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COMPARISON BETWEEN OBSERVED AND CALCULATED DISTRIBUTIONS OF TRACE SPECIES IN THE MIDDLE ATMOSPHERE

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INTRODUCTION

The number density of atmospheric minor constituents is characterized by large temporal and spatial variability. In the case of long-lived species such as the "source gases" (N_2O, CH_4, the chlorofluorocarbons, etc.), transport processes may account for much of this variability. In the case of fast-reacting species such as chemical radicals (OH, HO_2, O, NO, Cl, etc.), a large fraction of the variability is produced by the diurnal and seasonal variation of the solar insolation. However, as these radicals are usually produced by chemical or photochemical decomposition of long-lived species, their distribution is also indirectly controlled by transport processes. Finally, in the case of species whose chemical lifetime is approximately equal to the transport characteristic time of the atmosphere (ozone and nitric acid in the middle stratosphere, temporary reservoirs such as HO_2NO_2, $ClONO_2$, HOCl in given altitude ranges), chemistry and dynamics play an equally important role.

With the measurement, over a significant period of time and over a wide spatial range, of a number of trace species concentrations, it has become possible to produce climatological distributions of these compounds and even, for some of them, to infer reliable empirical models. As most of these models result from averaging a large number of observations, they may be compared to theoretical models which intend to simulate global average conditions by solving the conservation equations based on chemical, radiative and dynamical considerations. Such comparison allows the validation of both observational data and theoretical calculations. Moreover, such study leads to a better understanding of the basic processes which control the observed distributions and to the identification of inconsistencies between theory and observations.

Ideally, in order to investigate all processes involved, a comparison between theory and observations require on the one hand multidimensional models and on the other hand atmospheric data sets covering the entire earth. However, because the data available are limited and accurate multidimensional transport schemes are computationally expensive and difficult to achieve, "first order" validation of the currently known chemical processes in the stratosphere can be based on simpler one-dimensional calculations.

The purpose of this short paper is to identify major discrepancies between empirical models and theoretical models and to stress the need for additional observations in the atmosphere and for further laboratory work, since these differences suggest either problems associated with observation techniques or errors in chemical kinetics data (or the existence of unknown processes which appear to play an important role). The model used for this investigation [1] extends from the earth's surface to the lower thermosphere. It includes the important chemical and photochemical processes related to the oxygen, hydrogen, carbon, nitrogen and chlorine families. The chemical code is coupled with a radiative scheme which provides the heating rate due to absorption of solar radiation by ozone and the cooling rate due to the emission and absorption of terrestrial radiation by CO_2, H_2O and O_3.[2] The vertical transport of the species is expressed by an eddy diffusion parameterization.

COMPARISON BETWEEN THEORETICAL MODELS AND OBSERVATIONS

As the model used hereafter is one-dimensional and produces global average vertical profiles, the present

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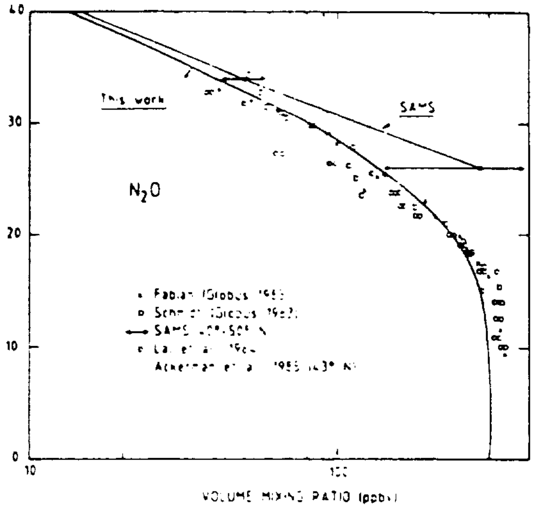

Fig. 1. Comparison between several observed distributions of nitrous oxide [3, 4, 5, 6] and a 1-D theoretical profile.

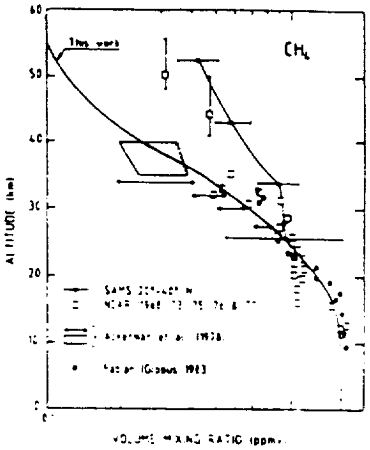

Fig. 2. Comparison between observed distributions of methane [3, 4, 7] and a 1-D theoretical profile.

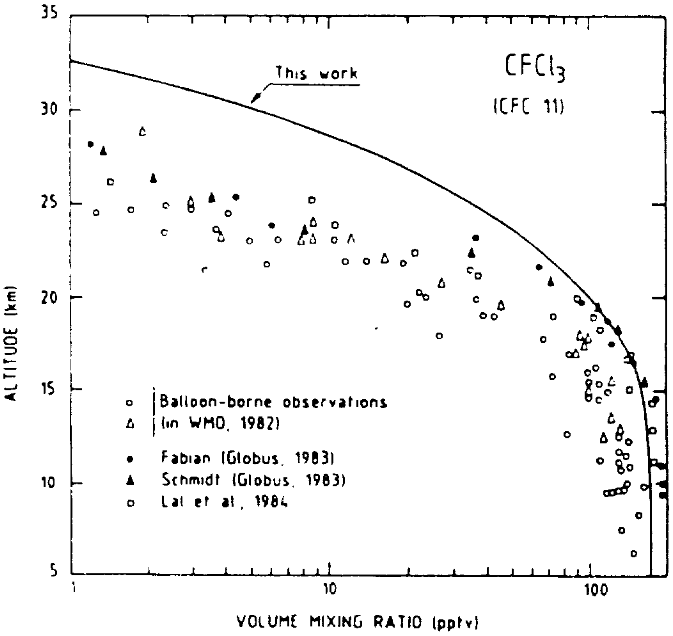

Fig. 3. Comparison between observed distributions of CFC-11 [3, 5] and a 1-D theoretical profile.

study will focus essentially on the long-lived trace gases. However, some important and unexplained discrepancies concerning the fast-reacting species will also be mentioned.

Source Gases

The calculated distributions of N_2O, CH_4, CCl_4, CH_3CCl_3, CFC-11 and CFC-12, are displayed in Figures 1-6. The agreement between theoretical and observed vertical distributions is good for N_2O

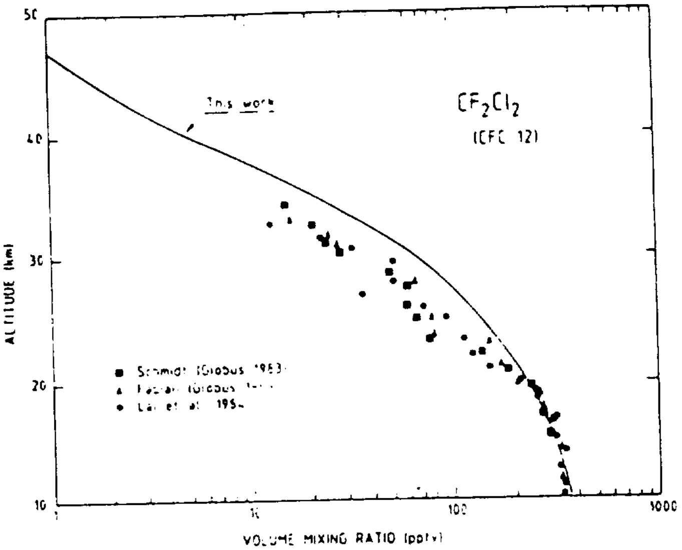

Fig. 4. Comparison between observed distributions of CFC-12 [3, 5] and a 1-D theoretical profile.

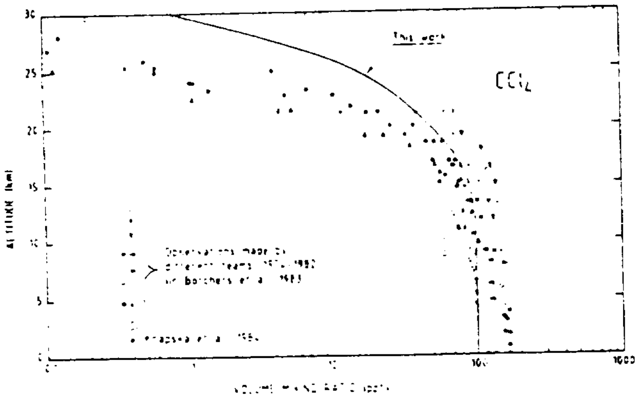

Fig. 5. Comparison between observed distributions of carbon tetrachloride [8, 9] and a 1-D theoretical profile.

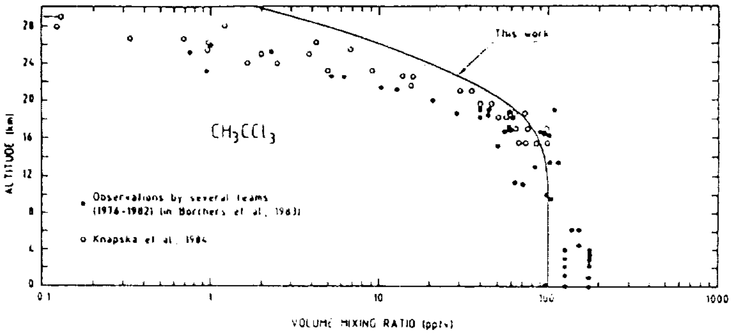

Fig. 6. Comparison between observed distributions of methyl chloroform [8, 9] and a 1-D theoretical profile.

and for CH_4. In the latter case however large differences in the observations exist above 30 km, making the comparison between model and observation difficult. The relatively good agreement, in the case of N_2O, is not surprising as the eddy diffusion coefficients which are used in the models (including the present model) are usually tuned to fit the vertical profile of this particular gas. For the precursor gases of active chlorine (e.g., the CFCs), the model tends to overestimate the mixing ratio, especially in the higher levels, except for CFC-12. Such discrepancy which appears in essentially all 1-D models has not yet been resolved. It can be due either to the use of an inadequate eddy diffusion coefficient or to an underestimated loss rate (or to both). Indeed, it has been shown from theoretical considerations [10] that the specified value of the 1-D eddy diffusion coefficient should be a function of the lifetime of the trace-constituent. Moreover, uncertainties remain in the calculation of the penetration of sunlight in the Schumann-Runge bands, leading to uncertain photodissociation rates of the chlorofluorocarbons.

The calculated lifetime of the source gases playing a major role in the stratosphere is given in Table 1.

TABLE 1 Calculated Lifetime of the Source Gases

Species	Lifetime (yrs)
N_2O	165.6
CH_4	10.0
CH_3Cl	1.5
CCl_4	68.8
CH_3CCl_3	6.6
$CFCl_3$(CFC-11)	86.6
CF_2Cl_2(CFC-12)	154.3
$CFCl_2CF_2Cl$(CFC-113)	129.8
CHF_2Cl(CFC-22)	16.2

Active Gases and Temporary Reservoirs

The concentration of active gases such as OH, HO_2, O, Cl, ClO, etc. is difficult to measure since their concentration is low and their chemical reactivity very high. A reliable comparison between theoretical model results and the few available data requires the knowledge of the solar zenith angle at the time of the measurement and the concentration in the observed air mass of the transport dependent long-live species which are the progenitor of the fast reacting compounds. From an examination of Figures 7 and 8, it can however be deduced that the most recent measurements of the OH radical [11, 12, 13, 14] have the same order of magnitude than values provided by theoretical models but that, in the case of HO_2, the values reported by Helten et al. [15] are in the lower stratosphere a factor 100 larger than predicted by

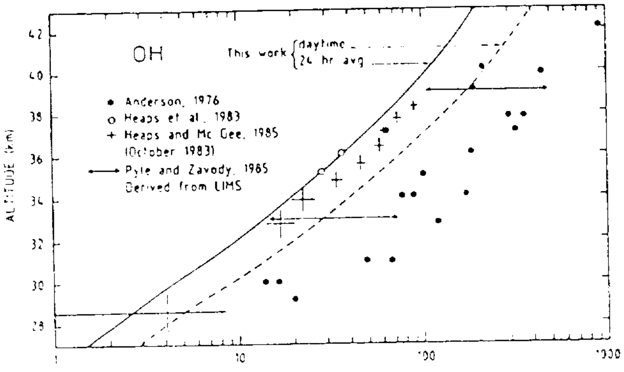

Fig. 7. Comparison between observed or indirectly deduced mixing ratio of OH [11, 12, 13, 14] and theoretical profiles (24 hour average and daytime average; mid-latitude; equinox).

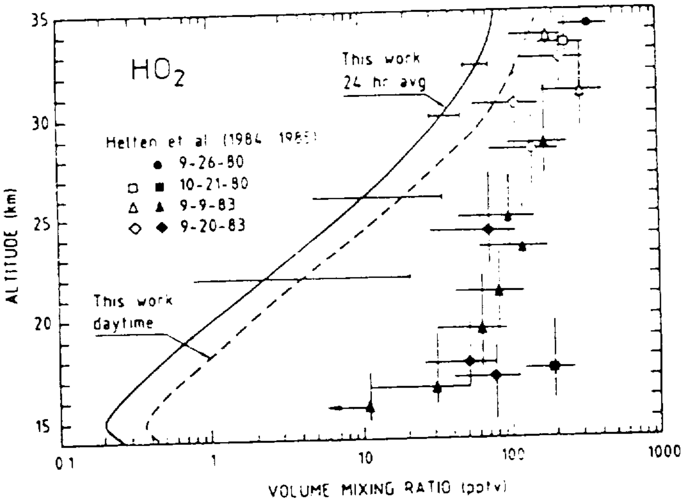

Fig. 8. Comparison between observed mixing ratio of HO_2 [15] and theoretical profiles (24 hour average and daytime average; mid-latitude; equinox).

theory. If additional measurements tend to confirm these data, the presently accepted chemical scheme is in error for the hydrogen species at least, in the atmospheric layer where the ozone concentration is the largest.

Efforts to measure the vertical distribution of temporary reservoirs have been reported only recently. Figures 9 and 10 show that, especially for $ClONO_2$, the data deduced from infra-red measurements, for example from the ATMOS experiment, are consistent with a 24 hour-averaged model calculation.

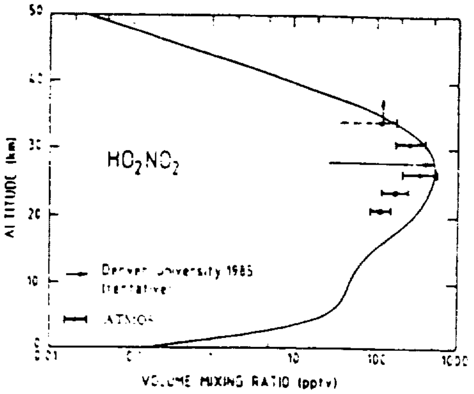

Fig. 9. Comparison between observations of HO_2NO_2 [16] and a 24-hour average theoretical profile (mid-latitude, equinox).

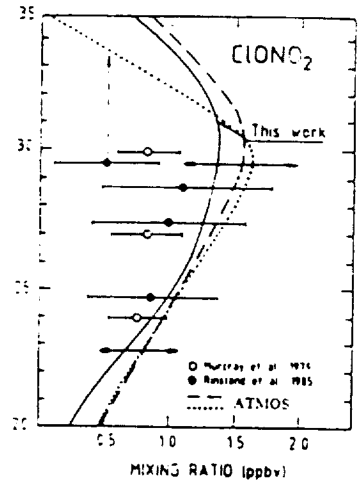

Fig. 10. Comparison between observations of $ClONO_2$ [17, 18, 19] and a 24-hour average theoretical profile (mid-latitude, equinox). The dotted line and the dashed line refer to ATMOS data at 30°N (sunset) at 47°S (sunrise) respectively.

Nitric Acid and Ozone

Finally, a comparison between theory and observations is performed for 2 gases (HNO_3 and O_3) which are produced in the stratosphere and whose lifetime varies significantly with altitude and latitude. In the case of HNO_3 (Figure 11), the agreement is fairly good between theory and observation below 30 km but above this height, most models seem to overestimate the HNO_3 mixing ratio. This discrepancy is emphasized by the fact that a new treatment of the HNO_3 LIMS data [20] indicates that the mixing ratio retrieved in the upper stratosphere should be reduced by as much as a factor 2-5.

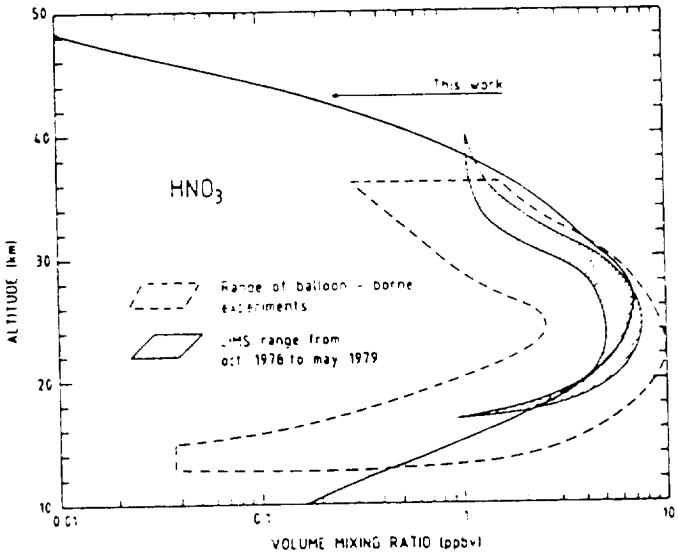

Fig. 11. Comparison between observations of nitric acid (balloon-borne experiments and LIMS data) and a theoretical profile (24 hour average, mid-latitude, equinox).

Ozone has been measured rather systematically and by different techniques over a number of years. The vertical profile provided by the US Standard Atmosphere [21] which is in close agreement with other data bases is compared in Figure 12 with a model calculation. The theoretical concentrations are obviously 20 to 40% lower than the observed values in the upper stratosphere. This ozone imbalance which was noted in several investigations [22, 23] is not yet explained. It could be due either to unknown additional production processes of ozone or to errors in some chemical or photochemical parameters. This problem is a major question as it reflects some unknown processes occurring in the atmospheric region where photochemical conditions apply and where the largest relative ozone depletions are predicted as a response to the emission of CFCs.

CONCLUSIONS

Models reproduce most of the observed distributions of the trace species belonging to the oxygen, hydrogen, nitrogen and chlorine families. Some discrepancies however remain, which reflect errors or uncertainties in the chemical scheme currently adopted in the models. More work is thus needed to identify the physical or chemical processes which could explain the cause of these discrepancies. A more detail comparison between observations and theory, which should account for the latitudinal and seasonal variation of the trace species concentration, should involve multi-dimensional models.

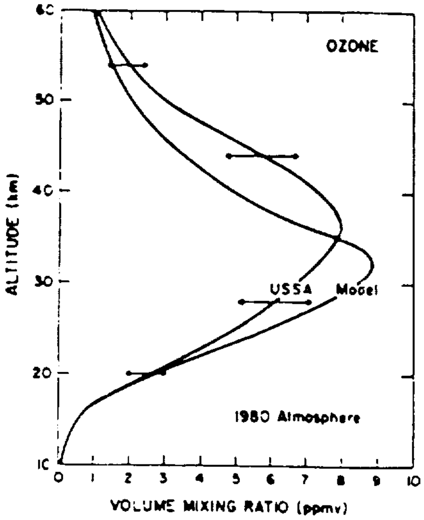

Fig. 12. Comparison between the U.S. Standard atmosphere model of ozone [21] and a theoretical vertical distribution.

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