanism between stratosphere and troposphere. (*B*) Calculated amplitudes of $q(\mu, t)$ for the $b(\mu)$ models in *A* and $K = 3 \times 10^{10}$ cm^2 sec^{-1}. Included are the observed amplitudes at the stations listed in Table 4.

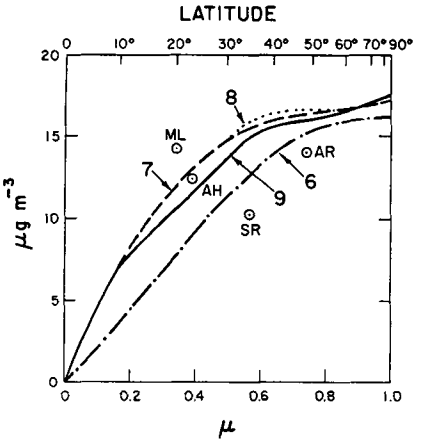

Fig. 6. Calculated amplitudes of $q(\mu, t)$ for $b(\mu)$ model 4, Fig. 5A and $K(\mu)$ according to curves 6 to 9, Fig. 2. Curve 6 is the same as curve 4 in Fig. 5B. Included are the observed amplitudes at the stations listed in Table 4.

the distributions of $K(\mu)$ to calculate possible distributions of $q(\mu, t)$. Figs. 5*B* and 6 serve to illustrate the important features of the results. The $q(\mu, t)$ values, Fig. 5*B*, were obtained with a constant K, curve 6, Fig. 2, in order to show the influence of the $b(\mu)$ distributions. We see that the amplitude of q for $\varphi < 40°$ is influenced only slightly by differences in $b(\mu)$, but that for $\varphi > 40°$ this is different, at least for this K model. The q values in Fig. 6 were obtained by applying the K models, curves 6, 7, 8, and 9, Fig. 2, to the same $b(\mu)$ distribution, curve 4, in order to show the effect of K on the O_3 distributions. The higher values of the K model 6 at lower latitudes result in lower q values, but for $\varphi > 40°$ the differences are small.

Our calculations were based on the assumption that $b(\mu)$ is symmetrical with respect to both hemispheres. The data from Antarctica suggest that this may not be so. In this case the amplitudes at the equator would not be zero. Clearly any asymmetry between the hemispheres with respect to stratosphere-troposphere exchange could easily be detected by O_3 data from equatorial regions in addition to data from the southern hemisphere.

The data of Table 4 are included in Fig. 5*B* and 6. The amplitudes agree reasonably well with the calculated values. This is to be expected since the budget considerations of tropospheric ozone (Junge 1962) which resulted in the expression for I were based on the amplitudes of the annual variations. The amplitude at Mauna Loa is somewhat large with respect to the calculated drop of q toward the equator.

If the data can be accepted as correct, this could point to either a pronounced reduction of K at the equator or to hemispherical asymmetry, or to both. But the latitude range of the present data is too narrow and their quality not good enough to draw conclusions in this respect.

The model calculations of O_3 presented here intend to demonstrate the general features to be expected, and the sensitivity of $q(\mu, t)$ with respect to both $K(\mu)$ and $b(\mu)$. The results seem to indicate that any uncertainty of $K(\mu)$ at lower latitudes or any asymmetry in $b(\mu)$ affects primarily the q values at $\varphi \leqslant 40°$. For $\varphi \geqslant 40°$, on the other hand, q is quite strongly influenced by the variation of b with μ because here the

uncertainties of $K(\mu)$ are neither large nor influential. Reliable and representative tropospheric O_3 data may therefore be quite useful in settling such questions as the asymmetry in tropopause exchange, the behavior of K in the tropics and the contribution of high latitudes to the global exchange between stratosphere and troposphere.

7. Conclusions

We can summarize the conclusions as follows:

(*a*) The seasonal variation of CO_2 is controlled by the biosphere over land, although the anthropogenic component is not negligible. The most uncertain factor is the seasonal variation of soil respiration, i.e. the value of ε. Until we have better data on this it will not be possible to draw quantitative conclusions concerning biological data, from observations of CO_2 fluctuations in the atmosphere. The maps of Lieth, however, seem to give quite reasonable figures.

(*b*) It seems hardly possible that detailed information could be obtained on the latitude dependence of K and the CO_2 source function from atmospheric CO_2 observations, even if the number and quality of the data were considerably increased.

(*c*) The model calculations for tropospheric O_3 suggest the possibility of studying global characteristics of the air exchange between stratosphere and troposphere. Reliable data on tropospheric O_3 for $\varphi < 30°$ may give information on hemispherical asymmetry of tropopause exchange processes and on the behavior of K in equatorial regions, whereas data for $\varphi > 30°$ may provide valuable information on the role of tropopause exchange in polar regions.

Studies of this kind require, however, that the various aspects of the tropospheric O_3 model used here be carefully checked.

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Note added in proof. On page 431 we mentioned that the observations of vertical O_3 distribution by Hering and Borden shows a roughly constant concentration of 50 $\mu g/m^3$ or a mixing ration inverse proportional to the air density. With our average value for $I = 4.7 \times 10^{14}$ g sec^{-1} we obtain an average vertical eddy diffusion coefficient for the troposphere of 7×10^4 cm^2 sec^{-1}, which appears very reasonable. If we assume the same flux for the average vertical profile at the lower stratosphere we obtain 6×10^3 cm^2 sec^{-1}, also in agreement with other estimates. This seems to us another indication that our budget figures for O_3 are quite consistent with other data.

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НЕКОТОРЫЕ АСПЕКТЫ СЕЗОННЫХ ИЗМЕНЕНИЙ ДВУОКИСИ УГЛЕРОДА И ОЗОНА

Делается попытка оценить сезонную функцию источника Q для CO_2 на основании данных о биосфере, полученных Лейсом, и данных о других источниках. Изменение респирации почвы является, по-видимому, наиболее неопределенным фактором. Результирующее изменение CO_2 в атмосфере рассчитывается с учетом горизонтального коэффициента обмена K, который изменяется с широтой. Сравнение с данными наблюдений Болина и Килинга показывает, что результаты не слишком чувствительны по отношению к предполагаемому изменению Q и K с широтой.

Величина K, меняющаяся с широтой, и предварительные результаты по озонному балансу использовались для расчета сезонных изменений тропосферного озона при заданных скоростях ввода озона из стратосферы. Делается заключение, что тропосферный озон может быть полезен для исследования глобального механика обмена между стратосферой и тропосферой и проблем, связанных с ним.