Tests of Photochemical and Dynamical Theories from Satellite Data [and Discussion]

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Tests of photochemical and dynamical theories from satellite data

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The launch of *Nimbus* 7 in 1978 led to the acquisition of global data sets for a number of stratospheric constituents: O_3, HNO_3, NO_2, H_2O, CH_4 and N_2O. These data have been used extensively in studies of atmospheric chemistry and transport. Some examples of these studies are presented in this paper.

1. Introduction

Interest in the chemical composition of the stratosphere has increased in recent years following the realization that man's activities could possibly change the concentration of ozone and hence also modify the temperature structure. This has led to important advances in both the measurement of stratospheric gases and the modelling of the chemistry, radiation and dynamics of the atmosphere. These models are now used routinely to study the present-day atmosphere and to predict its future development.

Because models are used to predict the future state of the atmosphere, it is important to have some idea as to the degree of confidence that can be placed in these calculations. The most obvious method of validating a model is to compare observations with calculations. Until recently, the available observations have come mainly from instruments on balloons and, sometimes, aircraft.

There are problems with this approach to model validation. Firstly, there are generally not enough observations to constrain the theory. For example, the concentration of OH in the stratosphere depends on the concentrations of many other gases, e.g. H_2O, $O(^1D)$, HO_2, HNO_3. If a model fails to reproduce an observed OH profile, is it because the theory describing OH chemistry in the model is wrong, or because the model has the wrong concentrations of H_2O, $O(^1D)$, or some other constituent involved in OH chemistry? Evidently for a test of OH chemistry the ideal would be to have measurements of all the atoms and radicals contained in the theory.

Secondly, comparison of models and data tends to be subjective. A discrepancy of perhaps 30% between observed and modelled ozone in the upper stratosphere is currently attracting considerable interest (WMO 1986). On the other hand much larger differences for OH, for example, are regarded as satisfactory. This arises to some extent because there is a reasonable record of ozone observations so that the mean profile and its standard deviation are fairly well categorized. For OH there are only a handful of measurements. How representative, then, is a single measured OH profile? It may be that the discrepancy between a model and a particular observation is caused by unusual dynamical conditions on the day of the measurement. Before 'validation' can be carried out it is clearly necessary to understand the variability of the gas being studied.

Data from satellites promise to remove many of the above problems. The great advantages of satellite payloads are, firstly, that many species can be measured simultaneously, by a number of different instruments if necessary; secondly, that satellite instruments can in principle operate for long periods so that statistically sound records can be built up; thirdly, satellites can provide the global cover that is vital when constituent concentrations depend on atmospheric transport.

Ozone has been measured from satellites by a number of backscattered ultraviolet (BUV) experiments for more than 15 years, but it is only from experiments launched since 1978 that global measurements of other constituents have become available. Important experiments include SAMS (the stratospheric and mesospheric sounder; see Taylor & Dudhia, this symposium) and LIMS (the limb infrared monitor of the stratosphere; see Russell & McCormick, this symposium), both carried on *Nimbus* 7; SAGE I and II (the stratospheric aerosol and gas experiment), which measured O_3 and NO_2 as well as stratospheric aerosol; instruments of the Solar Mesosphere Explorer (SME), which measured O_3 and NO_2; and ATMOS, a shuttle-borne interferometer operating in the infrared that has made measurements and identifications of many atmospheric constituents.

This paper will describe the use of data, from the LIMS and SAMS experiments, which have been used to test theories of the photochemistry and transport of the stratosphere. Section 2 will concentrate on two photochemical tests, one being the use of satellite data to derive OH concentrations and thus to test the photochemistry thought to control stratospheric hydrogen-containing radicals, and the second being a study of the diurnal variation of NO_2. Section 3 shows that, by using satellite data, estimates of variability can be obtained for species which are not measured. These variability estimates can themselves exert a powerful constraint on theory. Section 4 deals briefly with the problem of the spatial averaging involved in atmospheric models. Finally, in §5, it is shown that the latitude coverage provided by satellite data has led to an understanding of the role of equatorial dynamics in producing tracer distributions and hence to an improvement in the formulation of two-dimensional numerical models.

2. PHOTOCHEMICAL TESTS

(*a*) *The derivation of* OH *concentrations: a test of the chemistry of hydrogen-containing radicals*

OH is a most important constituent of the atmosphere. In the stratosphere and mesosphere it takes part in catalytic cycles, e.g.

$$\begin{aligned} &OH + O_3 \rightarrow HO_2 + O_2, \\ &HO_2 + O \rightarrow OH + O_2, \\ \hline \text{net}\quad &O + O_3 \rightarrow 2O_2 \end{aligned}$$

that can directly regulate the ozone concentration. The influence of hydrogen compounds is more far-reaching than this, however, because OH and HO_2 react with nitrogen and chlorine compounds to produce and destroy temporary reservoirs (e.g. HNO_3, HNO_4, HOCl, HCl), wherein reactive radicals are held in less reactive form. Thus

$$OH + NO_2 + M \rightarrow HNO_3 + M,$$

$$HO_2 + NO_2 + M \rightarrow HNO_4 + M,$$

$$HO_2 + ClO \rightarrow HOCl + O_2,$$

$$HCl + OH \rightarrow H_2O + Cl,$$

are all important reactions in the stratosphere.

There have been only a few measurements of OH and HO_2 within the stratosphere, and these are not consistent. For example, measured concentrations of OH by resonance fluorescence techniques (Anderson 1976) are somewhat larger than the lidar measurements of Heaps & McGee (1985), with model calculations falling between the two. The HO_2 measurements of Helten *et al.* (1984) are significantly greater than model calculations. (See WMO (1986) for a fuller discussion.) It is clearly important to know the concentrations of OH in the stratosphere and to test, if possible, the chemistry schemes included in photochemical models.

Pyle & Zavody (1985; hereafter P.Z.) attempted to tackle these problems by using data from the LIMS and SAMS instruments on *Nimbus* 7. They showed that OH concentrations could be derived from measurements made by these two instruments. Their first method relies on the steady state established between production and destruction of HNO_3. In sunlight, the timescale for steady state is a few hours in the upper stratosphere, but much longer at low altitudes and high latitudes. Equilibrium can be expressed

$$\frac{[HNO_3]}{[NO_2]} = \frac{k_1[OH]\,[M]}{k_2[OH] + J_3}, \tag{1}$$

where [ ] denotes the concentrations. Production of nitric acid by the three-body reaction of NO_2 and OH is balanced by its destruction, mainly by photolysis but also by the recombination with OH.

HNO_3 and NO_2 were measured by the LIMS instrument. Thus equation (1) can be solved for [OH], if the rate constants, k_1 and k_2, and the photolysis rate J_3 are known; k_1 and k_2 have been measured and J_3 can be calculated given the measured absorption cross sections and by using the LIMS ozone profile, which determines the transmission of solar radiation.

An alternative method of deriving OH is from its sources and sinks. The main source of OH is the reaction of $O(^1D)$ with water vapour

$$O(^1D) + H_2O \rightarrow 2OH \quad k_4$$

with the dominant sinks, in the upper and lower stratosphere respectively, being the following reactions:

$$OH + HO_2 \rightarrow H_2O + O_2 \quad k_5,$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \quad k_6.$$

The production and loss is somewhat more complex (see P.Z. for details) so that the tendency equation becomes

$$\begin{aligned} d([OH]+[HO_2]+[H])/dt = {} & 2k_4[H_2O]\,[O(^1D)] - 2k_5[OH]\,[HO_2] \\ & - 2k_6[OH]\,[HNO_3] - 2k_7[OH]\,[HNO_4] \\ & + k_8[CH_4]\,[O(^1D)] - 2k_9[H_2O_2]\,[OH] \\ & - k_{10}[CH_4]\,[OH]. \end{aligned} \tag{2}$$

To a very good approximation, the right-hand side can be set to zero, because the time to steady state is only a few tens of seconds. Equation (2) can then be solved for [OH] given the other parameters. [H_2O], [HNO_3] and [CH_4] were directly observed by LIMS and SAMS. [$O(^1D)$] and [HNO_4] can be derived assuming steady state with O_3 and NO_2, respectively. Finally, [HO_2] and [H_2O_2] can be assumed to be in steady state with [OH].

P. Z. calculated [OH] by the two methods outlined above. Profiles were derived at every LIMS observation point and zonal and monthly mean values were then calculated. Figure 1 shows examples of [OH] profiles at a number of different latitudes. Agreement between the two methods is generally good, especially in low latitudes. In the lower stratosphere at high latitudes, the time constant for the HNO_3 steady state becomes many days, and (1) is no longer valid. P. Z. showed that the disagreement in high latitudes was entirely consistent with theory.

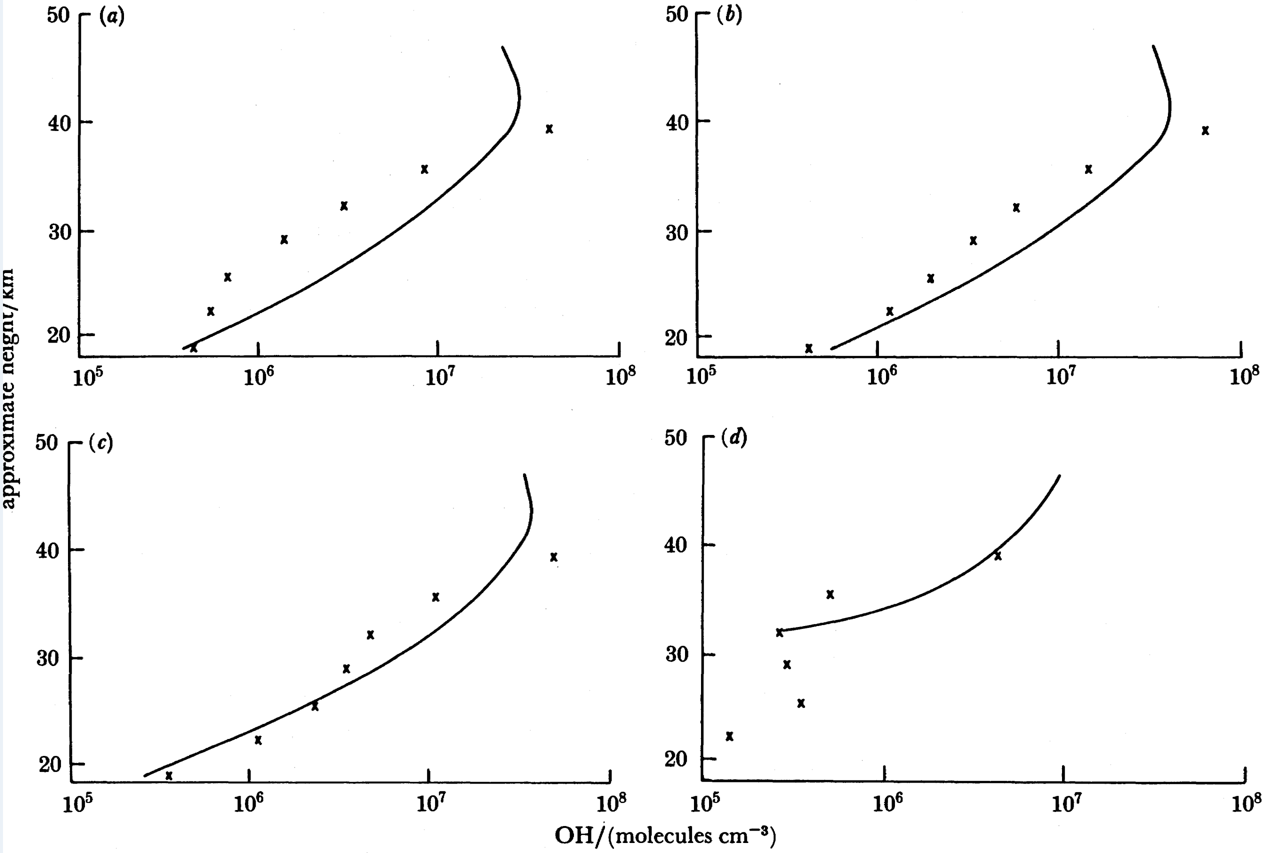

FIGURE 1. Profiles of OH (molecules cm^{-3}) derived from equation (1) (ratio, crosses) and equation (2) (sources and sinks, solid curve) for December 1978 at (*a*) 66° S, (*b*) 28° S, (*c*) 28° N, (*d*) 66° N. From Pyle & Zavody (1985).

Figure 2 compares OH profiles obtained from (2) with some available measurements. Agreement is satisfactory. The agreement can be quantified by carrying out an error analysis (indicated in figure 2) on the derived profiles. The profiles were recalculated varying, firstly, the concentrations of LIMS and SAMS measurements within their estimated errors (see Gille & Russell 1984; Jones & Pyle 1984), and, secondly, the reaction rate constants within their estimated errors.

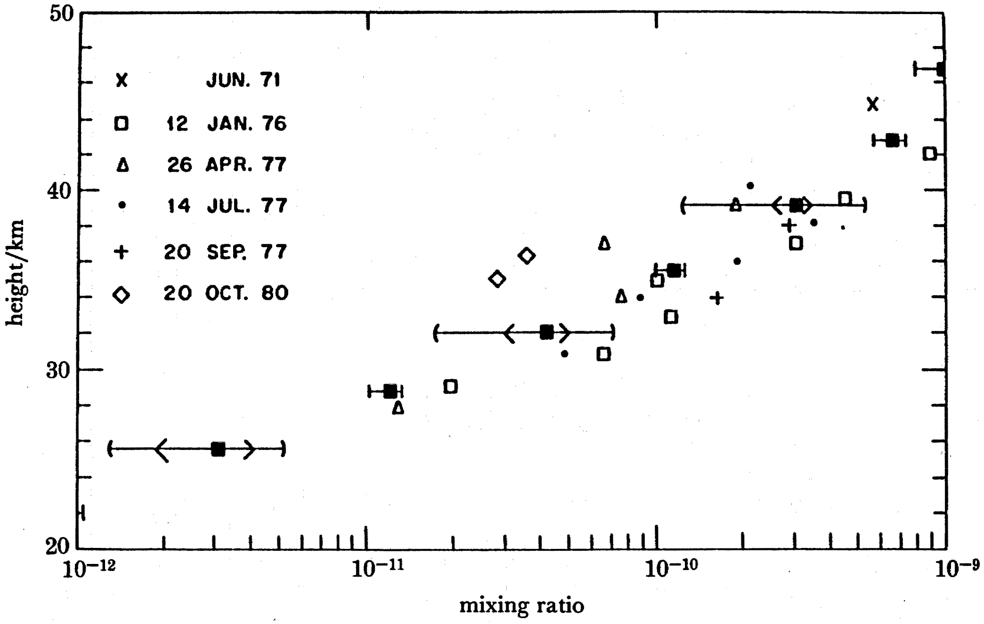

FIGURE 2. The November mean profile of OH volume mixing ratio (■) at 32° N derived from equation (2). The ⊢⊣ indicates twice the standard deviation about the monthly mean; (—) and ⟨—⟩ are estimated errors arising from anticipated errors in the kinetic data and LIMS measurements, respectively. Other symbols indicate available *in situ* measurements. See P. Z. for further details.

An important point to note is that the errors for the two schemes depend on different parameters. Thus (1) and (2) represent two independent methods of deriving OH. Agreement of the two schemes within the estimated errors (*ca.* ± 50 % in the middle stratosphere) would thus constitute a test of the chemistry included in the two schemes. Away from polar latitudes the two schemes generally do agree to much better than 50 %. These derivations therefore represent a modest, but important, test of some elements of the chemistry of hydrogen-containing radicals in the stratosphere.

(*b*) *A study of diurnal variations*

Study of the diurnal variations of stratospheric radicals should be a particularly suitable method of testing photochemical understanding. Over twenty-four hours the concentrations of many radicals undergo large excursions that are driven by the variation of solar insolation; on this timescale, transport effects are often of secondary importance.

Roscoe *et al.* (1986) compared the observed diurnal variation of NO_2 with calculations using a detailed numerical model. Figure 3 shows results from one particular balloon flight. It is seen that the gross features of the observations are well reproduced by the model. However, attempts to quantify the agreement proved inconclusive. For example, theory predicts that the decay of NO_2 during the night depends just on the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2,$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M.$$

Comparison of the modelled and observed decay of NO_2 should test this aspect of the theory. Roscoe *et al.* (1986) found, however, that the errors on the measured NO_2 were such that the

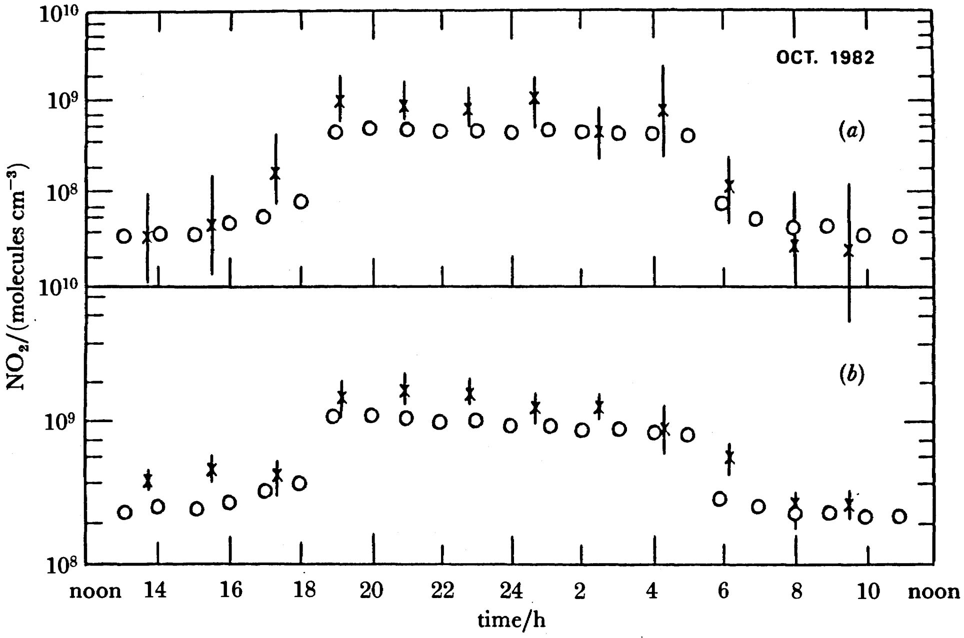

FIGURE 3. A comparison of the diurnal variations of NO_2 measured from a balloon (ϟ) and calculated in a model (○) at (*a*) 43.4 km and (*b*) 39.6 km. The abscissa covers a twenty-four hour period from noon to noon. After Roscoe *et al.* (1986).

night-time decay could not be determined to high accuracy, and the agreement with the model did not constitute a particularly critical test, even though these data represent the most complete set of diurnal measurements of NO_2 made from a balloon. Nevertheless their study did emphasize the importance of making quantitative tests.

Satellite measurements offer a way by which the required data can be obtained. For example, Solomon *et al.* (1986*a*) have used LIMS data to study the NO_2 variation at dusk. *Nimbus* 7 was in a Sun-synchronous orbit and measurements in low latitudes were made close to 1 p.m. and 11 p.m. local time. However, in high latitudes a wide range of local times was scanned during

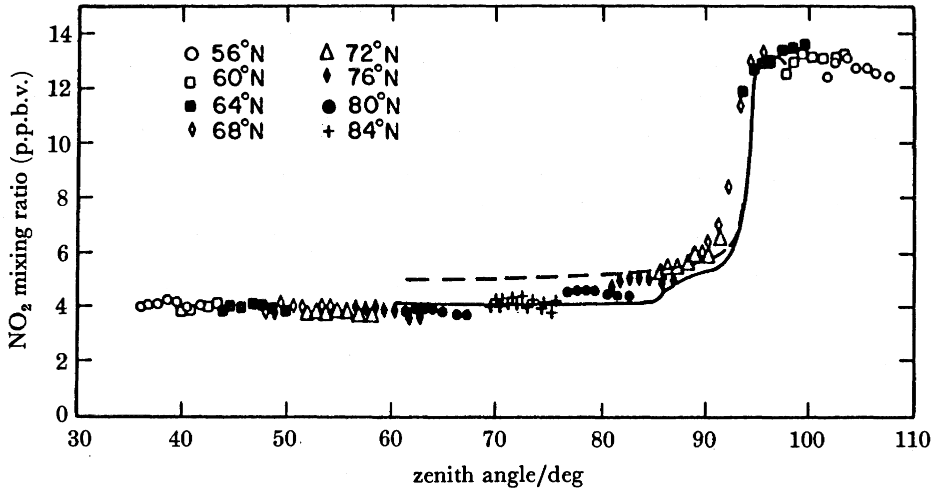

FIGURE 4. The variation of 5 mbar NO_2 mixing ratio (parts per billion by volume) with zenith angle at high northern latitudes in May. Lines —— and ––– are model calculations with different treatments of scattered radiation. Figure reproduced from Solomon *et al.* (1986*a*). (1 mbar = 10^2 Pa.)

a month; these data were used to study the rapid increase of NO_2 at dusk. Figure 4 shows the comparison of the LIMS data with a photochemical calculation. Qualitatively the agreement is good. Comparison is sensitive to the precise details of the scattering scheme used in calculations of photolysis rates. In future satellite experiments, this kind of analysis will be very important in studying the chemistry of radicals.

3. Estimates of variability

Estimates of the variability of constituent concentrations are important for a number of reasons. For example, it has already been stated that model validation simply by comparison of a modelled and an observed profile can be unsatisfactory because of lack of objectivity (is a 50% discrepancy 'serious' or 'satisfactory'?) and because of problems with the representativeness of the observed profile (if one observation only is available, is it representative of the mean state of the atmosphere?). If a large number of measurements are taken then a mean profile and its variance can be calculated. The variance then defines the degree of disagreement that is acceptable between a model and an observed profile.

A further reason for building up large sets of measurements is that comparison of modelled and observed variability is itself a good test of a photochemical model. For example, Solomon & Garcia (1984) argued that the variability seen in the ClO measurements of Weinstock *et al.* (1981) could be explained by variability in CH_4, produced perhaps by dynamical processes, and its influence on the chemistry of chlorine compounds through the reaction $CH_4 + Cl \rightarrow HCl + CH_3$. A further important study of variability was by Ehhalt *et al.* (1983) who showed that the variance of long-lived source gases could be explained dynamically in terms of an equivalent displacement height.

Both the above studies used balloon data. Pyle & Zavody (1987*a*) have used satellite data to study variability. In §2 it was shown that OH can be derived from the measurements on the *Nimbus* 7 satellite. For every observed profile a derived OH profile is obtained. Clearly with data taken nearly globally for many months it is possible to estimate, for example, the monthly and zonal mean OH and its variance at some latitude. The profile shown in figure 2 is in fact a monthly mean value and the 2σ variation is indicated.

Estimates of the variability of chlorine-containing radicals can also be made even though no satellite measurements of chlorine compounds have yet been made. As Solomon & Garcia (1984) have shown, if a profile of the total concentration of active chlorine ($Cl + ClO + HCl + HOCl + ClONO_2$) is defined, then its partitioning into the individual species can be calculated. The partitioning depends on the concentrations of OH, CH_4, etc. These compounds have either been observed from space or their concentrations can be derived.

Figure 5 shows examples of the predicted variability for two species. Figure 5*a* shows the variability for ClO, compared with the range of data from Weinstock *et al.* (1981), but not including the flights of 14 July 1977 and 28 July 1976. Notice that the more recent measurements with the resonance fluorescence technique have somewhat greater accuracy than the earlier measurements.

The variability predicted for H_2O_2 is large (figure 5*b*). This is to be expected (see Derwent & Eggleton (1981); Connell *et al.* (1985); Kaye & Jackman (1986)) when a species depends quadratically on its precursors (e.g. $[H_2O_2] \propto [HO_2]^2$).

These studies point to the need for a long series of measurements of important species such that their variability can be both calculated directly and then compared with modelled

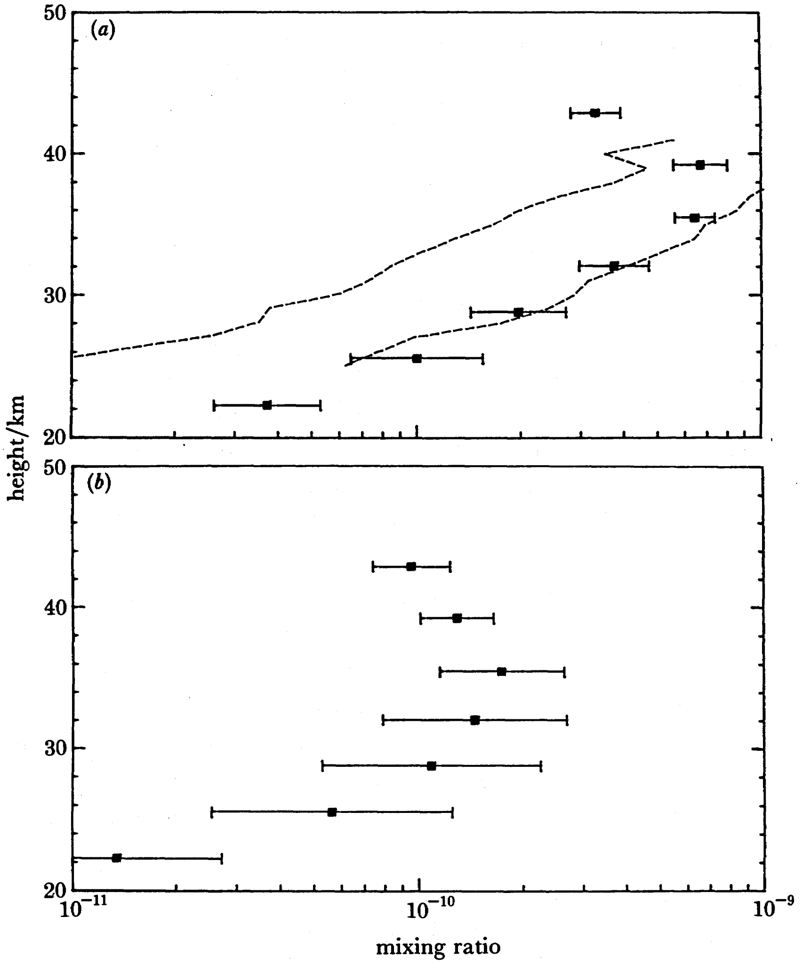

FIGURE 5. (*a*) Derived mean mixing ratio profile of ClO at 30° N, February. The error bars at each height show the $\pm 2\sigma$ variability in the computed values. The range of measured values (Weinstock *et al.* 1981, see text) is shown by the broken lines. Reproduced from Pyle & Zavody (1987*a*). (*b*) Derived mean mixing ratio of H_2O_2 at 30° N, February. The error bars at each height show the $\pm 2\sigma$ variability in the computed values.

variabilities. The validation of calculations with a photochemical scheme then involves not simply the comparison with a single measured profile, but the comparison with a mean profile and its variability.

4. SPATIAL AVERAGING IN NUMERICAL MODELS

Tuck (1979) has pointed out that errors may arise in numerical models when the continuity equations are averaged spatially. Eddy transport terms are then introduced and are usually treated in terms of empirical transport coefficients. Chemical eddy terms also arise because of the spatial covariance of reacting species. These terms are generally ignored.

For example, the rate of reaction between molecules X and Y averaged around a latitude circle (where $\overline{(\ )}$ represents the averaging operation) can be written

$$\underset{\text{(A)}}{k\overline{\mathrm{XY}}} = \underset{\text{(B)}}{k\overline{\mathrm{X}}\,\overline{\mathrm{Y}}} + \underset{\text{(C)}}{k\overline{\mathrm{X'Y'}}}, \tag{3}$$

where k, the rate coefficient is assumed to be a constant, and ( )′ denotes a local departure from the latitudinal average. In a latitudinal average, two-dimensional model, only term (B) can be treated explicitly; term (C) is the chemical eddy term which is usually ignored. Notice that if X and Y are positively correlated then term (C) will be positive and the model rate, (B), will underestimate the true rate, (A), and vice versa. Thus systematic correlations between reacting species will lead to a bias in the rates of their reactions as calculated in an averaged numerical model.

Pyle & Zavody (1987*b*) have used satellite data to investigate these averaging errors. For example, by deriving an atomic-oxygen concentration from every satellite measurement of O_3 they can then calculate the rate of reaction between O and NO_2 and hence term (A), the zonally averaged rate of the reaction, can easily be computed. Similarly, the zonal average concentration of O and NO_2 can be found separately and term (B) can then be calculated. The conclusion of their study is that the error introduced in zonal averaging is generally quite small, about a few percent. An exception was during the major warming of February 1979 when for some reactions at 60° N differences were found between terms (A) and (B) of approaching 10%.

It appears that the systematic errors introduced in two-dimensional models by the operation of zonal averaging are not large. This statement should be tempered by the consideration that satellite data represent the average from a portion of atmosphere a few kilometres deep, some tens of kilometres wide and perhaps a hundred kilometres along the line of sight. High-resolution *in situ* data is therefore still needed to test the hypothesis that variability on smaller scales could be an important source of errors in numerical models.

5. EQUATORIAL WAVES AND TRACER DISTRIBUTIONS

Satellite data, by virtue of global coverage, provide important details about the transport of stratospheric trace gases. For example, Leovy *et al.* (1985) have demonstrated by using LIMS ozone data the meridional transport associated with the 'wave-breaking' of planetary scale waves, as discussed by McIntyre & Palmer (1983). This section deals with a different dynamical example, the effect of equatorial waves on tracer distributions.

Jones & Pyle (1984) presented CH_4 and N_2O data from the SAMS experiment on *Nimbus* 7. An important and quite unexpected feature reported in their paper was the so-called 'double peak', whereby maximum mixing ratios on a constant pressure surface were found in the subtropics with a local minimum over the Equator. These double peaks were most pronounced from March to May with a suggestion of similar features, but much weaker, six months later (see also Taylor & Dudhia, this symposium). Jones & Pyle carried out two-dimensional simulations but were unable to reproduce, or explain, the double peaks.

Gray & Pyle (1986) proposed that the forcing of the semiannual oscillation, SAO, (a change in the equatorial mid-stratospheric zonal wind from easterly to westerly with a period of six months) was responsible for these double peaks. In the westerly phase of the forcing, which occurs around the equinoxes, an induced circulation with sinking air over the Equator and rising air in the subtropics is anticipated. Such a circulation would tend to produce double peaks in tracers like CH_4 and N_2O whose mixing ratios decrease with height in the stratosphere.

In their two-dimensional model, Gray & Pyle (1986) included a momentum forcing that was specified so as to reproduce the observed SAO of the zonal wind. This forcing produces an additional component of the model meridional circulation, which is then used to advect tracers in the model. Figure 6 shows the effect on the modelled N_2O fields of the inclusion of the forcing. With the SAO included, the model reproduces the double peak in the mid-stratosphere.

Subsequent studies have confirmed that the SAO forcing is responsible for the double peaks. Gray & Pyle (1987) have shown that by including detailed model-dependent treatments of momentum transport associated with equatorial Kelvin waves (responsible for the westerly phase of the SAO) and with gravity waves in the mesosphere, they are able to reproduce in detail the observed SAO and double-peak structure of CH_4 and N_2O. Features in the observed distributions of H_2O, NO_2 and O_3 can also be explained in terms of this model. In a separate, but complementary, diagnostic study, Solomon *et al.* (1986*b*) derived diabatic circulations with LIMS data. These circulations, which are consistent with the ideas of SAO forcing, were then used in a model to reproduce the N_2O and CH_4 double peaks successfully.

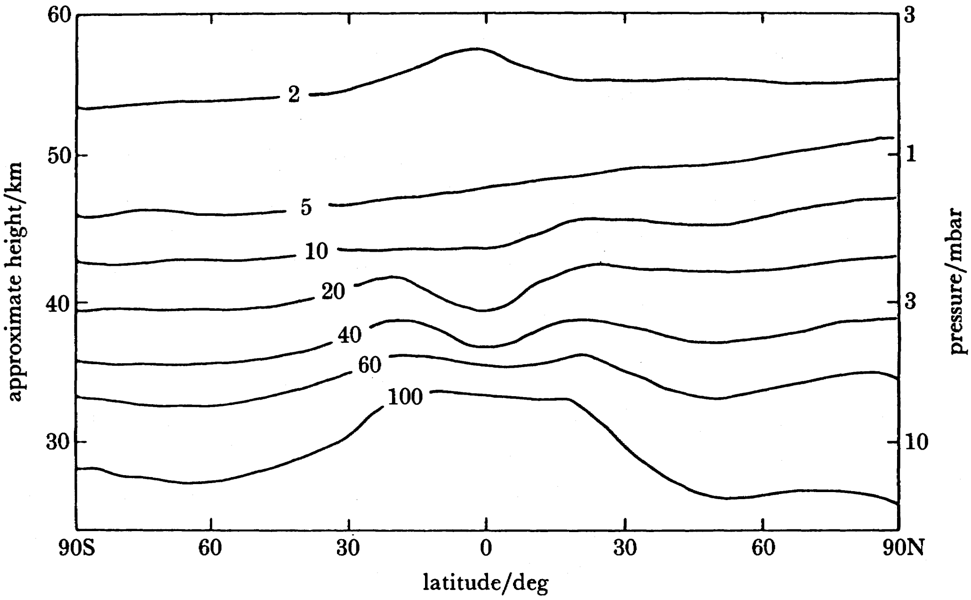

FIGURE 6. Latitude–height section of N_2O mixing ratio (parts per billion by volume) calculated by Gray & Pyle (1986). Note the double peak, most pronounced between 30° S and 30° N at 3 mbar. (1 mbar = 10^2 Pa.) (In this paper 1 billion represents 10^9).

6. CONCLUSIONS

Examples of a number of studies have been presented to demonstrate the use of satellite data in testing photochemical and dynamical theories of the stratosphere. The advantages of satellite data lie in the temporal and spatial coverage provided, so that it is possible to develop large data sets from which mean quantities and their standard deviations can be defined. It is argued that the variability, and not just the mean profiles, should be used in atmospheric chemistry studies. For example, comparison of predicted variability with that observed should in the future become an important facet of model validation. Variabilities may also be calculated for species which are not measured. The derivation of species concentrations with photochemical steady-state expressions offers the potential of a wide range of photochemical tests.

Studies of the spatial variation of species concentrations allow the interaction of chemistry and dynamics to be studied. For example, structures over subtropical latitudes have led to an understanding of the role of the semiannual oscillation in producing tracer distributions. Global data fields have demonstrated the idea of 'wave breaking'.

The studies discussed here have merely demonstrated the potential of satellite data. Only a few species have been directly measured thus far, and global and annual cycles have been observed for just O_3, CH_4 and N_2O. The data to be provided by the UARS satellite due to be launched in 1991 should provide a tremendous stimulus to theoretical atmospheric chemical and dynamical research. It is anticipated that many of the techniques discussed above will be used extensively in the investigation of these data.

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Discussion

M. E. McIntyre (*Department of Applied Mathematics and Theoretical Physics, University of Cambridge, U.K.*). In connection with some of the discrepancies between models and observation, the point by Tuck about the eddy anticorrelations of chemical reagents seems to merit careful attention. This is not only because of the very interesting arguments just presented by Dr Pyle that suggest the possibility of helping to explain several discrepancies at once, but also because of the nature of the fluid dynamics.

Our best understanding of the latter suggests the possibility of strong anticorrelations at much smaller scales, which could enhance the effects discussed by Dr Pyle. For instance, in the case of reagents being mixed into the winter-time mid-stratospheric 'surf zone', the implication of our present ideas about the dynamics of Rossby-wave propagation, Rossby-wave breaking, and geostrophic turbulence is that there could be significant anticorrelations at scales perhaps down to kilometres in the horizontal, and tens of metres in the vertical. There would almost certainly be strong anticorrelations at tens of kilometres and hundreds of metres respectively. The corresponding scales would not be drastically different in the upper stratosphere, perhaps larger by a factor 2 or 3. The time taken for mixdown to these scales is roughly of the order of a month or more. The potential-vorticity patterns seen in figure D1 of my comment on Professor Bowhill's contribution give some impression of the early stages of this mixing process, after allowing for the differences between potential-vorticity and passive-tracer behaviour. The whole process is probably less spatially homogeneous than might be suggested by figure D1, because the model simulation underestimates geographical effects like the Aleutian anticyclone. Again, further discussion can be found in an article in *Nature*. It can be added that the vertical mixing due to breaking gravity waves might modify this picture somewhat, but the likely spatial intermittency of such processes make them hardly likely to be able to smooth out the small-scale structure as would an artificial model diffusivity. Outside the surf zone, mixdown times may well be longer, and the effects on the chemistry correspondingly greater.

Reference

Juckes, M. N. & McIntyre, M. E. 1987 A high-resolution, one-layer model of breaking planetary waves in the stratosphere. *Nature, Lond.* **328**, 590–596.