Residence time and variability of tropospheric trace gases

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ABSTRACT

It is shown on the basis of theoretical considerations that time and space variations for tropospheric constituents should be approximately inversely proportional to their tropospheric residence time if the distribution of sources and sinks is similar. Compilation of available data seem to verify this. It is pointed out that such a relationship, if confirmed by further data, is a useful tool for atmospheric chemistry.

Introduction

At a time of increasing concern with the composition and chemical behaviour of the troposphere even in unpolluted areas, the study of the cycle of trace gases becomes more and more important. One of the most important parameters which characterizes these cycles is the atmospheric residence time. Together with the concentration distribution, it supplies important information on the global production and destruction rates as well as on the location of sources and sinks. Information on the global production and/or destruction rates is, however, difficult to obtain and up to the present time only very incomplete for most of the atmospheric trace gases. Any way to improve such information is, therefore, of special interest to air chemistry.

In this paper we try to demonstrate that the variability of trace gases is perhaps a useful parameter to derive information on the residence time. For various reasons we consider here only the tropospheric residence times: The troposphere comprises about 75% of the mass of the atmosphere and constitutes a well-mixed reservoir; the sources and sinks of the trace gases are located either within this reservoir or can be considered to be located at its boundaries (earth's surface, tropopause); the exchange between troposphere and stratosphere is so slow that the cycle of most trace gases is practically confined to the troposphere with the stratospheric branch of the cycle being of minor importance, and last but not least, since we have practically no information from the stratosphere it would be impossible to give complete estimates of time and space variations for the whole atmosphere.

In the literature the expressions "residence time" and "life time" of a gas within a reservoir are used in parallel. In general the removal rate S of a trace gas can result from actual chemical destruction S_c within the troposphere including its boundaries (e.g. the earth's surface) and/or from a flux S_f through these boundaries (e.g. tropopause) into other reservoirs (without chemical modification)

$$S = S_c + S_f \tag{1}$$

In the extreme case of $S_f = 0$, or $S = S_c$ one would be inclined to speak of a "life time", and in case of the other extreme $S_c = 0$, or $S = S_f$ one would prefer to speak of a "residence time". Since for most gases we have a mixture of both, we prefer "residence time" as the more general notation throughout this paper.

Theoretical considerations

With

$\varrho = \varrho(x_i, t)$ = air density as a function of the three coordinates $x_i (i = 1, 2, 3)$ and time t,
$m = m(x_i, t)$ = mixing ratio of a gas G by weight $(g_G g_{\text{air}}^{-1})$,
$q = q(x_i, t)$ = production rate of G, and
$s = s(x_i, t)$ = destruction rate of G, including the chemical processes along and the fluxes through boundaries,

the total air mass of the troposphere is

$$M_{\text{air}} = \int_t \varrho dV = \bar{\varrho} V \tag{2}$$

with $\bar{\varrho}$ the average value of ϱ with respect to the volume V of the troposphere t, and correspondingly

$Q = \bar{q} V$ and $S = \bar{s} V$

The total mass of G in the troposphere is

$$M = \int_t (\varrho m)\, dV = (\overline{\varrho m})\, V \tag{3}$$

by which the spatial average concentration $\overline{\varrho m}$ of G with respect to V is defined[1]. We now introduce the Hesselberg average

$$\hat{m} = \overline{\varrho m}(\bar{\varrho})^{-1} \tag{4}$$

and obtain

$$M = \bar{\varrho} \hat{m} V \tag{5}$$

Under steady state conditions which we will assume the time averages of $\tilde{M}$, $\tilde{Q}$, $\tilde{q}$, $\tilde{s}$, $\tilde{m}$ etc. should be constant if the period of averaging is sufficiently long. Since annual variations play an important role for the cycle of most trace gases this averaging period should be at least one year. This results in

$$T = \tilde{M}/\tilde{Q} = \overline{\tilde{\varrho}\tilde{m}}/\tilde{q} = \tilde{\varrho}\tilde{m}/\tilde{q} = \tilde{\varrho}\tilde{m}/\tilde{s} \tag{6}$$

with $\tilde{Q} = \tilde{S} =$ constant or $\tilde{q} = \tilde{s} =$ constant and

$T =$ residence time. (7)

We now consider the general expression for the transport of a tracer

$$\frac{\partial(m\varrho)}{\partial t} = -\sum_{i=1}^{3} \frac{\partial}{\partial x_i}[(m\varrho)\, \mu_{G_i}] + q - s \tag{8}$$

Here the velocities of G, u_{G_i}, are almost precisely the same as those of the air u_i, because they differ only by the inclusion of the molecular diffusion term in u_{G_i}, which is different for each gas but can, for all practical purposes, be neglected.

Following standard procedures we express the variable quantities m, q and s by

$$m = \tilde{m} + m',\ q = \tilde{q} + q',\ s = \tilde{s} + s' \tag{9}$$

where the dashes indicate the deviations from the space and time averages. If we consider (7) and the continuity equation for air equation (8) can be written

$$\frac{\partial(\varrho m')}{\partial t} = -\sum_{i=1}^{3} \frac{\partial}{\partial x_i}[(\varrho m')\, \mu_{G_i}] + q' - s' \tag{10}$$

A solution of (10) requires on the one hand the knowledge for the whole troposphere of $\varrho(x_i, t)$ and $u_{G_i}(x_i, t)$ which are the same for all trace gases and, on the other hand, of q' and s' together with the initial values and boundary conditions which are different for the individual trace gases. Such solutions of (10) would make it easy to study any relationship between the variations of the mixing ratio, m' and the residence time T, the topic of this paper. Since such solutions are only possible by the aid of general circulation models we will attempt to draw at least some general conclusions in this respect by simpler considerations and model calculations. These conclusions will then be compared with data available from the literature.

The four important quantities of each trace gas T, $\tilde{Q}$, $\tilde{S}$ and $\tilde{M}$ (or $\tilde{q}$, $\tilde{s}$, $\tilde{m}$) are related by the two expressions (6) and (7) leaving two of them undetermined. It is important to point out that the source function q is usually independent of m (and therefore $\tilde{Q}$ of $\tilde{M}$) in contrast to the sink function which for almost all atmospheric constituents is determined by m or rather $(m \cdot \varrho)$ in a more or less complex way,

$$s = s(m\varrho) \tag{11a}$$

For steady state conditions we have

$$\tilde{s}(m\varrho) = s = \tilde{q} \tag{11b}$$

which determines $\tilde{m}$ and thus T according to (6). Both q and $s(m\varrho)$ are essential for understanding the cycle of a trace gas but for most atmospheric constituents our knowledge concerning these quantities is very insufficient. For a number of interesting gases such as radon, H_2O and N_2O the important sources are all located at the earth surface so that q' is negative throughout the volume V of the troposphere but has highly positive values at the lower boundary. The standard deviation of q' is, therefore, fairly large. The sink on the other hand is farily uniformly distributed throughout

[1] We distinguish between concentrations ($m\varrho$) of gases given for instance in g cm^{-3} and mixing ratios given by weight ($g_G g_{\text{air}}^{-1}$) or by volume. Mixing ratios are conservative properties of the air whereas concentrations are not.

the troposphere (radon by radioactive decay, H_2O by condensation, N_2O by photodissociation) so that the standard deviation of s' is small or at least small compared with that of q'. These considerations will be useful later in our discussion. If it is possible to assume for s a first order reaction, as it is more or less the case for the examples just mentioned, we have $s = s_0 \cdot \varrho m$ with $s_0 =$ constant. With (4) and (6) we then obtain the well known relationship $T = s_0^{-1}$.

In this paper we are interested in relationships between the variability of m and T. Starting point of this study was the observation that for atmospheric gases the relative fluctuations of m decreased with increasing T (Junge, 1963). This is fairly easy to understand qualitatively but it proved to be more difficult to find quantitative relationships. However, in the subsequent discussion we will draw some general conclusions which can be supported by numerical model calculations.

We assume the case where the standard deviations σ^* of s' and q' obtained by averaging over the whole troposphere and over a suitable time period are related by

$$\sigma^*(s') \ll \sigma^*(q') \tag{12}$$

If we further assume the normal case that q is independent of m (and thus q' independent of m') m' depends according to (10) only on q' and, of course, on the meteorological transport processes which are, however, the same for all atmospheric constituents. Under these conditions gases with identical source functions q (and thus also q' and $\tilde{\bar{q}}$) should have the same m' and the same $\sigma^*(m')$. In view of (6) and (7) and the fact that $\tilde{\bar{q}}$ is fixed, the two quantities $\tilde{m}$ and T can still be freely chosen for the gases. If we define the *relative* standard deviation by

$$\sigma(m') = \sigma^*(m')/\tilde{m} \tag{13a}$$

we have with (6)

$$\sigma(m') = \sigma^*(m')\,\tilde{s}/T\tilde{\bar{q}} \tag{13b}$$

This relation shows that for gases with the same source function q, $\sigma(m')$ varies inversely with the residence time T. Although condition (12) is at most only approximately valid for certain tropospheric trace gases, this result is of interest to us as it indicates that an inverse relationship between $\sigma(m')$ and T may be expected under certain conditions, in apparent agreement with observations as shown below. It should be noted that condition (12) implies two things, considering that $s = s(m)$: First of all, regardless of the spatial distribution of q, m must be fairly uniformly distributed within the troposphere which means that the tropospheric mixing time must be short compared to the residence time throughout the troposphere. This condition is approximately satisfied in the model calculations discussed below. Secondly (12) also implies that the sink function $s(m)$ must be rather unfiorm, as for instance with a homogeneous gas reaction occurring throughout the troposphere and not, for instance, a destruction mechanism at the earth' surface. But even in the almost ideal case of a homogeneous gas reaction of first order and a well mixed troposphere, there remains the variation of s with altitude due to the decrease in gas density for a uniform mixing ratio.

In order to see more directly what may be expected we studied the tropospheric behavior of trace gases by a simplified numerical model in more detail. In this numerical model we assumed a latitude independent west wind circulation with a vertical wind profile up to the tropopause similar to that actually found in mid latitudes (Table 1). This west wind circulation passes alternatively over continents and oceans of equal length of 6 000 km approximating actual conditions. Horizontal mixing was assumed to be constant with altitude with an eddy diffusion coefficient of 3×10^{10} cm^2/sec a value generally accepted to be realistic for mid latitudes. Vertical mixing was effected by eddy diffusion with eddy diffusion constants as a function of altitude given in Table 1. We further assumed the continental surface to be a uniform source for the trace gas but not the ocean surface (or vice versa). The sink function was assumed to be first order in $m\varrho$ throughout the troposphere. The assumption of sources and sinks are approximately typical for a number of atmospheric trace gases as discussed above. We calculated the two dimensional (longitude and height) steady state distribution of m which shows, of course, only space but no time variations and from this the corresponding value of $\sigma(m')$.

This model approximates realistic conditions in the atmosphere for trace gases. Although

Table 1. *Vertical profiles of the average hemispheric speed V of the westwind circulation and the vertical eddy diffusion coefficient D used in the model calculations*

Height z (km)[a]	V (m sec^{-1})	D (10^5 cm^2 sec^{-1})
0.1	2.2	1.9
0.5	2.8	1.95
1.0	3.6	2.0
3.0	8.1	2.0
5.0	12.6	2.0
10.0	17.9	2.0

[a] For very small z $D \approx 8 \times 10^6$ z (km).

$\sigma(q')$ will be larger than $\sigma(s')$ condition (12) is not quite fulfilled. The calculations covered the range of 5 days $\leq T \leq 1.5$ years; we did not go beyond 1.5 years because for these T values the convergence for steady state conditions was too slow so that the computer time became extremely long. The results can be expressed by

$$\sigma(m') = a \cdot T^{-b} \qquad (14)$$

with $a = 2.16 \times 10^{-2}$, $b = 0.95$ and T in years. The deviation of b from 1.0 may reflect the fact that assumption (12) is not fulfilled. But (14) is certainly a fairly good approximation of (13). More elaborate model calculations for other space and time variations of q and s will, of course, be necessary to see how generally valid this result is.

In our model calculations we varied T but kept the distribution of q and s constant. It is clear that with a constant T but with variations of q and s the parameter a in (14) would cover a certain range. Fig. 1 shows that the values given by (14) are smaller by a factor of about three than the tentative average value derived from the actual observations in the atmosphere. It is likely that the simplifications in our model are responsible for this difference. All the following factors will enhance the variability and, therefore, increase a:

1. In our model no time variations due to synoptic, meso- and large scale circulations were included.

2. Our model has no latitude variations of any parameter.

3. q was assumed to be constant over land; under actual conditions all area sources will vary with soil conditions, population density, etc.

4. Our model does not include seasonal variations nor differences between the two hemispheres.

It is quite clear from this discussion that we have to expect statistical relationships between $\sigma(m')$ and T due to the fact that the spacial and time distributions of q and s are different for each individual gas. This will result in a certain range of a-values in (14) and should be considered in any evaluation of actual data on T and $\sigma(m')$ as in Fig. 1.

With respect to the constant b in (14) there may be variations too. The actual data in Fig. 1 and our theoretical considerations seem to indicate that b can be expected close to one, but this again has to be demonstrated on a broader basis. Recently, Gibbs & Slinn (1973) tried to estimate the relationship between σ and T by a simple model in which q and s show time variations. If the characteristic time for the source and sink variations is short in comparison with T, their model suggests a relationship $\sigma \propto T^{-1/2}$; for other conditions the exponent may have other values.

In summary we may say that the theoretical conditions do not allow to draw general conclusions. It is fairly sure that if condition (12) is valid inverse proportionality between σ and T according to (13) is to be expected. But for more realistic conditions deviations may occur for both constants a and b in (14), the magnitude of which cannot be estimated at present.

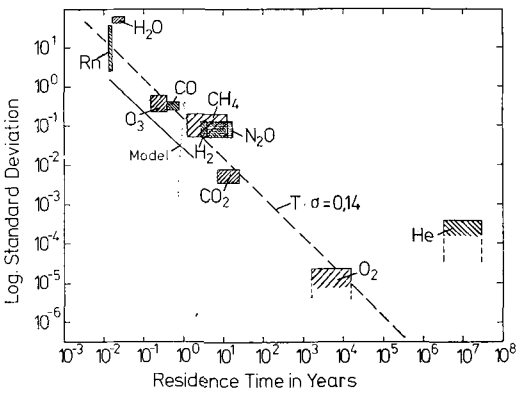

Fig. 1. Relationship between log standard deviation σ and residence time T for the troposphere based on the data in Table 1.

At the conclusion of this section a few remarks about the residence time T and the Hesselberg average $\hat{m}$ should be made. Recently Bolin & Rhode (1973) pointed out that in natural reservoirs which are not well mixed and which are not governed by first order exchange processes the average age of a gas molecule is different from the residence time of the reservoir (which they called turn over time). The average transient time of a particle, i.e. the expected life time of a molecule entering the reservoir is, on the other hand, identical with the residence time. Although this clarification does not effect our discussion directly it is certainly worth keeping these distinctions in mind for future discussion and nomenclature. But there is another aspect which is of concern to our discussion. For the troposphere there are two processes which are often overlooked in calculating T: The exchange with the ocean and with the stratosphere. This exchange occurs for all gases, even if there is no gradient across the tropopause or if solution equilibrium with the ocean surface water exists. This exchange reduces the residence time of all gases including the noble gases to finite values, but it does not result in fluctuations of m, unless there are net fluxes across the boundaries.

Broecker & Peng (1973) have demonstrated that the stagnant film model is adequate to calculate the transfer rates of most gases between the atmosphere and the ocean. In this case the flux of a gas through the air-ocean interface is controlled by the concentration gradient across the stagnant film layer which has a global average thickness of $z = 3 \times 10^{-3}$ cm. The concentration of any atmospheric gas with a partial pressure of p (atm) at the upper boundary of the film is

$$c = p \cdot s/v \text{ (mole/cm}^3\text{)}$$

with s = solubility coefficient = volume of gas at STP absorbed by one volume of water if the pressure of the gas is one atmosphere, and $v = 2.24 \times 10^4$ cm^3 = volume of one mole at STP.

Assuming zero concentration below the film the flux is

$$F = c \cdot \frac{d}{z} \quad \text{(mole/cm}^2 \text{ sec)}$$

with d = diffusion coefficient of the gas in water in cm^2/sec.

If we take into account that the troposphere comprises 0.75 of the mass M of the atmosphere and that the ratio of total earth surface to ocean surface is 1.41, the global average mass of an air column of 1 cm^2 cross section in exchange with the ocean water is

$$M = 0.75 \times 1.41 \times p \cdot H/v = 1.06 p \cdot H/v \text{ (mole/cm}^3\text{)}$$

with H = scale height of the atmosphere = 8.4×10^5 cm. The tropospheric residence time due to ocean exchange is therefore

$$T_0 = 1.06 H \cdot z/s \cdot d \cdot 3.15 \times 10^7 \text{ (years)}.$$

For N_2 we have $d = 0.95 \times 10^{-5}$ and $s = 0.024$ for 0°C resulting in $T_0 = 380$ years. Since d varies little with the gases T depends almost completely on s. Broecker & Peng distinguish essentially two groups of gases: N_2, O_2, CO, H_2, A_r, CH_4 which have residence times of the order of several hundred years and CO_2, N_2O, which have residence times of the order of 10 years.

The gas exchange across the air-ocean interface does not result in variations of m, if solution equilibrium exist. We may call exchanges of this type "silent". Another "silent" exchange occurs through the tropopause for gases which have no gradient of m in the tropopause region, as for instance CO_2, O_2 etc. The residence time of the troposphere with respect to the stratosphere T_s is about 5 years. The total residence time T_t for tropospheric gases is thus

$$\frac{1}{T_t} = \frac{1}{T} + \frac{1}{T_0} + \frac{1}{T_s}$$

where T is the residence time due to net sources and sinks as considered earlier. It is clear from our discussion that for any relation between $\sigma(m')$ and the residence time only T should be considered. If the oceans are net sources as with CO, N_2O, and H_2 the contribution of this net source is, of course, to be included in T.

A few words about the special meaning of the Hesselberg average value $\hat{m}$ may be in order. It was necessary to introduce this average value because the mixing ratio is a quantity which is related to ϱ. The spatial average m would be defined by

$$\bar{m} = \frac{1}{V} \int_t m dV.$$

Since for most atmospheric gases the distribution is given in terms of mixing ratios m rather than in terms of concentrations ($m\varrho$), it is easier to calculate $\bar{m}$ instead of $\hat{m}$. It is, therefore, necessary to know under what conditions the distinction between $\hat{m}$ and $\bar{m}$ becomes important.

For a trace gas which is vertically well mixed and for which the main differences occur in horizontal directions, ϱ can be considered constant and both average values become identical for all practical purposes. This is also true if the vertical variations remain small. For estimating the effect we assumed a linear variation of m with altitude z

$$m = m_0 - z \cdot \varepsilon$$

with m_0 = surface value, and ε = vertical gradient of m.

We further assume $\varrho = \varrho_0 e^{-z/H}$ within the troposphere, i.e. isothermal conditions as an approximation. For an average tropopause height of 12 km, the deviation of $\hat{m}$ from $\bar{m}$ is 12 % if at the tropopause m is either $\frac{1}{2}m_0$ or $2m_0$ and 22 % if it is $\frac{1}{4}m_0$ or $4m_0$. For O_3 or CO, m varies by a factor of about two in the vertical within the troposphere. For gases with residence times equal or longer than O_3 or CO we can, therefore, use $\bar{m}$ instead of $\hat{m}$. For Rn and H_2O, however, this is not possible. Unfortunately, the data for Rn are too incomplete to calculate a true $\hat{m}$ average, so that H_2O is the only gas for which the actual $\hat{m}$ average is computed.

Compilation of data

In the subsequent section available data on residence times and spatial variations of trace gases within the troposphere will be compiled. Such data are still extremely meager, but some progress during the last 10 years has been made. We will discuss the various gases in decreasing order of their residence time. All estimates are listed in Table 2 and plotted in Fig. 1.

He. Helium is the gas with the longest known residence time. It is produced by radioactive decay in the earth's crust of U^{238} and TH^{232} at almost equal rates and only about 2 % by decay of U^{235}. The total production can be estimated from the amount of these substances in the earth's crust and the fraction of helium which is released from the soil. Both quantities are not too well known but the residence time of He of about 10^7 years can be considered to be accurate within one order of magnitude (e.g. Damon & Kulp, 1958). He must escape from the thermosphere and the mixing ratio observed in the atmosphere is assumed to represent steady state conditions. Because of this situation, Glueckauf (1951) made careful analyses and found a constant mixing ratio of 5.239 ± 0.002 ppm or within the relative limits of $\pm 4 \times 10^{-4}$. This uncertainty apparently reflects the accuracy of the method and not be actual variations in the atmosphere, although some measurements were made comparatively near the large helium sources of the United States. From Fig. 1 we estimate the actual variations of He to be orders of magnitude smaller than the accuracy of Glueckauf's method. The He data, therefore, cannot contribute to our present problem.

O_2. Oxygen is normally considered to be a "permanent" gas of the atmosphere. But the only gases which can be considered "permanent" are the noble gases other than Helium which have practically no net sources nor sinks, so far as we know. All other atmospheric gases do have sources and sinks including the main constituents N_2 and O_2, corresponding to finite residence times. For O_2 the residence time is primarily controlled by the biospheric oxygen cycle. The marine part of this cycle is hard to estimate but the data indicate that the oxygen cycle within the ocean is closed to some degree, so that the net exchange with the atmosphere is smaller and perhaps comparable with the cycle through the land plants. The cycle through the land plants can be estimated fairly reliably by the known CO_2 cycle. The best estimate given for the total CO_2 production is 1.7×10^{17} g CO_2 yr^{-1}. This is based on careful comparisons of observed seasonal CO_2 variations in the atmosphere and model calculations under the reasonable assumption that the rate of decay of organic matter is about equal during summer and winter (Junge & Czeplak, 1968). This figure is in good agreement with those of other authors, recently compiled in the SCEP Report (1970). The uncertainty of this value is estimated to be less than a factor of ± 1.3. With a total CO_2 content of our atmosphere (for 320 ppm CO_2) of 2.6×10^{18} g CO_2, the resulting CO_2 residence time is $T_{CO_2} = 15$ years. This is longer than the total T_{CO_2} of about 6 years (see later) because of oceanic exchange.

Table 2. *Estimates of residence times and standard spatial variations of tropospheric trace gases discussed in this paper. Estimated uncertainty factors of these quantities are also included*

Estimated uncertainty factors of these quantities are also included

Gas	Residence time T (yr)	Uncertainty factor	Standard spatial variation	Uncertainty factor
He	1×10^7	3.0	$< 4 \times 10^{-4}$	[a]—
O_2	5×10^3	3.0	$\leq 2.4 \times 10^{-5}$	[a]—
CO_2	15.0	1.5	5×10^{-3}	1.5
N_2O	8.0	2.0	8×10^{-2}	1.5
H_2	6.5	2.0	8×10^{-2}	1.4
CH_4	4.0	3.0	1×10^{-1}	2.0
CO	0.6×10^{-1}	2.0	5×10^{-1}	1.3
O_3	2.5×10^{-1}	1.5	4×10^{-1}	1.5
H_2O	2.2×10^{-2}	1.3	5×10^{1}	1.2
Rn	1.4×10^{-2}	1.1	1×10^{1}	4.0

[a] Only upper limits can be given.

For photosynthesis and organic decay the exchange of O_2 and CO_2 is stochiometric. With 20.95% O_2 and 0.032% CO_2 by volume in our atmosphere the corresponding residence time of O_2 is

$$T_{O_2} = T_{CO_2} \frac{20.95}{0.032} = 9\,700 \text{ years.}$$

This is the value based on photosynthesis of land plants alone. It is perhaps not unreasonable to assume a net oceanic O_2 exchange with the atmosphere of the same magnitude. This would reduce the actual value to $T_{O_2} = 5 \times 10^3$ years with an uncertainty factor of perhaps 2.0. Machta & Hughes (1970) give $T_{O_2} = 2 \times 10^3$ years.

For an estimate of δ_{O_2} the best data available are those by Machta & Hughes (1970). They made 78 measurements over a large variety of locations from 49° N to 37° S and found an average O_2 content of 20.946% by volume with a "precision or geographical variability, or both", of ± 0.0005 corresponding to a relative precision of $\pm 2.4 \times 10^{-5}$. Since O_2 variability and accuracy of the measurements cannot be distinguished, we have to take this value as an upper limit for σ, the tropospheric variability, including seasonal variations by photosynthesis. The seasonal variations of O_2 can be estimated from those of CO_2 which are of the order of ± 4 ppm. Considering the concentration ratios of CO_2 and O_2 as above, we obtain relative O_2 variation of about $+2 \times 10^{-5}$. This value is close to that by Machta & Hughes indicating that the true spatial variations may indeed be very close to $\pm 2.4 \times 10^{-5}$. The uncertainty factor of σ can, of course, not be given in this case.

CO_2. The residence time of CO_2 is usually estimated to be about 6 years. Recently Machta (1971) attained values as low as 2 years based on measurements from bomb produced $C^{14}O_2$. But it should be considered that these values refer primarily to the exchange with the ocean. As mentioned above for O_2 the best estimates of the residence time due to photosynthesis of land plants is $T_{CO_2} = 15$ years with an estimated uncertainty factor of 1.5. Because the exchange with the ocean does not contribute much to the tropospheric variability and because we have not included oceanic exchange for the other gases for the same reasons it is fair to assign this value to CO_2 for the present discussion.

The variability of CO_2 in the troposphere is primarily controlled by the seasonal uptake of land plants in temperate latitudes. In tropical areas with continuous growth uptake by plants and release from the soil compensate each other to some degree on a local scale throughout the year, so that effects on tropospheric variability are much smaller. The same applies to the exchange with the oceans. Here there are definite source areas in the tropics and sinks polewards, so that the exchange is not quite "silent" as perhaps with other gases.

Representative values for the spatial variations were provided by Bolin & Keeling (1963), Bolin & Bischof (1970) and the Deutsche Forschungsgemeinschaft (1971). From the Pacific data of Bolin & Keeling one obtains $\sigma = 4 \times 10^{-3}$ if both hemispheres are considered for an annual average. Bolin & Bischof obtained values for σ as a function of altitude between 2 and 10 km from data over large parts of the northern hemisphere. σ decreases from 6×10^{-3} at 2 km to 3×10^{-3} in the upper troposphere.

In west Germany (Deutsche Forschungsgemeinschaft, 1971) CO_2 is continuously recorded on three remote stations on mountains or high level terrain. The standard deviation of the daily average values from the monthly mean values for each station, averaged over all three

stations and for a period of about 2 years, is 2×10^{-2}. Although this value refers to time variations it can be considered representative for special variations over Central Europe. This value can be considered a reasonable extrapolation to zero height of the values of Bolin & Bischof.

Comparison of all these data and considering the troposphere as a whole, an average σ of $\pm 5 \times 10^{-3}$ seems to be a reasonable figure with an estimated uncertainty factor of ± 1.5.

N_2O. A comprehensive study of tropospheric N_2O was recently published by Schütz et al. (1970). This study supersedes the data obtained earlier and can be used as a basis for our considerations. These authors estimate that the residence time is shorter than 70 years, perhaps less than 10 years but this estimate is rather uncertain. Recently Hahn (1972) obtained new data from the Atlantic showing supersaturation and Seiler & Schmidt (1973) compiling data on gases in ocean water estimated the oceanic source for N_2O alone to be 2.1×10^{14} g/year. Together with a production estimate of 0.5×10^{14} g/year from soil by Schütz et al. (1970) this results in a residence time of 8 years. In Table 2 we assumed an uncertainty factor of ± 2.

The average mixing ratio of 0.25 ppm in the troposphere was obtained by several hundred measurements at the earth's surface, on mountain stations and in the upper troposphere. The standard deviation is about 0.08 with an estimated uncertainty factor of ± 1.5.

H_2. For hydrogen only very recently sufficient data became available to consider this gas here. Schmidt (1973) studied the tropospheric distribution of H_2 and its budget in a comprehensive way and found that it has considerable anthropogenic sources (mostly from automobile exhaust) besides natural production by OH oxidation of CH_4 and in ocean water. The estimated residence time from all sources combined is 6.5 years with an assumed uncertainty factor of 2. The study by Schmidt of the global distribution of H_2 was performed with the aid of a very sensitive recording device in ground air over the oceans and by air craft in the upper troposphere so that a large volume of data became available including the southern hemisphere. The variations of H_2 in the troposphere turned out to be smaller than indicated by previous measurements based on individual samples, for instance those taken by Ehhalt, 1971 over the North Atlantic Ocean (private communication). On the basis of his large number of data Schmidt found a standard deviation of 5% within the northern and 2% within the southern lower troposphere with a difference between the hemispheres of about 4%. From this it can be estimated that the global tropospheric standard deviation is 8% with an uncertainty factor of 1.4. Recently Östlund (1970) made measurements of HT over about one year which indicated $\sigma(m') = 0.1$. This is slightly larger than the H_2 value. Although for both gases H_2 and HT the sinks should be similar there will be differences in $q(x_i, t)$ because HT is supposed to originate primarily from nuclear industries.

CH_4. Koyama (1963) in a study of CH_4 production in paddy fields, estimated the residence time to be 20 years. Because this estimate was based on extrapolations of laboratory measurements to the production of the whole earth's surface, it cannot be very reliable. Earlier estimates by Hutchinson (see Junge, 1963) gave 100 years. Ehhalt (1967) made it certain that there are other important sources besides soil production under natural or agricultural conditions so that T_{CH_4} may be only a few years. Recently Ehhalt (1973) gave estimates between 4–7 years based on production and destruction by OH radicals which can lead to values as low as 1.8 years. We assume here an estimate of 4 years with an uncertainty factor of 3 indicating that this value may still change.

The measurements prior to 1962 were summarized by Junge (1963), newer data were obtained by Ehhalt (1967) and Martell (1970). All these data show values between the limits of about 0.7 and 1.6 ppm (volume) with a reasonable average around 1.1 ppm and an estimated σ of ± 0.2. However, recent data from an east–west voyage over the North Atlantic summer 1971 (Ehhalt, private communication) showed only a standard deviation of 5% and data by Lamontagne et al. (1973) from a north–south trip in the Pacific indicate a similar steadiness, but a 10% decrease in the southern hemisphere. On the basis of these recent but more comprehensive data σ seems to be primarily controlled by the hemispheric difference (similar to CO) so that we adopt $\sigma = 0.1$ with an uncertainty factor of 2.

CO. The CO cycle is recently very much debated and much new information has been compiled. We know of at least three important

sources of CO, anthropogenic, ocean surface waters and oxidation of CH_4 by OH radicals. Sinks for CO are the soil, the stratosphere and again reaction with OH radicals within the troposphere. The first estimates on the residence time based on the anthropogenic production gave 2–3 years (Robinson & Robbins, 1969). On the basis of C^{14} data Weinstock (1969) concluded that the residence time, most likely due to considerable production by CH_4 oxidation, was as short as 0.1 years. However, the considerable difference in CO mixing ratio between the northern and southern hemisphere is only compatible with the assumption that the anthropogenic source is still the dominant one (Seiler, 1973). The average CO mixing ratio in the northern hemisphere is about 0.16 ppm as compared to 0.05 ppm in the southern hemisphere, with a global tropospheric average of close to 0.1 ppm. The most recent budget evaluation by Seiler (1973) gives a residence time of 0.5 years which we accept here and we estimate the uncertainty factor of this value to be 2.

The highest concentrations of CO occur near cities and polluted areas but these areas are rather small with respect to the total volume of the troposphere. There are only few data from the lowest layers over unpolluted continental areas. In clean air masses in Central Europe 1–3 ppm CO have been observed. Over the North Atlantic and most likely over the North Pacific as well tropospheric mixing ratios vary between 0.1 and 0.2 ppm, with much lower values in the southern hemisphere.

The tropospheric σ value is, therefore, primarily controlled by the large difference between the two hemispheres and must be close to 0.5 with an estimated uncertainty factor of 1.3. This value is again based on the compilation of data by Seiler (1973).

O_3. The estimates of the tropospheric residence time of O_3 seem to converge toward a value of 3 months or 0.25 years (Junge, 1962); Fabian & Junge, 1970). We estimate the uncertainty factor of this value to be ± 1.5.

The data about the O_3 distribution within the troposphere are not very abundant. Most values are obtained near the earth's surface, which is the sink and this results, of course, in considerable fluctuations. We are here primarily interested in data above the planetary boundary layer. In general, the large scale horizontal spatial variations are relatively small as demonstrated by Junge (1962). If we assume the seasonal variations in both hemispheres to be in opposite phase with an amplitude of $\pm 30\%$, this leads to large-scale horizontal variations of the same order. More pronounced are the vertical variations. The data obtained by Hering & Borden (1965) are perhaps the most representative, although the accuracy for the troposphere is somewhat doubtful. Converted into mixing ratios they found the following annual averages:

altitude	0	2	4	6	8	km
mixing ratio	5.7	5.8	6.4	8.4	13.5	$(g_{O_3}/g_{air}) \times 10^8$

We see that on the average the mixing ratio decreases by a factor of 2–3 from the tropopause to the earth's surface. This gradient together with an average vertical eddy diffusion coefficient of about 2×10^5 cm^2 sec^{-1} corresponds to the above given residence time so that this gradient seems to be reasonably well founded (Schütz et al., 1970).

More recent studies of the variability of tropospheric ozone by Pruchniewicz (1970) show that superimposed upon the large scale variations is a small scale variability at the 500 mb level from one day to another of about $\pm 20\%$. It can be assumed that these time variations reflect to a large extent spatial variations within the troposphere, due to horizontal differences and changes in the vertical motions associated with synoptic scale pressure systems. All this by no means very abundant observational material from the free troposphere indicates that σ must be around ± 0.3, this value being dominated primarily by the vertical gradient.

The O_3 fluctuations within the planetary boundary layer are much larger and have to be considered for the final value of σ. Since the boundary layer amounts only to about 10% of the volume of the troposphere, the low O_3 concentrations often observed near the earth's surface cannot modify σ too much. We estimate that σ will be increased to about ± 0.4 which we will accept as the final value for the whole troposphere. The uncertainty factor is estimated to be ± 1.5.

H_2O. Water vapour is a very variable constituent in the troposphere. The variability is controlled primarily by the horizontal and vertical temperature distribution. The mean residence time for water vapour is fairly well known due to reasonably good global water vapour

and precipitation data. It is about 8 days (0.022 years) with an estimated uncertainty factor of ± 1.3 (see Junge, 1963).

The spatial variability of the H_2O mixing ratio for the whole troposphere can be estimated by considering the temperature variability within the troposphere assuming constant relative humidity. From average temperature cross sections of the troposphere (*Handbook of Geophysics*, 1960) we plotted the frequency distribution of occurring temperatures. This distribution was converted into a distribution of water vapour densities for 50% relative humidity and this in turn into water vapour mixing ratios by using formulas for the air density as a function of altitude. From this distribution the Hesselberg average was calculated and the logarithmic standard deviation considering the decrease of area towards the poles and the actual heights of the tropopause as a function of latitude. The calculations were made both for the January and July cross sections. The values obtained were:

	January	July
$\bar{\varrho}$	0.617×10^{-3}	0.612×10^{-3} g cm^{-3}
$\bar{m}\bar{\varrho}(H_2O)$	2.62×10^{-6}	3.53×10^{-6} g cm^{-3}
$\bar{m}$	4.24×10^{-3}	5.78×10^{-3} g $(g_{air})^{-1}$

The geometric standard deviations are 45 and 46 respectively. Considering the fact that by using average temperature distributions and constant relative humidities the σ-values will be on the low side and that this is only partly compensated by the extreme seasons, we assume $\sigma(m')$ to be 50 with an uncertainty factor of 1.2.

Rn. The radon sources are the continents. Its residence time is for all practical purposes identical to its radioactive life time of 5.5 days. Within the troposphere we estimate the reduction of this value by absorption in ocean and rain water to be less than 20%. As a final value for our purpose we, therefore, choose 5 days (1.4×10^{-2} years) with an uncertainty factor of 1.1.

Unfortunately, the distribution of Rn in the troposphere is not well known. Earlier data summarized by Junge (1963) show differences between surface air over the continents and oceans by a factor of hundred which decreases in the upper troposphere considerably. In Antarctica concentrations range around 1–2 pcm^{-3} (Lambert et al., 1970) whereas in normal continental surface air in the northern hemisphere values of 50–400 pcm^{-3} are normal decreasing by factors of 10 or more in the upper troposphere.

It is difficult to obtain from these data representative σ values. Our estimate is $\sigma = 10$ with a considerable uncertainty factor of about 4. Due to large fluctuations and the scarcity of the data, this value is the least reliable one of all gases in Table 2.

Discussion

Fig. 1 indicates that by and large σ and T seem to be inversely proportional to each other. Deviations which occur can be due either to inaccuracies of the data and/or to the scatter expected from the theoretical considerations as a result of the differences in the global distribution of $q'(x_i, t)$ and $s'(x_i, t)$. But the scatter seems to be less than expected which may indicate that the various factors responsible for $\sigma(m')$ cancel each other out to some degree or are not so critical.

The dashed curve in Fig. 1 gives good reasons to expect the actual He fluctuations to be smaller by several orders of magnitude, perhaps much too small to be ever measured with presently available techniques. The reason for the deviation of H_2O may be the following: Its distribution is primarily controlled by the vertical temperature profile especially over the tropics where the highest and lowest temperatures are encountered. This distribution in turn is primarily responsible for $\sigma(m')$. For most of the other gases, on the other hand, it is the horizontal difference of sources and sinks which is important for $\sigma(m')$. We mentioned this possible scatter due to differences in $q(x_i, t)$ and $s(s_i, t)$ already in our theoretical considerations. It should be mentioned that in the first drafts of Fig. 1 about two years ago there were still strong deviations for N_2O and CH_4 from the dashed curve. With the accumulation of new data of T for N_2O and of $\sigma(m')$ for CH_4 the scatter has decreased and it was quite encouraging to see that the recent values of H_2 fall in line with the other data.

The approximate relationship indicated in Fig. 1 would be

$$T \cdot \sigma(m') = 0.14 \text{ (years)}$$

Such a relationship if confirmed by future studies would be of considerable interest to global air chemistry because it would provide a possibility to arrive at estimates of T and thus of $\tilde{Q}$ or $\tilde{S}$ solely on the basis of measurements of spatial and/or time variations of the respective constituent. An interesting case is for instance N_2. It has a biological cycle which can roughly be estimated. If the average ratio C/N in the land biomass is 15 (see Bowen, 1966), the residence time of N_2 would be of the order of 10^6 years in view of the carbon cycle. On the basis of Fig. 1 one would expect a $\sigma(m') \approx 10^{-7}$, but it remains doubtful if such low values can ever be determined, quite apart from the fact that N_2 acts as the carrier gas and a mixing ratio cannot be determined.

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ВРЕМЯ ЖИЗНИ И ИЗМЕНЧИВОСТЬ ТРОПОСФЕРНЫХ ГАЗОВЫХ ТРАССЕРОВ

На основе теоретических соображений показано, что временные и пространственные изменения тропосферных составляющих приближенно должно быть обратно пропорционально их времени жизни в тропосфере, если распределение источников и стоков подобно. Сравнение имеющихся данных повидимому подтверждает эту точку зрения. Указывается, что такое соотношение, если оно подтвердится дальнейшими данными, является полезным инструментом атмосферной химии.