United Nations
Environment
Programme

Distr.
LIMITED

UNEP/CCOL/8/3/Add.[illegible]

Original: ENGLISH

Co-ordinating Committee
on the Ozone Layer
Eight Session

Nairobi, 24-28 February 1986.

RECENT RESEARCH RESULTS AND ONGOING ACTIVITIES RELEVANT TO THE WORLD PLAN OF ACTION ON THE OZONE LAYER

Contribution
by the

United Kingdom of Great Britain
and Northern Ireland

INTRODUCTION

Since the Seventh session of CCOL, Stratospheric ozone research in the United Kingdom has continued at a high level, particularly at the Meteorological Office, Harwell, British Antarctic Survey (BAS), Rutherford Appleton Laboratory (RAL) and Oxford and Cambridge Universities. The work is funded by government departments, by the Science and Engineering Research Council and by Chemical Manufacturers Association. Seven scientists from the UK have made significant contributions to the WMO/NASA/UNEP Ozone Layer Assessment, including four of the chapter authors.

The Department of the Environment and the Meteorological Office have jointly set up a Stratospheric Ozone Review Group, to prepare a review of our current understanding (on a much smaller scale than the Assessment) and to coordinate future UK activities.

1. ATMOSPHERIC MEASUREMENTS AND INTERPRETATION

1.1 Ground based

The Meteorological Office has continued measurement of columnar ozone abundance using Dobson instruments. The standard instrument was taken to St Helena in the S Atlantic in order to check the instrument there, and to Boulder to check its own calibration against the world standard.

The British Antarctic Survey has continued ozone observations at Argentine Islands and Halley Bay using Dobson spectrophotometers. A decline in ozone amount in the austral spring at halley Bay has been reported (Nature, 315, 207 (1985)). An ultraviolet spectometer, built by the Physics and Engineering Laboratory of DSIR, New Zealand, will be installed to measure NO_2 at Halley Bay during 1986.

A Zeeman Modulator radiometer has been built at Oxford University to measure stratospheric column abundances of NO in absorption using the sun as a source. Because of problems with water vapour absorption, the measurements have to be made from a high mountain site, and in autumn of this year the apparatus was transported to Pic du Midi and an observing run of approximately one month's duration was obtained. The data appear to be of good quality and are currently being analysed. This 'proof of concept' expedition is expected to be followed by a longer series of runs in the future, when it is hoped that the seasonal variability of the species will be measured, perhaps in tandem with uv measurements of NO_2 and Dobson measurements of ozone. Measurements in the southern hemisphere are also planned.

1.2 Aircraft

Further measurements of trace species near jet streams have been made in the NE Atlantic by the Meteorological Office Hercules aircraft. The results are being analysed and, together with those from previous flights, are being combined with TOMS ozone data from the Nimbus 7 satellite and potential vorticity fields to estimate stratosphere-troposphere exchange.

1.3 Balloons

The Meteorological Office has constructed instruments to attach to a balloon intended to fly round the world in the southern sub-tropical jet, scheduled for June 1986. Instruments will measure ozone, water vapour, temperature, pressure and wind-shear, and will be lowered up to 1 km below the balloon by winch.

At Oxford University a new improved Balloon Pressure Modulator Radiometer has been developed to measure NO and NO_2 in the stratosphere from high altitude balloons. The first flight of the new BPMR was made in September 1985 from France as part of the second MAP-GLOBUS campaign, when measurements were obtained throughout a 14-hour flight. This data has yet to be analysed, but the analysis of data from earlier flights of the previous BPMR Mk I (from 1975 to its loss after a flight in 1983) has made progress. The results clearly show the simultaneous fall in NO_2 and rise in NO after sunrise, as predicted by photochemical models. The steady decay of NO_2 during the night due to the production of N_2O_5 has also been followed, as has the peaking of the NO abundance during the afternoon. A tentative detection of N_2O_5 itself was made; this has since been confirmed by ATMOS. The current programme with the new radiometer is aimed at improving the sensitivity and precision of the measurements to allow more rigorous and quantitative tests of photochemical theory to be made in future.

Modelling, in a collaboration between Oxford and Cambridge Universities, of nitrogen oxides measured from balloons has continued and a paper is in the press (J. Geophys. Res. 1986). This modelling has concentration species with sheet time constants. The observed diurnal variations of NO_2, for example, has been modelled well; inferences concerning the role of N_2O_5 can be made by studying the precise shape of the diurnal cycle. Modelling of longer lived gases (CH_3Cl, CH_3CC_3, F11, F12, F112, F114, F22, F115 etc) has been carried out jointly between the Rutherford Appleton Laboratory (RAL), Cambridge, MPI Lindau and MPI Mainz (FRG).

1.4 Satellites

The measurements of temperature, methane, and nitrous oxide made by the Stratospheric and Mesospheric Sounder on Nimbus 7 are being used at Oxford to study the dynamics of the stratosphere. The minor constituents are being used as tracers in the input to a model which is then solved for the motions, particularly in the vertical. Interesting, seasonally-variable patterns resembling hemispheric Hadley-type cells have been discovered in the stratosphere. A separate model, initialised by SAMS temperature measurements, is being used to study the conditions under which stratospheric sudden warmings are initiated.

Analysis of satellite data from the LIMS and SAMS experiments has also continued at RAL and Cambridge. Using data on CH_4 and H_2O it has been demonstrated that the increase of the water vapour mixing ratio with stratospheric altitude is consistent with a source just from methane oxidation. (In this work the two groups also collaborated actively with the Meteorological Office.)
Further work with satellite data includes a study of radical variability on various spatial and temporal scales, following up the successful study of the OH radical inferred from satellite data. These derived radical concentrations are also being used to assess the importance of the spatial averaging procedures used in 1-D and 2-D models. Finally, the temperature dependence of NO_2 is being studied to investigate our understanding of NO_x photochemistry, and especially, its chemical change.

Work at RAL on derivation of OH latitude/height fields and the related HO_2 and H_2O_2 amounts from LIMS data has been completed and accepted for publication in 1985. The OH fields are not measurable directly from space, so that the derived OH values fill a vital gap in stratospheric knowledge, in view of the central role of OH in the photochemistry, particularly of O_3 destruction.
Differences between modelled and observed O_3 and HNO_3 may arise from neglect of cross-terms in the model's averaging process. To investigate this possibility correlation studies have been used to examine the temperature dependence and interdependencies of various constituents such as O_3, NO_2 and H_2O based on LIMS data. These relationships are found to be too weak to account for the differences in O_3 and HNO_3.

A flight of the ATMOS interferometer on board Spacelab 3 took place in April 1985. These produced the first high-resolution (0.01 cm^{-1}) spectra of the ozone layer region from space, from a total of 19 solar occultation events.
Retrieval of constituent concentrations is the responsibility of JPL, Oxford, RAL, and others, and good progress is being made including positive identification of N_2O_5 and $ClONO_2$ for the first time in the atmosphere. RAL scientists have been involved in analysis of the spectra to measure H_2O, CH_4, O_3, HNO_3 and (tentatively) H_2O_2. Computer links between JPL and RAL have been set up allowing interactive use of the ATMOS PRIME computer and spectral processing software. The new spectra recorded by ATMOS represent a unique set of new observations of the middle atmosphere, and RAL scientists are heavily involved in exploiting these new measurements.
At Oxford, the ATMOS measurements are being analysed for profiles of methane, water vapour, nitric oxide and ozone. The results so far appear to confirm, and shed further light on, the stratospheric circulation discovered by SAMS. The water and methane data appear to confirm that oxidation of the latter is the main source of the former in the ozone layer. Vibrational temperatures are being computed from the CO_2 bands in the spectra, particularly for the upper-state bands which show evidence for radiative non-equilibrium effects of importance to the energy balance of the middle atmosphere. The study of these is continuing.

Analyses continue of data received at the Meteorological Office from Stratospheric Sounding Units (SSUs). A study of the seasonal evolution of the stratosphere is nearing completion. Emphasis is being placed on the southern hemisphere, a region that received comparatively little attention before the advent of data from satellites. Maps of Ertel's potential vorticity are being used to relate systematic changes in the circulation to non-conservative processes.
It is intended to use the stratosphere-mesosphere model to assimilate temperature and wind measurements from the UARS satellite, which is scheduled for launch in 1989. The aim is to improve the quality of analyses and to dispense with the geostrophic approximation used, at present, to calculate winds from temperatures. Data from the SSU and SAMS radiometers are being used in preparatory work.

Development work at Oxford University is now well advanced on an improved version of the Stratospheric and Mesospheric Sounder, known as ISAMS, for flight on the Upper Atmosphere Research Satellite (UARS). This will measure ozone, water vapour, carbon monoxide and N_2O, NO, NO_2, N_2O_5 and HNO_3. At present, preparations are being made for laboratory testing of the instrument prior to delivery to NASA in early 1988.

2. LABORATORY MEASUREMENTS

2.1 Spectroscopy

At Cambridge University the measurement and analysis of the infra-red spectra of important atmospheric species such as SO_3 and CH_3Cl have been carried out at very high resolution (0.005 cm^{-1}). These are being extended to other species including hydrocarbons and NO_3.

This has been the first full year of operation of a BOMEN high resolution Fourier transform spectrometer at RAL, and new spectroscopic measurements have been made in support of a number of satellite experiments. The facility includes a wide range of absorption cells and gas handling facilities to provide gas samples at the most important temperatures and pressures representative of the lower and middle atmospheres of the Earth and of planetary atmospheres. Sophisticated software is used for the derivation of spectral parameters. The range of coolable gas and absorption cells covers paths lengths from 1 mm to 500 m.
Spectroscopic parameters being measured at RAL for the interpretation of ATMOS solar occultation spectra include HNO_3 in the 1300-1350 cm^{-1} region, and N_2O_5. Similar support for ISAMS and balloon-borne experiments covers CH_4 (self-broadened line widths and absolute line strengths in the V_4 branch at room temperature; temperature

dependence of N_2 - broadened lines) and NO (self - and N2 - broadened widths and line strengths for transitions in the 1-0 band and their temperature dependence; very low pressure spectra).
Attempts to record the IR Spectrum of the NO_3 radical are being made using the $NO_2 + O_3$ generation method; many novel aspects of the reaction kinetics have emerged.
The above work is being undertaken at RAL in collaboration with Oxford University. In addition, the relative line positions of HF, H_2O and CH_4 have been measured to very high accuracy at RAL, in support of HF measurements to be made by the Halogen Occultation Experiment on UARS.

2.2 Chemical Kinetics

Cambridge University have developed a laboratory method for studying reactions of HO_2 which avoids interference by hydrates of HO_2 and is used at total pressures corresponding to those in the lower stratosphere. It is based on flash photolysis combined with infra-red diode-laser spectroscopy. Measurements of the rate of recombination of HO_2 radicals have been published. It has been shown that the calculated strength of the v_3 band of HO_2 is a factor of 7 too high. Measurements of IR band strength are being extended to NO_3 and DO_2. Because of the importance of the pressure dependences formed for reactions of hydrogen radicals, this work is being extended by applying the highly sensitive but difficult technique of mid-infra-red laser magnetic resonance spectroscopy to study atmospheric reactions of HO_2 with NO, NO_2 etc in the pressure range 10-50 Torr.

Rate coefficients for the reactions: $Cl + HO_2 \rightarrow HCl + O_2$ (1a); $Cl + HO_2 \rightarrow OH + ClO$ (1b) and $ClO + HO_2 \rightarrow HOCl + O_2$ (2) have been determined at Harwell from measurements of the kinetic behaviour of HO_2 and ClO in the photolysis of $Cl_2 - H_2 - O_2 - N_2$ mixtures using the molecular modulation technique. The following values were obtained for the rate coefficients at 308 k: $k_{1a} = (4.4 + 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; $k_{1b} = (9.4 + 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_2 = (6.2 + 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. None of these rate coefficients showed any significant change with pressure over the range 50 - 760 Torr. These results do not suggest any changes to the recommended values of k_1 or k_2 for the stratospheric modelling and thus no change in calculated ozone concentrations. Further investigation of the pressure dependence of k_2 at $T < 250K$ may be required.

A stopped flow kinetic spectrometer was used at Harwell to investigate the reactions of chlorine nitrate with HCl, HBr and H_2O by observation of the decay of $ClONO_2$ in the presence of excess gaseous H-containing reagent. At room temperature and under the experimental conditions the overall reaction: $ClONO_2 + HX \rightarrow HNO_3 + ClX$ occured rapidly for X = Cl and Br but more slowly for OH. The kinetics of the reactions were complex and were probably dominated by heterogeneous reaction pathways occurring on the reaction vessel surface. This makes assessment of reaction rates in the stratosphere very uncertain. However extrapolating to the stratospheric conditions obtaining at the altitude of maximum $ClONO_2$ mixing ratio (27 km), gives an overall decay coefficient for chlorine nitrate of $10^{-9}s^{-1}$ by the heterogeneous reaction $ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$. Compared with the 24 hr averaged photo-dissociation rate at this altitude of $10^{-4}s^{-1}$ these data therefore suggest that removal of $ClONO_2$ in the stratosphere via reaction with HCl is of very minor importance.

Differing absorption cross-sections of $ClONO_2$ over the wavelength range 200-400 nm have been reported in the literature. Therefore the cross-sections have been redetermined by the Harwell Laboratory by measuring the optical density of known pressures of $ClONO_2$, corrected for absorption by OClO and NO_2 impurities (present at less than 0.1% concentration), in a cylindrical quartz cell using a stabilised deuterium lamp. A photo-diode array was used to record wide band spectra in the 200-400 nm region. The results showed good agreement over the whole wavelength range with the lower of the values previously reported, which should therefore be used for stratospheric calculations.

3. MODELLING

3.1 3-Dimensional Model

A 3-D numerical model of the stratosphere and mesosphere is being developed by the Meteorological Office and Oxford University and used to study the dynamics of the middle atmosphere, in particular the interaction between this region and the troposphere. Much higher spatial resolution is being used than hitherto; it has been realised that strong jet streams develop in the middle atmosphere which must be resolved for a successful simulation of the circulation. The major stratospheric warming of the northern winter 1984/85 has been reproduced closely in a 10-day forecast with the model. The dynamics of the event are under investigation, in particular the non-conservative role of radiation. The model is also being used in idealised experiments to study the effect on the stratosphere of large-scale features in the tropospheric circulation. Studies continue to improve the representations in the model of radiative processes and gravity wave breaking. Simple ozone chemistry is included; eventually the full chemistry of the region will be incorporated, and the model will be used as a tool for the interpretation of satellite measurements of minor constituents (such as those made by UARS).

3.2 2-Dimensional Models

A collaborative programme of 2-dimensional modelling is being carried out by Rutherford Appleton Laboratory and Cambridge University with emphasis on comparison with satellite data. A study which includes a detailed treatment of the semi-annual oscillation in low latitudes has demonstrated the important role played by equatorial dynamical processes in driving tracer distributions. Specifically, some unexpected features observed by SAMS in the behaviour of CH_4 and N_2O can now be well reproduced. It has also been shown that latitudinal and seasonal changes in O_3 and night-time NO_2 seen by LIMS are consistent with this model. The semi-annual oscillation study is in the press (Quart. J. Roy. Met. Soc., 112, 1986).

In the past year the SAO has been produced in the model by inclusion of the appropriate Kelvin wave equations, so that the empirical forced momentum term has been replaced by "real physics". The double peaked latitudinal dependence observed at certain seasons in CH_4 and N_2O are still successfully generated in the model.

At Cambridge University a 2-dimensional modelling study of perturbations to the stratosphere is underway. This will include the effects of increasing F11, F12, CH_4, N_2O and CO_2, both separately and as multiple perturbations.

3.3 1-Dimensional model

Results from the British Antarctic Survey's stratospheric 1-D photochemical computer model have been published (Quart. J R Met Soc, 111, 1013 (1985), showing that a Lagrangian-mean vertifal velocity of a few tens of metres per day (downward) is required iin the Antarctic summer, in order to reconcile measurements of total ozone and lower-stratospheric temperature with calculated chemical depletion of ozone. The change from continuous to interrupted photolysis, when the sun first sets after the long polar day of mid-summer, has a marked effect on the concentration of N_2O_5 and, to a lesser extent, $ClONO_2$, with a consequent decrease in the rate of ozone loss. These effects cannot be assessed correctly unless the forcing due to solar radiation is followed exactly.
Further studies will investigate the development of reservoir species during the polar night, with a view to establishing their concentrations at the onset of photolysis in the spring.

3.4 Diurnal Model

The work at RAL on comparisons between the Diurnal Model and balloon observations of NO and NO_2 has produced interesting results, showing an unexpected reduction of NO and NO_2 in the 1982 flight (possibly related to the 'El Chichon' volcano). These have been submitted for publication. An ESA funded study of Solar Occulation Missions has also made use of this model to analyse the errors arising at dawn in limb absorption measurements of rapidly changing species.

3.5 Trajectory Model

In collaboration with NASA Langley, NCAR, NOAA Aeronomy Lab (Boulder) and RAL, the photochemical-trajectory modelling approach developed at the Meteorological Office has used LIMS observations to demonstrate an increase of about 0.1 ppbv of HNO_3 per day along mid-stratospheric trajectories which remains essentially in the ozone and water vapour mixing ratios from the same points. Suggestions were made about possible mechanisms for this hitherto unsuspected source of HNO_3. The initialisation scheme has been reformulated for the main body of work done by this approach; the work is being prepared for publication in collaboration with RAL. The technique has also been used to examine the temperature history of air parcels circulating over Halley Bay (76°S, 27°W) in Antarctica during recent Octobers; the work is shedding some light on limitations in possible explanations of the large ozone column reductions recorded there in recent years.

4. Further information

Further information on the work described in this report can be obtained from the following:

British Antarctic Survey - Dr M J Rycroft
British Antarctic Survey
High Cross
Madingley Road
Cambridge
CB3 ET

Cambridge University - Professor B A Thrush FRS (laboratory studies)
Dr J Pyle (models)
Department of Physical Chemistry
University of Cambridge
Lensfield Road
Cambridge
CB2 1EP

Harwell - Dr A E J Eggleton
Environmental and Medical Sciences Division
Building 551
AERE Harwell
Oxfordshire
OX11 ORA

Meteorological Office - Dr A F Tuck
Meteorological Office
London Rad
Bracknell
Berkshire
RG12 2SZ

National Physical Laboratory	-	Dr P Woods National Physical Laboratory Queens Road Teddington Middlesex TW11 0LW
Oxford University	-	Dr F Taylor University of Oxford Department of Physics Clarendon Laboratory Parks Road Oxford OX1 3PU
Rutherford Appleton Laboratory	-	Dr J Harries Rutherford Appleton Laboratory Chilton Didcot Oxfordshire OX11 0QX