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Residence time and spatial variability for gases in the atmosphere

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ABSTRACT

The relation between spatial variability and residence time for gases in the atmosphere is studied using a two-dimensional numerical model. Results indicate that although the residence time shows a strong dependence on the variability, other factors, mainly the distribution of sources, also play an important role. If nothing is known about the location of the sources and sinks, the uncertainty in the estimate of the residence time from variability measures will be at least a factor of 10. The situation is greatly improved when one has indications of where the source is located.

Verification of the model, using gases in the atmosphere for which variability estimates and independent estimates of the residence time were available, proved difficult because of the uncertainties associated with these estimates. The general features of decreasing variability with increasing residence time and a strong dependence on the source configuration were, however, confirmed.

1. Introduction

What is the relation between concentration variations and residence time for gases in the atmosphere? Intuitively, it is easy to understand that gases with long residence times have smaller variations in space and time, than gases with short residence times. Is it then possible to formulate a formal relation between these two quantities? The question was discussed by Junge (1963) and Junge et al. (1971), but the first mathematical model for the relation was proposed by Gibbs and Slinn (1973). Using a simple stochastic model, they derived the relation

$$\hat{\sigma} \sim \tau^{-1/2},$$

where $\hat{\sigma}$ stands for the variability in concentration (the standard deviation divided by the mean) and τ stands for the residence time. The variability they had in mind was the temporal variability at one point caused by the different histories of the arriving air masses. We are not familiar with any practical applications of this model.

In pursuance of his earlier work, Junge (1974) formulated a different mathematical model. From theoretical considerations he deduced an inverse relation between the variability and the residence time

$$\hat{\sigma} \sim \tau^{-1}.$$

According to Junge, this relation is valid under the constraints that the gases should have the same source function and that the sink should be much less variable in space than the source. He found further support for this relation by using a simple two-dimensional model and finally by comparing the relation with data for some gases in the atmosphere for which measurements of the variability and independent estimates of the residence time were available.

For a well-mixed reservoir in steady-state the average residence time is equal to the turnover time, i.e., to the mass in the reservoir divided by the outflow (Bolin and Rodhe, 1973). This gives the possibility of estimating the fluxes in and out of the atmosphere without actually measuring them, provided that one has an estimate of the residence time.

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Junge's relation provides a tool for estimating the residence time, and has been used extensively during recent years. In a literature search, we found 44 articles referring to Junge's article (Junge, 1974) up to 1981. In most of these articles, the Junge relation was used to estimate the residence time from different measures of variability; either temporal variability at a fixed point or estimates of the spatial variability in the troposphere. Junge, then developing his model, mainly used data on spatial variability.

Before we continue, we should try to clarify what is meant by variability and what the causes may be for differences in variability. To begin with, we would like to distinguish between spatial variability and temporal variability at one point. An ideal measure of variability would take into account both temporal and spatial variations. This would, however, not be very useful because of the measurements which we are likely to have available. Either we could expect to have the concentration as a function of time at a few points or a spatial cross-section, for example from measurements on a "pole-to-pole"cruise. There is no reason to believe that the temporal variability at one point should be the same as the variability obtained from a spatial cross-section. In fact, the temporal variability has been shown to be strongly dependent on where the measurements are made and how variable the weather conditions are at that point (Levy et al., 1982). For these reasons, we have confined our further treatment to spatial variability only.

If we consider the spatial variability, problems arise with regard to the definition. Since the density of air changes with height, we should use the mixing ratio of the gas as our measure of abundance. If we then had a vertical–latitudinal cross-section of the mixing ratio for some gas, we would get a good measure of the variability by computing the mean and the standard deviation of our measurements. Often one has to be content with less—a vertical profile, or data obtained at ground level only. It is not evident that variability estimates based on such different data sets should show the same dependence on residence time.

Factors other than the residence time are bound to influence the variability. Such major factors are the spatial distributions of sources and sinks. Other factors are changing meteorological conditions and changes with time of the "strengths" of sources and sinks. One way to investigate how these factors influence the variability/residence time relation is to use some sort of model of the atmosphere. We choose to use a two-dimensional height–latitude gridpoint model. How well a model of this type represents essential features of the atmosphere is open to doubt. Models of this kind, however, have been extensively used for studies of atmospheric trace substances (Hidalgo and Crutzen, 1977; Rodhe and Isaksen, 1980; Pearman and Hyson, 1980).

2. Model description

The model used for this investigation is a two-dimensional model developed by Isaksen and Rodhe (1978). It is a gridpoint model of the atmosphere based on the continuity equation. The grid extends from pole to pole with a latitudinal spacing of 10° and from 1 to 50 km height with a vertical spacing of 2 km. The mean meridional and vertical wind velocities are adopted from Newell et al. (1972). The turbulent diffusion parameters are based on the work by Hidalgo and Crutzen (1977). The model has been used previously to study the tropospheric sulfur budget (Rodhe and Isaksen, 1980). One main problem with models of this type is the parameterization of the eddy diffusion. The turbulent eddy diffusion coefficients are, on account of the limited data used for their estimation, very unreliable. An even more serious drawback is that it is impossible, with this parameterization scheme, to model certain characteristics of the atmospheric circulation, such as the transport up through the tropical troposphere by means of "hot towers", i.e. high-reaching cumulonimbus clouds.

In order to perform simulations to study the residence time/variability relation, we have introduced 3 different source functions, 3 different sink functions, and 3 different measures of the variability in our model.

The 3 different source functions are called "anthropogenic source", "rain forest source", and "ocean source". The latitudinal distribution of each source is presented in Fig. 1. All sources are located at the earth's surface.

— "Anthropogenic source" is obtained from oil consumption data. It has a strong peak around 40° to 60° N (Europe and North America) and is a typical emission field for industrial pollutants such as SO_2, CO etc.

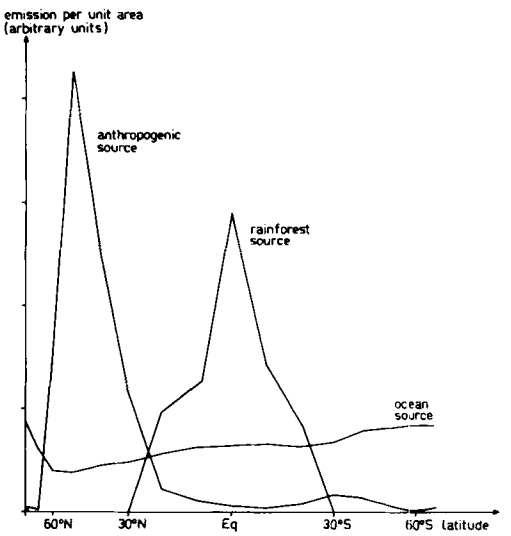

Fig. 1. Latitudinal distributions of model source functions.

— "Rain forest source" is proportional to the area covered by rain forest in each latitudinal band. A possible trace gas with this source function could be COS. The spatial variability (the standard deviation divided by the mean) of the emission is about the same for these two source functions, 1.90 and 1.86, respectively.
— "Ocean source" is proportional to the area covered by oceans for each latitudinal band. The variability for this source function is lower than for the others, 0.25.

The 3 sink functions used are "uniform sink", "dry deposition sink", and "stratospheric sink".

— "Uniform sink" means first-order decay in the whole atmosphere.
— "Dry deposition sink" implies that the sink acts only upon the lowest level of the model with a constant deposition velocity.
— "Stratospheric sink" means that the gas is inert in the troposphere and is subject to first-order decay above the tropopause.

Finally, our 3 measures of variability are the standard deviations divided by the mean computed from the following gridpoints:

$\hat{\sigma}_t$ — (for tropospheric)—from pole to pole including 4 lowest levels of the model (up to 7 km);
$\hat{\sigma}_s$ — (for surface)—from pole to pole but only the lowest model level (1 km);
$\hat{\sigma}_{2p}$ — (for two-point)—from only 2 gridpoints, at 60° N and 60° S at the lowest level.

3. Results of the numerical experiments

The model was run using the formulation described in Section 2 for the 9 different source/sink configurations and for varying residence times. The results for $\hat{\sigma}_t$ and $\hat{\sigma}_s$ are summarized in Figs. 2 and 3. The bars show the variation throughout the year caused by the model's seasonally changing turbulent eddy coefficients and wind fields.

The turn-over time is varied from $\frac{1}{16}$ years up to 64 years by varying the strength of the sink. The lower limit is chosen so that the atmosphere can still be considered well-mixed within a latitude band. For the cases with a stratospheric sink (7, 8 and 9), the transport time to the stratosphere sets a lower limit of around 2 years. The upper limit is chosen for practical reasons. For longer turn-over times, it becomes too time consuming to run the model until the steady state is reached.

We start our discussion of the results by considering our most comprehensive measure of the variability $\hat{\sigma}_t$ (Fig. 2). A striking feature is the wide range of variability we obtain for the different source/sink configurations given a fixed residence time. The range is approximately a factor of 10 for $\tau = \frac{1}{16}$ year and decreases slightly with increasing residence time. The corresponding range in residence time, for a given variability, is even larger, since the slope of the curve is less than 1.

Another easily detectable feature of the results is the systematic difference in variability for different source functions. Quite naturally, we get the lowest variability with the ocean source function, the source with by far the lowest variability. The rain forest source gives 2.5 times higher variability and the anthropogenic source gives the highest variability, 2.5 times higher than the rain forest source.

The above-mentioned difference of a factor of 2.5 between the variability for the "anthropogenic source" and the "rain forest source" vanishes for short residence times (0.25 years). The lack of difference seems reasonable if we remember that the two sources have nearly the same variability (1.90 and 1.86). The difference between the two is that the "anthropogenic source" is heavily biased towards the northern hemisphere, whereas the

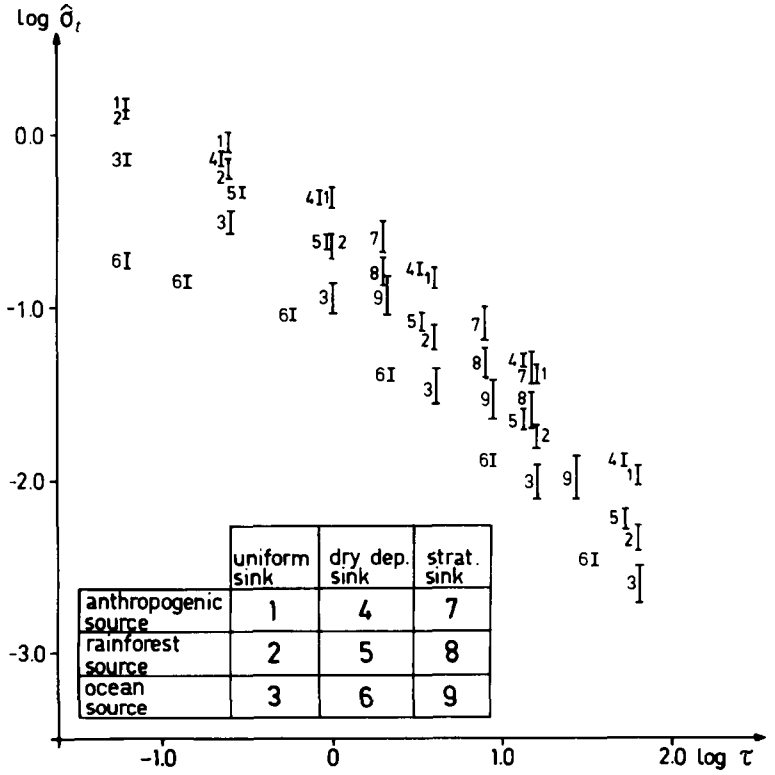

Fig. 2. The tropospheric variability ($\hat{\sigma}_t$) as a function of residence time (τ).

"rain forest source" is almost symmetric relative to the equator. This, in combination with the slow mixing across the equator, explains the difference in variability seen for residence times comparable to and longer than the interhemispherical mixing time (of the order of one year, cf. Czeplak and Junge, 1974).

The influence on the variability of the sink function seems to be less important. It is only for the "ocean source" that we see a clear dependence on the sink function; the "stratospheric sink" gives higher variability than the "uniform sink", and the "dry deposition sink" gives (for short residence times) lower variability.

For each of the 9 different source/link configurations, we computed the best fit, in a least square sense, to the model $\hat{\sigma}_t = A \cdot \tau^B$ to the midpoints of the "data bars" shown in Fig. 2. The result is presented in Table 1. We see that the exponent in all cases is somewhere between the -0.5 proposed by Gibbs and Slinn (1973) and the -1 obtained by Junge (1974). The slope of all 9 curves increases with increasing residence time, approaching Junge's model.

If we consider our second measure of variability $\hat{\sigma}_s$ (Fig. 3), we see that the picture is qualitatively the same as for $\hat{\sigma}_t$. The main differences are the much wider range for the variability of the combinations "ocean source" + "uniform sink" and "ocean source" + "stratospheric sink" (cases 3 and 9) and a less distinct difference between "anthropogenic source" and "rain forest source", at least for short residence times. From a practical point of view, $\hat{\sigma}_s$ is a good measure of variability, while as it retains much of the features of $\hat{\sigma}_t$, it is much easier to estimate from measurements.

Our last measure of variability $\hat{\sigma}_{2p}$, the estimate using only 2 points, shows an altogether more complex behaviour. This is hardly surprising, since only 2 grid points are used and the interaction

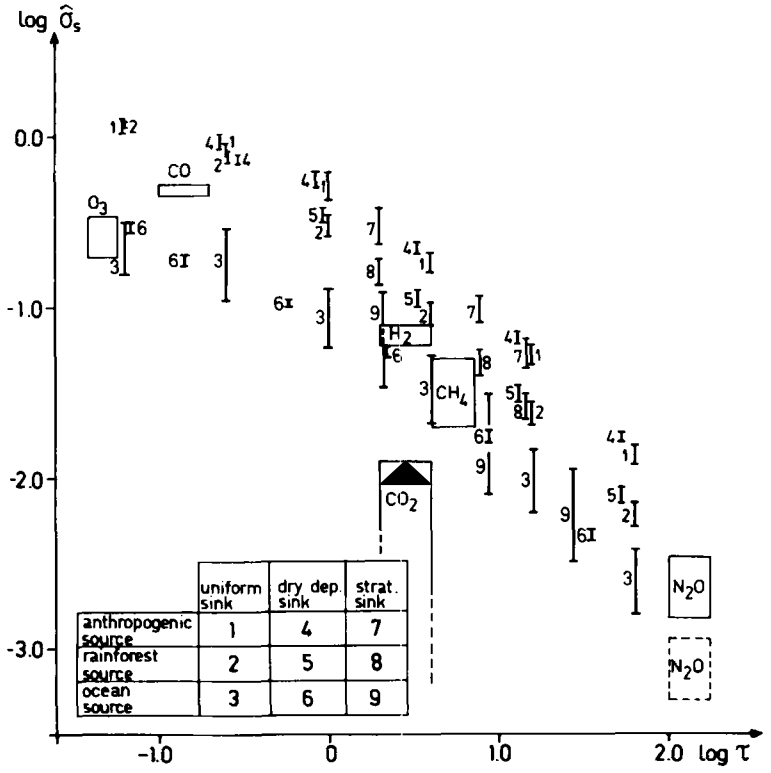

Fig. 3. The surface variability ($\hat{\sigma}_s$) as a function of residence time (τ).

Table 1. *Coefficients for a least square fit of the model for* $\hat{\sigma}_t$ *for the different source/sink configurations*

	Uniform sink		Dry deposition sink		Stratospheric sink	
	A	B	A	B	A	B
Anthropogenic source	0.31	−0.72	0.32	−0.75	0.49	−0.87
Rain forest source	0.18	−0.83	0.20	−0.86	0.31	−0.91
Ocean source	0.095	−0.82	0.048	−0.63	0.25	−0.91

between the transport fields and the source/sink configuration may give either almost the same concentration at the 2 points or give vastly different ones. The fact that the range of variability in this case was 3 or 4 orders of magnitude for a given residence time clearly indicates that this kind of data is insufficient for estimating the residence time.

The time of occurrence of the yearly maxima and minima of the variability is determined by an interaction between the source/sink configuration and the governing mixing pattern. For the anthropogenic source, for example, the minimum occurs at the end of the northern hemisphere's winter season, the season with the most effective mixing in the northern hemisphere. The details of the change of variability in the model during the year is of only limited interest, since it is dependent on the way the seasonal changes in the weather patterns are introduced into the model (the wind fields and turbulent eddy coefficients are exchanged 4 times per year). However, the modelled range of variability might be taken as an indication of how much the variability may change with changing meteorological conditions.

4. Data comparison

It is of interest to compare the results obtained in our numerical model with data. There are, however, rather few compounds, within the range of residence time that we are interested in, for which there exists good data on spatial variability and independent estimates of residence time. If we take the trace gases considered by Junge (1974) as a starting point, we can immediately rule out Rn, H_2O, O_2 and He as having either too short or too long residence times for comparison with the model. This leaves us with CO_2, N_2O, H_2, CH_4, CO, and O_3. We will examine data for these 6 gases to see if they might be used to test our model. The independent estimate of the residence time will for all cases be based on estimates of the fluxes in and out of the atmosphere and on an estimate of the total mass of the trace gas in question. For the estimates of the variability, we have tried, for each estimate, to use data from one measurement group only to avoid the problems connected with intercalibration between measurement groups.

4.1. *CO*

The residence time of CO in the atmosphere is estimated to be 0.1–0.2 years (Freyer, 1979). We have used 2 different data sources to estimate the CO spatial variability. From the latitudinal distribution deduced by Seiler (1974), we obtained a variability of 0.54. Since Seiler's estimate is based on ground-level measurements, it should be compared to our $\hat{\sigma}_s$. From the measurements by Heidt et al. (1980), we estimated a spatial variability of 0.47. These measurements were made on board an airplane flying from 70° N to 60° S at an altitude varying from 0.1 km to 7 km. This is neither quite equivalent to our $\hat{\sigma}_t$ nor our $\hat{\sigma}_s$, but we choose to insert the value in our $\hat{\sigma}_s$–τ plot (Fig. 3), where it is seen to fall somewhere between "anthropogenic source" and "ocean source". The main sources of CO are, as reviewed by Freyer (1979), thought to be the oxidation of CH_4 (1500–5000 Tg yr^{-1}) and an anthropogenic source (450–640 Tg yr^{-1}). The main sink is thought to be oxidation by OH. This implies a fairly uniform source/sink configuration and does not contradict our model.

4.2. *CH_4*

CH_4 has an estimated atmospheric residence time of 4–7 years (Freyer, 1979). As in the case of CO, we have 2 different estimates of the spatial variability. From the latitudinal distribution of Ehalt (1978), we can estimate the variability to $5.0 \cdot 10^{-2}$. This should be compared to our $\hat{\sigma}_s$, since the data are obtained at the ground. From the same flight (GAMETAG), where measurements of CO were obtained, we also have measurements of CH_4 (Heidt et al., 1980). This set of data implies a variability of $2.0 \cdot 10^{-2}$. This lower variability (compared to that of Ehalt) could reflect that most of these data were obtained above the boundary layer. We choose, however, to interpret this difference as our uncertainty in the variability and insert both values in our $\hat{\sigma}_s$–τ plot (Fig. 3). As for CO, the range for CH_4 falls somewhere between "rain forest source" and "ocean source", but for CH_4 closer to "ocean source". The main sources for CH_4 are considered to be paddy fields (280 Tg yr^{-1}) and swamps and marshes (190–300 Tg yr^{-1}) and the main sink is thought to be oxidation by OH (Freyer, 1979). As for CO, this implies a source function that has a lower variability than an anthropogenic source but which is still not uniform.

4.3. *CO_2*

CO_2 introduces complexities that have not been taken into account in our model. The sources and sinks exhibit a strong seasonal variation mainly due to biological activity. This means that the variability will fluctuate during the year, superimposed on the changes caused by changing weather conditions. If we estimate the variability from the latitudinal cross-section deduced by Bolin and Keeling (1963), it varies for different months from a maximum of 0.013 in August down to very low values. The turnover time of CO_2 is estimated to lie between 2 and 4 years (Bolin et al., 1979). Introducing this into Fig. 3, we see that the estimated variability for CO_2 is lower than that for CH_4, although CH_4 has a longer estimated residence time in the atmosphere. The 2 main sources for CO_2 (which are also the main sinks) are the exchange with the oceans ($100 \cdot 10^{15}$ g C yr^{-1}) and photosynthesis on land ($53–78 \cdot 10^{15}$ g C yr^{-1}) (Bolin et al., 1979). When compared to our model, CO_2 has a lower variability than any of the source/sink configurations. This might be explained by the low variability in sources and sinks for CO_2, and that the sources are approximately the same as

the sinks averaged over the years. However, the strong seasonal variation in sources and sinks for CO_2 makes all comparison with our model doubtful.

4.4. H_2

The residence time for H_2 is currently estimated to be between 2 and 4 years (Conrad and Seiler, 1980). This figure is fairly uncertain because of the uncertainties involved in the estimates of the individual sources and sinks. From the measurements by Schmidt (1978), we estimate the tropospheric variability to be between 0.06 and 0.08. Since this estimate is derived from latitudinal cross-sections at ground level, it should be compared to $\hat{\sigma}_s$ (Fig. 3).

According to Conrad and Seiler (1980), there are four main sources for H_2: automobiles and industry (20 Tg yr^{-1}), burning of biomass (10–25 Tg yr^{-1}), oxidation of CH_4 (10–35 Tg yr^{-1}) and oxidation of hydrocarbons (10–35 Tg yr^{-1}). The main sink is uptake by soil (70–110 Tg yr^{-1}). Since approximately 50% of the emissions is anthropogenic, we would expect a fairly high variability. However, the variability is seen to be only moderate and slightly lower than what the model predicts for a rain forest source. The discrepancy between the model and the data for H_2 may of course be explained by the inadequacy of the model itself. However, we can not exclude the more interesting possibility of a longer residence time in the atmosphere for H_2 than currently estimated.

4.5. O_3

From the meridional cross-section presented by Fabian and Pruchiewicz (1977), we obtain an estimate of the variability comparable to $\hat{\sigma}_s$ of between 0.20 and 0.35. The variability varies seasonally, but to a much lesser extent than for CO_2. The estimate of the ozone residence time is very uncertain due to the controversy about the gas phase production in the troposphere (Crutzen, 1973; Chameides and Walker, 1976; Chatfield and Harrison, 1976). If we accept the presence of a large tropospheric source of ozone, the residence time will be between 2 and 3 weeks (Galbally and Roy, 1980; Fishman et al., 1979; Rodhe et al., 1982). The two main sources for ozone in the troposphere are considered to be injection from the stratosphere (1000 Tg yr^{-1}) and gas phase production in the troposphere (2000 Tg yr^{-1}). The main sinks are destruction at the surface (1100 Tg yr^{-1}) and gas phase destruction (2000 Tg yr^{-1}) (Rodhe et al., 1982).

In view of ozone's source/sink configuration, with most production and destruction taking place rather homogeneously within the troposphere, the low variability obtained is not surprising. We notice that the variability of O_3 is lower than that for CO, although O_3 has a shorter estimated residence time.

4.6. N_2O

The tropospheric residence time of N_2O is estimated to be in the range 100–174 years (Weiss, 1981). From the data presented by Weiss (1981), we calculated latitudinal cross-sections and from these, the variability. The range of variability, arising from different ways of treating the collected data, was $1.5 \cdot 10^{-3}$–$3.5 \cdot 10^{-3}$. As the data were collected on sea cruises and at ground-level stations, this should be compared to $\hat{\sigma}_s$ (Fig. 3).

We face here another complication; the distribution is not in a steady-state. Weiss (1981) reports that the concentration is rising at a rate of about 0.2% per year. This increase in the source strength, together with a long N_2O residence time, will affect the variability. Calculations with a simple box model indicate that the variability should be reduced to about a third in the steady state case. This is in accordance with Weiss' (1981) statement that the interhemispherical difference should be reduced by 0.5 p.p.b. in the steady-state case. The estimated reduced variability is also introduced into Fig. 3 (dashed lines).

The range for N_2O (the revised values) indicates a source that gives about the same variability as the ocean source. There seems to be a fair agreement that the main sink for N_2O is photolysis in the stratosphere. The sources are more uncertain; there has been an ongoing dispute about the possibility of the ocean as a major source, but this idea seems to be discarded now (Weiss, 1981; McElroy, 1980). The other proposed sources are emissions from natural ecosystems and emissions caused by man's land use. How variable the total source is depends on the partitioning between these two sources. In general, though, we conclude that the data for N_2O are not inconsistent with our model.

5. Discussion

This investigation of the relationship between variability and residence times for atmospheric trace gases has the following aims:

— To clarify the concept of variability and

— To investigate the reliability of residence time estimates based on measurements of variability.

The concept of variability was addressed in the introduction. The main point was the distinction between variability in time (at a fixed point) and spatial variability. We confined our further treatment to spatial variability only.

To investigate variability/residence time relationships, we used a two-dimensional model of the atmosphere. The results indicate that if an estimate of the variability is the only information available, the uncertainty in the estimate of the residence time will be more than a factor of 10. The situation is greatly improved if some information about the expected source/sink configuration is available. The model shows that if the locations of the sources and sinks are known, then the uncertainty in the estimate of the residence time is decreased to about a factor of 2.

These results were obtained from one specific model of the atmosphere. It is possible that models with different parameterization schemes would have given different results. To test the validity of our model results, we compared them with measurements for trace gases in the atmosphere.

The concentrations of trace gases in the atmosphere show a more complex behaviour than is possible to resolve in our model. Some gases have strong seasonal variation in source and sink strength. Others were clearly not in the steady-state, the emissions increasing. This makes the comparison between model results and the real world difficult. In addition, there is the uncertainty about the measurements behind the variability estimate and especially of the flux estimates for many of the trace gases. We must conclude that there are not enough data to verify the model in any great detail.

If the data are not good enough to verify the details of the model, neither do they contradict it. The general feature of decreasing variability for increasing residence time is clearly established. The data also support the hypothesis that the source/sink configuration has a strong impact on the variability.

Based on the above considerations, we propose the following scheme for estimating residence time by this method.

(i) Try to obtain an estimate of the variability comparable either to our surface variability measure $\hat{\sigma}_s$ or to our tropospheric variability measure $\hat{\sigma}_t$.

(ii) If nothing is known about the source/sink configuration, then the estimate has to be based on the envelope of the bars in Figs. 2 or 3. This will give an uncertainty in the estimate of more than a factor of 10.

(iii) If there are indications of where the sources and sinks are located, try to fit that in with the model, taking into consideration especially how variable the source is and where it is located with respect to the equator. This will give a better estimate, but the uncertainty will still be appreciable (at least a factor of 2).

In this presentation, we have placed much emphasis on the uncertainties connected with the estimation of the residence time from measurements of the variability. It is important to keep these uncertainties in mind, but they do not disqualify the method. The difficulties in making flux estimates are widely recognized and the residence time obtained by the method may have uncertainties of at least the same magnitude as when using the variability method. The variability/residence time relation also gives the possibility of checking whether all major sources and sinks have been properly accounted for.

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