The modelling problems associated with spatial averaging

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SUMMARY

The problem of spatial averaging in photochemical models of the stratosphere is considered. It is shown that correlation between reacting species, or between species and temperature, can lead to a bias in the model treatment of the reaction rate. Using satellite data it is demonstrated that for reactions controlling the ozone budget the resulting error is generally not large, although it may be appreciable during times of strong dynamical activity. Finally, we speculate that the errors could be more significant for species with strong gradients in the vertical, or for variability on a smaller scale than is resolved by satellite measurements. This could afford an explanation of some current modelling problems.

1. INTRODUCTION

The general problem of spatial averaging in numerical models of atmospheric chemistry was first discussed by Tuck (1978, 1979, see also Allam et al. 1981). He pointed out that, because of the averaging approximations usually invoked, the global average in a one-dimensional model and the zonal average in a two-dimensional model may not correspond to the true global and zonal averages.

Consider reaction between A and B with rate constant, \( k \), assumed for simplicity to be independent of temperature and pressure. Letting \([\cdot]\) denote a concentration, \( \bar{\cdot} \) a zonal average and \( \cdot^\prime \) a departure from the zonal average, then the zonally averaged rate of reaction between A and B is

\[
\tilde{k}[A][B] = \tilde{k}[\bar{A}][\bar{B}] + \tilde{k}[\bar{A}^\prime][\bar{B}^\prime].
\]  

(1)

The term on the left we call the true rate. The first term on the right is the rate which would be calculated in a two-dimensional model. We call this the model rate. The model rate and the true rate are not, in general, equal. They are only equal if A and B are uncorrelated in which case the second term on the right-hand side of Eq. (1), the eddy term, is zero. If A and B are positively correlated then the eddy term itself is positive and the model rate will be less than the true rate. If A and B are anticorrelated then the eddy term is negative and the model rate will be greater than the true rate.

Similar arguments would apply to the case of the global average in a one-dimensional model, or the case of diurnal averaging (see e.g. Fabian et al. 1981). Indeed any type of average will have an associated covariance problem. This applies to all scales, from the global, down to the microscale. For molecules to react they must come into contact and thus the calculation of the ‘true’ average rate implies a knowledge of all spatial and temporal variations.

In practice, the situation is even more complicated. The rate constant \( k \) is usually temperature and, for three-body reactions, pressure dependent, hence its correlation with constituents A and B also has to be considered. For the case of a variable \( k \), three eddy terms are present, and the true rate is given by

\[
\tilde{k}[A][B] = \tilde{k}[\bar{A}][\bar{B}](1 + r_{A,B} \sigma_A \sigma_B + r_{k,A} \sigma_k \sigma_A + r_{k,B} \sigma_k \sigma_B)
\]

where, for example, \( r_{A,B} \) is the usual cross-correlation coefficient between the quantities A and B, and \( \sigma_A \) is the standard deviation of A, normalized by its average value.
\( \tilde{k} \), the 'average' value of the rate constant in the above expression is normally calculated from the average temperature and this can give rise to a further error. If the temperatures have a normal distribution, it can easily be shown that for an exponential temperature dependence of

\[ k = k_0 \exp(-E/RT) \]  (2)

where \( E \) is the activation energy and \( R \) the gas constant, the average coefficient is approximately given by

\[ \bar{k}(T) = k(T) \left\{ 1 - \frac{\sigma_T^2 E}{RT} (1 - E/2RT) \right\} \]  (3)

\( \bar{T} \) is the mean temperature of the sample and \( \sigma_T \) the standard deviation of the temperature values.

The error can be quite significant. For the case of the \( k[O][O_3] \) loss and a temperature of 250K with 10K standard deviation, it is equal to about 5%.

Finally, there will also be averaging problems associated with the treatment of photolysis; we have ignored these, preferring to concentrate in this study on the effect of the spatial covariance of species concentrations. We discuss our photolysis approach in section 2 and return to the topic briefly in section 4. Let us stress that we do not think averaging errors in photolysis calculations are necessarily small; indeed, these errors would merit a future study. Notice that there are other sources of error in numerical models; in particular the kinetic or photochemical data may be in error or the photochemical scheme may be incomplete. For example, if in consequence the penetration of ultraviolet radiation is treated incorrectly then this would have a major impact on the calculated species distributions. All these errors are potentially important and some error is inevitable; nevertheless, we will not consider them. Because of the difficulty of treating global and zonal averages in models of one and two dimensions, the problem outlined by Tuck has generally been ignored by modellers. The problem of concentration variations on smaller scales has not been considered at all. On the other hand, many models include a treatment of the diurnal averaging problem, simply because this can be done in a straightforward manner.

In this paper we use data from the LIMS (limb infrared monitor of the stratosphere) experiment on Nimbus 7 to investigate the problem of treating zonal and global averages in numerical models. We are motivated by a desire to understand current discrepancies between models and measurements. For example, models generally underpredict ozone in the upper stratosphere by between 20 and 50%, although Natarajan and Callis (1989) have pointed out that if ATMOS observations are used to constrain a calculation of ozone, then the observed ozone can be reproduced within its experimental error. Two-dimensional model calculations at Cambridge (Chipperfield 1990) show only a small discrepancy with observations but it is nevertheless interesting that underprediction by all models appears to be a consistent result. The ozone balance in this region is between production by photolysis of \( O_2 \), which will have probably only a small averaging problem, and destruction by a variety of two-body reactions. If there are anti-correlations between the species removing ozone, e.g. between O and \( NO_2 \) and O and \( ClO \), then, from Eq. (1), it is possible that a numerical model would overestimate the rate of ozone destruction and hence ozone would be underestimated by the model. This aspect of the ozone budget has been studied here. It is found that generally the differences between the true and model rates are small for the cases considered, except at the time of a major stratospheric warming.

We consider two other problems in addition to that of the ozone budget at 40 km;
(i) the problem of matching the observed HNO₃ profiles in the mid stratosphere and (ii) the problem of simultaneously modelling a number of source gases, e.g. N₂O and CH₄.

The satellite data have limitations in spatial resolution which are inherent in any remotely-sensed data and tell us nothing about spatial variations with scale less than a few kilometres in the vertical or less than perhaps a hundred kilometres along the instrument line of sight. In the final part of this paper we speculate that spatial variations on these or smaller scales may be important for atmospheric chemistry.

2. THE DATA

The LIMS experiment, launched in October 1978 on board the Nimbus 7 satellite, measured radiation emitted at stratospheric altitudes by H₂O, O₃, NO₂ and HNO₃ (Gille and Russell 1984). With a sun-synchronous orbit, the experiment had a coverage from 84°N to 64°S with thirteen orbits each day. Retrieved data for the seven months of the mission have been archived with a grid spacing of 1.5 km in the vertical and 4 deg in latitude along the orbit. Data are available for both day and night.

For our study, we have considered two time-periods: the month of May for 'typical' conditions, and February for disturbed data. (A major stratospheric warming occurred in late February 1979, following a strong disturbance early in the month.) We have selected soundings in both time-periods at three latitudes: 60°S, the equator, and 60°N, and each latitude band was about half a degree wide. Only the day-time soundings were used. There were about 300 soundings in each group except at 60°S in May where we had just 160 soundings.

We first placed the LIMS data on a height grid with a resolution of 0.5 ln(p/p₀) with p₀ = 1013 mb, equivalent to a height resolution of about 3.5 km. All the terms appearing in Eq. (1) were then calculated for each sounding. The sun elevation angle was made the same for all soundings in a group, equal to the average angle at the latitude band and time period for data in that group. This is done because our interest here is in the effect of spatial averaging. Ideally, concentrations taken at one particular time, a 'snapshot', would be used in this study. However, to increase the amount of data we have had to use samples taken over one month. If the appropriate zenith angle for each sounding were to be used, then two error-sources would be introduced, one associated with the spatial covariances and the second associated with the zenith-angle variation. However, we prefer here to consider just the spatial covariance and therefore assume that all the data were indeed taken at the same time. In the subsequent analysis, model rates, 'true' and average, are compared with each other. Neither is necessarily the rate of reaction found in the atmosphere, but this does not matter since we are investigating errors in modelling practice associated with spatial averaging. For this the data used are perfectly adequate.

The success rate of retrieving any of the LIMS species depends on its concentration and the temperature at the relevant height. Whereas O₃ and H₂O were retrieved in almost all the soundings up to (and above) the height of 50 km, the number of successful retrievals for HNO₃ and NO₂ decreases at heights above about 35 km. So that the model errors for the different loss reactions should be more comparable, only those soundings were used where all the LIMS species were retrieved at the height considered. An exception was made with HNO₃ which was not required to be present above 38 km for the calculation of the radical concentrations (see below). In this way the comparison could be extended up to a height of 47 km in most cases. (N.B. It follows that, owing to the selection of soundings according to whether retrieval was or was not possible, the variability, and hence model errors, are underestimates. For example, the
standard deviation of the temperature data in February, at 60° N and 29 km, was 13.0 K when all the soundings were considered, and 10.4 K when the restricted range was used. The average temperature was 3.8 K higher here for the full range. The differences arise mainly because fewer NO₂ and HNO₃ retrievals are made at the lower temperatures.)

Apart from the species measured by LIMS, concentrations of other species can be derived from the LIMS measurements. For example, Pyle and Zavody (1985) have described the derivation of OH and HO₂ from the sources and sinks of the hydrogen-containing radicals. In the same study, NO and O(3P) were derived on the basis of equilibrium with measured NO₂ and O₃, respectively.

A further approximation is invoked in this study. We wish to derive ClO from the LIMS data. Unfortunately, measurements of chlorine species have not yet been made from space. However, if we assume that we know the profile of total odd chlorine ([ClOy] = [Cl] + [ClO] + [HCl] + [ClONO₂] + [HOCI]) then the partitioning between the various members of the family depends only on measured quantities (see Table 1).

<table>
<thead>
<tr>
<th>TABLE 1. THE PHOTOCHEMICAL SCHEME</th>
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<tbody>
<tr>
<td>O₃ + hν → O¹(¹D) + O₂</td>
</tr>
<tr>
<td>O₂ + hν → 2O₂</td>
</tr>
<tr>
<td>O + NO₂ → O₃ + NO</td>
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<tr>
<td>O + NO₂ → O₂ + OH</td>
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<tr>
<td>O + ClO → O₂ + Cl</td>
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<tr>
<td>O + O₂ + M → O₃ + M</td>
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<tr>
<td>OH + O₃ → HO₂ + O₂</td>
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<tr>
<td>HO₂ + NO → OH + NO₂</td>
</tr>
<tr>
<td>O(¹D) + CH₃ → OH + CH₂</td>
</tr>
<tr>
<td>OH + CH₄ → H₂O + CH₃</td>
</tr>
<tr>
<td>Cl + CH₄ → HCl + CH₃</td>
</tr>
<tr>
<td>N₂O + hν → N₂ + O(¹D)</td>
</tr>
<tr>
<td>N₂O + O(¹D) → 2NO</td>
</tr>
<tr>
<td>NO₂ + OH + M → HNO₃ + M</td>
</tr>
<tr>
<td>HNO₃ + OH → NO₂ + H₂O</td>
</tr>
<tr>
<td>HNO₃ + hν → NO₂ + OH</td>
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<tr>
<td>O₃ + hν → O₂ + O</td>
</tr>
<tr>
<td>Cl + O₃ → ClO + O₂</td>
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<tr>
<td>Cl + H₂ → ClO + H</td>
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<tr>
<td>Cl + HO₂ → ClO + OH</td>
</tr>
<tr>
<td>ClO + NO → CI + NO₂</td>
</tr>
<tr>
<td>HCl + OH → HOCI + O₂</td>
</tr>
<tr>
<td>HOCl + OH → ClO + H₂O</td>
</tr>
<tr>
<td>HOCl + hν → Cl + OH</td>
</tr>
<tr>
<td>ClO + NO₂ + M → ClONO₂ + M</td>
</tr>
<tr>
<td>ClONO₂ + hν → ClO + NO₂ + O₂</td>
</tr>
</tbody>
</table>

Assuming a fixed profile is, we believe, a fair approximation. There is no stratospheric sink of ClOy and its major source gases have been measured. Furthermore, for our argument the absolute concentration is unimportant. It is the spatial variability that is of interest and this should be modelled reasonably well, with the exception that only zonal mean fields of CH₃ (which determines the HCl/ClO ratio in the upper stratosphere) are generally available from the SAMS instrument (Jones and Pyle 1984). The variability of stratospheric chlorine compounds is discussed in detail in a further paper (Pyle and Zavody 1987). Table 2 presents the steady-state expressions used in this study. Rate constants and data for the photolysis calculations are from various recent compilations as described in Pyle and Zavody (1985).
TABLE 2. PHOTOCHEMICAL STEADY-STATE EXPRESSIONS

\[
\begin{align*}
[O] &= (J_1 + J_{1k})[O_2]/(k_1[O_2][M]) \\
[Cl] &= k_4[O] + k_{20}[NO] \\
[ClO] &= k_{10}[O_3] \\
[Cl] &= k_{25}[OH] \\
[HC] &= k_{12}[CH_4] + k_{21}[HO_2] + k_{20}[H_2] \\
[ClO] &= J_{2k} + k_{25}[OH] \\
[HOCl] &= k_3[HO_2] \\
[ClO] &= J_{2k} + k_{20}[O] \\
[ClONO_2] &= k_{25}[NO_2][M]
\end{align*}
\]

3. THE CALCULATION OF AVERAGES

The LIMS data have been used to calculate terms in the ozone continuity equation. Our simplified expression for ozone production and loss becomes

\[2J_2[O_2] = 2k_3[O][O_3] + 2k_4[O][NO_2] + 2k_4[O][HO_2] + 2k_4[O][ClO]\]  (4)

in which \(J\) is the photodissociation coefficient.

We have chosen this simple expression for purpose of illustration. Other terms could be included but nevertheless Eq. (4) contains the main rate-determining reactions for ozone production and destruction. Before we consider the terms individually we note that production of ozone involves a photolysis reaction for which species covariances do not arise.

After calculating the terms appearing in Eq. (4) for all the individual soundings, and for the average LIMS values in each group, the average product terms were computed for both cases. The losses obtained by using the two methods were compared and the differences (‘model errors’) are shown in Fig. 1(a–c). (Note the change of scale for Fig. 1(c).) It can be seen that, under conditions of nearly zonal flow, the total model error is usually under 1%. The largest errors occur at 60°N in February when, during the period of the sudden warming, the variability in the species and temperatures is the highest. The model losses in, in almost every case, lower than the true losses at heights below 38 km; thus the model should be expected to overestimate ozone by comparison with observations. Above this height, the model losses tend to be higher; the errors, however, are well below 2%, to be compared with the 20–50% underestimate of \(O_3\) at around 40 km in recent studies of models of one and two dimensions.

The errors at the equator and in the summer hemisphere are always very small. Errors increase somewhat into the winter hemisphere. For example, at 60°S in May the errors in the calculated zonally averaged rate of the \(O + O_3\) reaction are greater than 5%.

In order to understand the magnitude and sign of the model errors, let us consider the different loss reactions at 60°N in February in turn.

The approximate contributions to the model error for the \(k_3[O][O_3]\) losses are shown in Fig. 2. The rate constant \(k_3\) is highly temperature dependent (\(E/R = 2100K\) in Eq. 2) and, in this case, the error in the average value of \(k_3\) exceeds the errors due to the eddy terms. The error is largest at about 43 km (\(\sigma_T = 17-9K, \bar{T} = 262-8K\), and is equal to 13-8%.

At any given height, not only \(k_3\) but also \(O\) and \(O_3\) have a temperature dependence. Analysis of satellite measurements has shown that in the upper stratosphere \(O_3\) varies
Figure 1. Percentage difference between the true zonal average rate of the reactions in Eq. (4) and the rate that would be calculated in a two-dimensional model. a (---), $k_3[O][O_3]$; b (----), $k_2[O][HO_2]$; c (-----), $k_4[O][ClO]$; d (-----), $k_4[O][NO_2]$; e (------), total. The rates were calculated using LIMS satellite data: (a) for 60°S, February 1979, (b) for the equator, February 1979, (c) for 60°N, February 1979 (note the change of scale).
with temperature with a temperature exponent equal to about 1000 K. Owing to the long life-time of $O_3$, transport and the gradient of the mixing ratio become increasingly important at lower heights, causing the exponent to decrease to zero and become negative in the lower stratosphere. It follows from the above that the error arising from the correlation between $k_3$ and $O_3$ is expected to be positive where the two quantities are correlated, i.e. above 35 km, and negative where the temperature dependence of $O_3$ has become negative—just as we have found from the data.

As can be seen from Table 1, the primary source of $O$ is photolysis of $O_3$ and, assuming photochemical equilibrium, the concentration of $O$ is given by

$$[O] = \left( J_1 + J_{10} \right) [O_3]/k_5[M][O_2].$$

The $J$ term is substantially independent of temperature; hence the temperature dependence of the numerator is given by that of $O_3$. In the denominator, the rate constant $k_5$ varies with temperature approximately as $\exp(510/T)$. (We have in fact used in our calculations the more usual form of $T^{2.5}$ for the temperature dependence. In the following discussion for convenience we have used the—nearly equivalent—exponential form.) The number of molecules per unit volume of air, $M$, and molecular oxygen, $O_2$, are inversely proportional to temperature and, for small changes in temperature this is equivalent to an exponential temperature dependence of approximately $\exp(2T_s/T)$ where $T_s$ is the mean stratospheric temperature at a given pressure level. It follows that the denominator varies with temperature as $\exp(K/T)$ where $K$ is in the range of 800 to 1200 K. If changes of temperature were the only cause of ozone variability—or, alternatively, if the variabilities of $O_3$ and temperature had a common cause—then in the upper stratosphere very small variability would be expected for atomic oxygen; at first sight a most surprising result.

$O$ and $O_3$ are strongly correlated in the lower and mid stratosphere but, because the relative variances of both $O$ and $O_3$ in this case are always smaller than that of the rate constant, the error due to this term is the smallest. Even for the very variable high-latitude winter stratosphere the model error is less than 4% at all the heights considered. The correlation decreases with height and, at heights above 35 km, $O$ and $O_3$ are often anticorrelated, giving rise to a change in sign of the error term. The anticorrelation is
caused by a combination of the temperature dependence of O$_3$ and the positive temperature dependence of the rate coefficient for the O + O$_2$ reaction. The total error peaks at about 30 km and is equal to 12% at 22 km.

The model errors for the O + HO$_2$ reaction are substantially smaller. Because of the very weak temperature dependence of the rate coefficient ($E/R = 200$ K), using the average temperatures for its calculation leads to errors of less than 1%. Another consequence of the small temperature dependence is a low variance for $k_5$, leading to small errors from the $k_3$[O][HO$_2$] terms. The dominant source of error in this case is always the term arising from the correlation/anticorrelation between O and HO$_2$.

The errors for the $k_4$[O][ClO] term are also low. The temperature dependence of the rate coefficient is small ($E/R = -120$ K), hence its contribution is again small. The correlation between O and ClO is positive below about 30 km and negative above. In February at 60° N, the correlation calculated for O and ClO was very strong in the lower stratosphere (for about 220 soundings, 0.95 at 19 km, 0.91 at 22 km), giving rise to significant errors here. In the regions where Cl chemistry is important, however, the model errors do not exceed 5%. For the $k_4$[O][NO$_2$] term $k_4$ is considered to be independent of temperature and hence we only have to consider the error arising from correlation between O and NO$_2$. Although some pattern is evident in the correlation coefficients between the two quantities (e.g. at the equator, positive correlation at most heights; at high latitudes, negative correlation in the lower and higher stratosphere and positive correlation in the mid stratosphere), the correlation coefficients are low and hence the model errors are also small. The correlation is highest in February at 60° N (for about 260 soundings, 0.52 at 29 km and 0.59 at 32 km) and this, combined with the large variability in NO$_2$, leads to errors of about 5% in the model.

4. DISCUSSION AND SPECULATION

Although the eddy terms and errors arising from using average temperatures in the rate constant calculations are much too small to explain the discrepancies between model and experimental O$_3$ values, we believe that variability on a smaller scale may play an important role. The variability discussed above was of planetary scale. The satellite retrievals represent mean values of the species mixing-ratios for volumes of air a few kilometres deep and extending a few hundred kilometres in the horizontal plane. Variability on a smaller scale cannot be resolved. It should also be noted that the GCM calculations of Grose et al. (1987) and the air parcel trajectory study of Austin et al. (1987) avoid zonal averaging yet also underestimate ozone in the upper stratosphere. If there is a major averaging problem then it may be associated with variability on scales that cannot be resolved at the moment by satellite measurements.

Figure 3, following Kley et al. (1980), shows simultaneous, high-resolution measurements of O$_3$ and H$_2$O. Note the vertical structure and the anticorrelation of the O$_3$ and H$_2$O variations. Consider the variation at 31 km in more detail. The ozone mixing ratio is about 6-6 ppmv compared with an average value (obtained by drawing a smooth curve through the data) of about 8.2 ppmv. Similarly H$_2$O has increased from the mean of about 3 ppmv to 4-1 ppmv. How does the mean value, inferred from the average curves, for the rate of OH + O$_3$ compare with the true value? The production of HO$_x$ is proportional to [H$_2$O][O(1D)] which will be little different for the observed curve and the average curve at 31 km since H$_2$O and O$_3$ are anticorrelated. If we assume that HO$_2$ is constant for the two curves (and this does not necessarily follow) then we can calculate OH. At 30 km the partitioning of OH and HO$_2$ is dominated by
Figure 3. Vertical profiles of H$_2$O and O$_3$, taken from Kley et al. (1980).

\[ \text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad k_8 \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2 \quad k_9 \]

from which it can be shown that

\[ [\text{OH}] = (\text{HO}_2) \left( 1 + \frac{k_8[O_3]}{k_9[\text{NO}]} \right) = [\text{HO}_2] \frac{k_9[\text{NO}]}{k_8[O_3]}. \]

If we assume that NO is constant (and this would surely not be true) then a 28% decrease in O$_3$ (from 8·1 to 6·6 ppmv) would lead to a 28% increase in OH. It can easily be shown that this leads to a 4% difference in the rates of OH + O$_3$ calculated using the observed and average curves; not entirely negligible compared with a discrepancy between models and observations of between 20 and 50%. Of course, the details of this argument are very speculative. Nevertheless, the impact of these laminar structures does need to be examined in detail in a more rigorous theoretical and observational study.

There are very few observations of these laminar structures as they call for particularly sensitive measurement techniques. If they were to show an increase in amplitude with altitude then naturally their influence in the averaging problem becomes more important. In this context the use of lidar techniques to measure ozone in the upper stratosphere and mesosphere could be particularly important.
While the measurements of fine vertical structure are very limited, support for our idea is perhaps given by the very high resolution barotropic modelling study of Juckes and McIntyre (1987). Their calculation shows extremely large variability on relative small spatial scales in middle latitudes as the polar vortex is eroded. These structures could play an important role in atmospheric chemistry.

A further point should be made. The problems of averaging are cumulative so that contributions of a few percent from global-scale variations, from small-scale variations and perhaps from diurnal variations could all add to a significant contribution.

Nevertheless, the cases we have considered thus far have tended to have small differences between true and model means. For a bimolecular reaction, the concentrations variations enter quadratically in the rate expression. Thus to get a difference between true and model rates of 20% requires perturbations to the mean concentrations of around 45%. For gases with relatively weak horizontal and vertical gradients like stratospheric ozone and water vapour, this is extremely difficult to achieve.

There are gases which have strong gradients in the stratosphere. Source gases, like N$_2$O, F 11, F 12, which are produced or released in the troposphere and have only sinks in the stratosphere decrease rapidly with altitude above the tropopause. For these gases the dynamically induced variability by, for example, gravity waves or simply interleaving of layers of air could produce significant vertical structure in the gas concentration profile (see Ehhalt et al. 1983).

These structures, we hypothesize, could explain another longstanding modelling problem. Simultaneously modelling all the source gases is a current problem in models of both one and two dimensions (see e.g. WMO 1986). For example, using a two-dimensional model, Jones and Pyle (1984) were able to reproduce the observed CH$_4$ profiles well, but the model overestimated the observed N$_2$O in the upper stratosphere. With an improved dynamical representation in the same model Gray and Pyle (1986) found that the observed N$_2$O was modelled well but that the observed CH$_4$ was now underestimated. If we look more closely at the photochemistry of CH$_4$ and N$_2$O we find that the continuity equation, ignoring transport, can be written

\[
\frac{d[\text{CH}_4]}{dt} = -k_1[O(1D)][\text{CH}_4] - k_2[\text{OH}][\text{CH}_4] - k_3[\text{Cl}][\text{CH}_4]
\]

\[
\frac{d[N_2\text{O}]}{dt} = -J_{N_2\text{O}}[N_2\text{O}] - k_4[O(1D)][N_2\text{O}].
\]

For N$_2$O the destruction is dominated by the photolysis term. Thus N$_2$O is destroyed mainly by photolysis, which has no averaging problem, while CH$_4$ is destroyed by bimolecular reactions which will have an averaging problem. Furthermore, CH$_4$ will be anticorrelated with H$_2$O and, hence, probably with OH so that the model rate of the reaction OH + CH$_4$ should overestimate the true rate. This is in the required sense to explain the discrepancy noted above. Unfortunately, we are again not in a position to confirm this suggestion as the required high-resolution data are not available. However, a systematic study of a series of source gases might provide further clues.

Although we have assumed that the photolysis reaction does not have an associated averaging problem, Hunten (1983) has pointed out that the photolysis rate at any level will depend on fluctuating concentrations of O$_3$ and O$_2$ above the level in question, which Hunten argues could systematically increase the photolysis rate for a gas like N$_2$O. Thus if CH$_4$ and OH are indeed anticorrelated, both factors would lead to better agreement between model and observations for both CH$_4$ and N$_2$O. Of course, another explanation could be that the absolute value of the photolysis rate is calculated incorrectly, a not
unlikely result at wavelengths around 200 nm. Furthermore, there would be an averaging problem associated with temperature dependent absorption cross-sections, such as for N$_2$O, which we have not included.

A further problem in modelling stratospheric species has been the tendency for models to overestimate the HNO$_3$ in the stratosphere above about 30 km. As can be seen from Table 1, the source of HNO$_3$ is the reaction

$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ \hspace{1cm} (6)

and HNO$_3$ is destroyed by photolysis and through the reaction

$\text{HNO}_3 + \text{OH} \rightarrow \text{NO}_3 + \text{H}_2\text{O}$. \hspace{1cm} (7)

In the lower and middle stratosphere, loss reaction (7) is only a small fraction of the total loss which is dominated by photolysis at all the heights considered here. Reaction (6) has a fairly strong temperature dependence, about $\exp(1000/T)$ if the dependence of M on T is included, and hence all three eddy terms are important.

The approximate break-down of the errors for reaction (6) are shown for February at 60°N in Fig. 4. There is significant cancellation of errors caused by the correlation coefficients being approximately equal, but of opposite sign, for OH and NO$_2$, and k and NO$_2$. The largest error is about 4%, with the model underestimating the production of HNO$_3$. The other latitudes show similar but much smaller errors. Notice that the errors here are small because of cancelling contributions. In principle the averaging errors could be large in cases like this.

For all the data considered, NO$_2$ and H$_2$O were found to be weakly correlated in the lower stratosphere and weakly anticorrelated in the upper stratosphere. At around 30 km, the expression for OH/HO$_2$ is approximately given by

$$\frac{\text{OH}}{\text{HO}_2} = \frac{k_5 \text{NO}}{k_8 \text{O}_3}$$ \hspace{1cm} (8)

so that OH should be in phase with NO. As NO is proportional to NO$_2$ (the correlation coefficient between the two was often found to be as high as 0.98 and exceeded 0.5 in

![Figure 4](image)

Figure 4. Contributions to the model error in the term $k[\text{OH}][\text{NO}_2][\text{M}]$ from (a) (⋯⋯), averaging the temperature dependent rate constant and from correlations between (b) OH and NO$_2$ (−−−−), (c) k and OH (−−−−), (d) k and NO$_2$ (−−−). The total error is shown by the solid line, (e). From LIMS satellite data for 60°N, February 1979.
all our samples), the fairly strong correlation between OH and NO$_2$ is to be expected in the lower and middle stratosphere. In the upper stratosphere, the NO + HO$_2$ reaction is no longer the dominant loss reaction for HO$_2$ and the correlation between OH and NO$_2$ becomes very small and of either sign.

The errors arising from the eddy terms in reaction (7) are shown for February at 60°N in Fig. 5. The total model errors are of similar magnitude to those in the HNO$_3$ production term but, for this case, the HNO$_3$ loss due to this mechanism is only 10–30% of the total loss at heights up to 45 km. It is only above these heights that the model error in total HNO$_3$ loss becomes even marginally significant, the model underestimating the total loss by about 2.8%. We note that the production and loss errors are of the same sign.

![Figure 5](image_url)

**Figure 5.** Contributions to the model error in the term $k[OH][HNO_3]$ from (a) (· · ·), averaging the temperature-dependent rate constant, and from correlations between (b) OH and HNO$_3$ (— -- —), (c) $k$ and OH (— — —), (d) $k$ and HNO$_3$ (— — —). The total error is shown by the solid line (e). From LIMS satellite data for 60°N, February 1979.

5. CONCLUSION

We have examined the problem caused by spatial averaging in models of one and two dimensions using satellite data from the LIMS instrument on Nimbus 7. The differences between the true and modelled zonal averages are usually quite small. For example, the ozone balance can generally be calculated to an accuracy of better than 5% using zonally averaged satellite data, if it is assumed that unresolved scales are not important. An exception was during the sudden warming of February 1979 when errors approaching 10% were found. For HNO$_3$ production, the errors in zonal averaging were similarly small. These conclusions are generally similar to those reached independently by Kaye (1987) in a study which came to the authors' attention during completion of this manuscript. It is found theoretically that when two reacting species are anticorrelated, the modelled rate of reaction is an overestimate of the true rate. This has interesting implications. We have speculated that a number of long-standing modelling problems could be related to this fact. These are the tendency for models to underestimate ozone in the upper stratosphere, the problem of modelling simultaneously a number of source gases, and the tendency for models to overestimate HNO$_3$ in the middle stratosphere. In all of these examples, incorrectly averaged rates could contribute to the problem. Our arguments are conjectural and rely perhaps on small-scale structure of the kind observed.
by Kley for H₂O and by many workers for O₃ in the lower stratosphere (e.g. Dobson 1973). Further evidence could possibly be given for these suggestions by a more extensive study of source gases but confirmation (or refutation) will require fast-response measurements of high sensitivity to resolve any small-scale structure. In situ techniques or lidar sensing are both possible candidates. We believe our speculations deserve further consideration.

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