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Ozone loss in Antarctica: the implications for global change

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SUMMARY

Although stratospheric ozone loss had been predicted for many years, the discovery of the Antarctic ozone hole was a surprise which necessitated a major rethink in theories of stratospheric chemistry. The new ideas advanced are discussed here. Global ozone loss has now also been reported after careful analysis of satellite and groundbased data sets. The possible causes of this loss are considered. Further advances require a careful coordination of field measurements and large-scale numerical modelling.

1. INTRODUCTION

It is a paradox that, although the stratospheric science community had predicted the possibility of ozone depletion for many years, the discovery of the ozone 'hole' over Antarctica came as a complete surprise: theory did not predict such dramatic ozone depletion, nor that it would occur in the lower stratosphere over Antarctica. Molina & Rowland (1974) had suggested that the build up of chlorofluorocarbons (CFCs) in the atmosphere could eventually lead to a depletion of ozone by a catalytic cycle involving Cl and ClO.

$$\begin{aligned} & Cl + O_3 \rightarrow ClO + O_2 \\ & ClO + O \rightarrow Cl + O_2 \\ \text{net:}\quad & O + O_3 \rightarrow 2O_2, \end{aligned}$$

where Cl and ClO are the eventual breakdown products of the CFCs after they have reached the region of strong ultraviolet radiation in the middle and upper stratosphere. This idea formed the basis of model calculations of ozone depletion by the CFCs until the celebrated announcement of Antarctic ozone loss by Farman *et al.* (1985). Model calculations of the kind performed by Molina & Rowland showed the largest ozone reduction, in percentage terms, in the upper stratosphere around 40 km and indicated that the ozone loss would grow gradually with increasing amounts of chlorine in the stratosphere. The loss was calculated to occur mainly in the upper stratosphere because it was here that models predicted the largest mixing ratios of ClO. At lower altitudes, HCl and $ClONO_2$ were calculated to be the most abundant forms of chlorine. Moreover, the concentration of atomic oxygen increases with altitude. Low concentrations of atomic oxygen in the lower stratosphere make the above catalytic cycle less effective.

The first obvious evidence of stratospheric ozone depletion came with the discovery of the springtime Antarctic ozone hole. Observations show that the ozone loss occurs rapidly, with most of the ozone in the polar lower stratosphere, between approximately 15 and 20 km, being removed in about six weeks in the Antarctic spring. Figure 1 shows the ozone data from Halley Bay in 1987. On 15 August the profile measured is normal for the time of year. Two months later massive ozone loss has occurred throughout the lower stratosphere. Thus, the observed loss conflicts with that predicted in both its speed (weeks rather than years) and location (the lower stratosphere rather than the upper stratosphere); the discovery of the ozone hole has led to a major rethink of theories of ozone depletion.

It is not our intention here to describe the many different theories put forward to explain the Antarctic ozone loss, but rather to present the picture which has emerged since 1985. This will be done in § 2. Theories have advanced rapidly and new orthodoxies have arisen, some of which may be no more enduring than the old. There has been much discussion, with an associated mystifying jargon, on a variety of ideas about how various processes occurring deep within the low pressure system of the winter polar stratosphere (the polar vortex) can influence lower latitudes. These questions and the general issue of middle latitude ozone loss are discussed in § 4. This includes some discussion of results from a campaign, the European Arctic Stratospheric Ozone Experiment (EASOE), which took place between November 1991 and March 1992. Atmospheric models have, in recent years, advanced in their ability to include the complex interactions between atmospheric chemistry and dynamics. General circulation models with detailed chemical schemes offer the opportunity to study some

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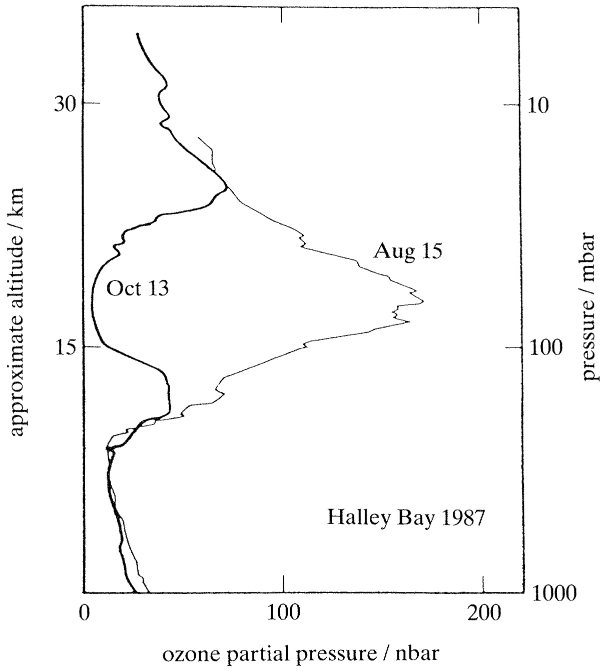

Figure 1. Ozone profiles measured at Halley Bay, 76°S on 15 August and 15 September 1987 (from SORG, Stratospheric Ozone 1988, HMSO, with permission).

of the many questions which still remain about the impact of polar ozone loss on the global distribution of ozone. Some preliminary calculations with such a model are presented in § 5.

2. PRESENT THEORIES OF POLAR OZONE LOSS

The search for an understanding of the Antarctic ozone loss naturally involved the question of why it should have occurred in that part of the globe in the spring time. In winter, the circulation in the polar stratosphere of both hemispheres is dominated by a low pressure vortex of strong westerly winds. In the Antarctic the winds are basically circumpolar. At the centre of this vortex temperatures can remain low during winter and early spring. In contrast the northern hemisphere winter circulation is more disturbed, or variable. The centre of the vortex does not usually correspond to the pole, often being displaced by a high pressure system centred over the Aleutians, and the minimum temperatures are generally several degrees higher than in the south.

It is the lower temperatures in the south which provide the first clue to the Antarctic oxone loss. Temperatures drop low enough for the formation of polar stratospheric clouds (PSCs) whose frequent occurrence has been well documented by satellite observations during the 1980s (McCormick *et al.* 1989). PSCs form at temperatures a few degrees above the frost point, below about 195 K, and are believed to be composed initially of nitric acid trihydrate. As the temperature drops, water ice can form (Toon *et al.* 1989).

It has been hypothesized (Solomon *et al.* 1986) that the PSCs act as surfaces for heterogeneous reactions which convert chlorine from reservoir forms, such as HCl and $ClONO_2$, into radicals which can destroy ozone. Several reactions are proposed.

$$\begin{aligned} N_2O_5 + H_2O &\rightarrow 2HNO_3, & (1)\\ ClONO_2 + H_2O &\rightarrow HNO_3 + HOCl, & (2)\\ N_2O_5 + HCl &\rightarrow HNO_3 + ClONO, & (3)\\ HCl + ClONO_2 &\rightarrow HNO_3 + Cl_2. & (4) \end{aligned}$$

In all cases, it is assumed that the nitric acid produced in the reaction stays in the solid phase. Reactions (2), (3) and (4) all turn chlorine from relatively stable forms to much more reactive forms. HOCl, ClONO and especially Cl_2 are all rapidly photolysed to liberate chlorine atoms. Reactions (1)–(4) would also act as a sink for nitrogen oxides in the polar lower stratosphere so that if, for example, ClO is indeed present it is then much less likely to be converted back to the reservoir $ClONO_2$ by the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$. Thus, these heterogeneous reactions offer a suitable explanation of the high levels of ClO, in concentrations greater than 1 p.p.b.v., which have been measured recently in the Antarctic polar lower stratosphere (Anderson *et al.* 1989; de Zafra *et al.* 1989; Brune et al. 1989) and for the observations of low levels of nitrogen oxides (see, for example, Fahey *et al.* (1989) for a detailed discussion of nitrogen oxides in the presence of polar stratospheric clouds).

Even with the high levels of ClO observed in the lower stratosphere, the catalytic cycle of Molina & Rowland (1974) (and Stolarski & Cicerone (1974)), which is described in the introduction, would be relatively inefficient in the spring time of the polar lower stratosphere because of the low concentrations of atomic oxygen expected to be present at that time. Molina & Molina (1987) suggested an alternative catalytic cycle, which does not involve atomic oxygen, but which is capable of producing rapid ozone loss:

$$\begin{aligned} ClO + ClO + M &\rightarrow Cl_2O_2 + M, & (5)\\ Cl_2O_2 + h\nu &\rightarrow ClO_2 + Cl, & (6)\\ ClO_2 + M &\rightarrow Cl + O_2, & (7)\\ 2 \times (Cl + O_3 &\rightarrow ClO + O_2), & (8)\\ \hline \text{net } 2O_3 + h\nu &\rightarrow 3O_2. \end{aligned}$$

The formation of the chlorine monoxide dimer in reaction (5) is favoured by low temperatures, making this cycle especially suitable in the Antarctic. Note that this cycle also requires sunlight; the depletion over the Antarctic occurs in the springtime with the return of solar illumination. Another cycle involving both bromine and chlorine compounds

$$\begin{aligned} BrO + ClO &\rightarrow Br + Cl + O_2,\\ Br + O_3 &\rightarrow BrO + O_2,\\ ClO + O_3 &\rightarrow ClO + O_2,\\ \hline \text{net } 2O_3 &\rightarrow 3O_2, \end{aligned}$$

is also believed to be important.

A further component of the explanation again involves the polar vortex. Measurements made during the Airborne Antarctic Ozone Experiment in 1987 showed a very strong gradient of some chemical species as aircraft flew towards the centre of the polar vortex. For example, source gas concentrations (e.g. the CFCs) fell dramatically (Heidt *et al.* 1989; Loewenstein *et al.* 1987) indicating that the air nearer the vortex centre had in the past been at much higher altitudes where the source gases were destroyed: the air is 'old'. Air at somewhat lower latitudes had higher concentrations of these gases. This has important implications. The total amount of chlorine in any measured parcel of air in the stratosphere should be reasonably constant, being the concentration as the air entered the stratosphere at the tropopause. Low concentrations of the CFCs therefore imply higher concentrations of other chlorine compounds such as, for example, HCl and $ClONO_2$. These compounds, but not the CFCs, can be turned into 'active' chlorine (i.e. Cl and ClO) on polar stratospheric clouds. The strong horizontal gradients of many chemical species are a robust feature of polar observations (see, for example, Profitt *et al.* (1989)). The strong wind gradients around the vortex act as a barrier to horizontal mixing. Thus, for example, once ozone depletion occurs, mixing with lower latitude air, rich in ozone, does not happen to any large extent and the ozone depletion remains until the dynamical breakdown of the polar vortex in the late spring.

The above constitutes an explanation of the ozone hole which in outline is broadly accepted, although many details are the subject of debate. Thus, heterogeneous reactions on PSCs formed in the cold polar winter turn chlorine into reactive form; when sunlight returns the elevated levels of chlorine can destroy ozone rapidly in catalytic cycles involving the chlorine monoxide dimer and also bromine monoxide; removal of nitrogen oxides, either reversibly ('denoxification') or irreversibly ('denitrification'), from the polar vortex and the lack of mixing with lower latitudes maintain the ozone depletion until the dynamical conditions change with the approach of summer.

3. SOME HETEROGENEOUS REACTIONS

The surface reactions (1)–(4) discussed above have been studied in the laboratory during the last few years (e.g. Tolbert *et al.* 1988; Hanson & Ravishankara 1991). Reaction efficiencies on both ice surface and cold sulphate aerosol have been studied and there is now reasonable quantitative data for chemical modelling studies.

An important unresolved question is how efficiently the chlorine can be turned into reactive forms (i.e. Cl and ClO) by heterogeneous reactions (although evidence from polar campaigns indicates that the process operates on a timescale of hours), and by what mechanism. For example, the importance of reaction (4) will depend on the relative abundances of HCl and $ClONO_2$. Simple stoichiometry tells us that if equal amounts of HCl and $ClONO_2$ are available, then all of this chlorine can be converted to Cl_2. On the other hand if the ratio of HCl to $ClONO_2$ is 2:1, then for every two atoms of Cl liberated one molecule of HCl remains. (See figure 2). If the abundance of $ClONO_2$ is even less, then the amount of chlorine produced in active form is correspondingly reduced. Additional production of active chlorine can only occur if chlorine nitrate, reformed for example by reaction between ClO and NO_2, subsequently reacts with the remaining HCl. It should be recalled that the polar lower stratosphere is substantially denitrified, so this extra cycling may not be particularly effective. Indeed, numerical models, including just reactions (1)–(4), have had some difficulty in producing the observed high levels of active chlorine required to reproduce the observed rapid loss of ozone (see, for example, Prather (1991); Crutzen *et al.* (1992)).

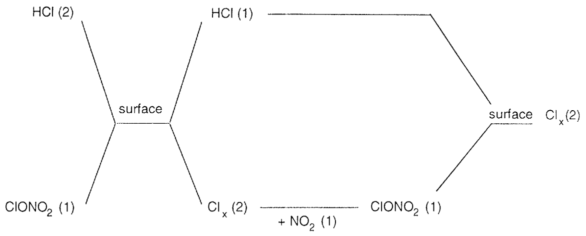

Figure 2. A schematic of the sequence of surface reactions between HCl and $ClONO_2$.

A reaction which is being studied currently may provide the solution. The reaction

$$HCl + HOCl \rightarrow Cl_2 + H_2O \qquad (9)$$

certainly proceeds rapidly on ice surfaces (Hanson & Ravishankara 1992). There is, however, some dispute about its efficiency on sulphate aerosol. Model calculations including this reaction do lead to a better representation of the observed polar ozone loss. The HOCl can be produced either heterogeneously (reaction 2) or by the rapid gas phase reaction between ClO and HO_2. The recycling, shown in figure 3, may be a more efficient means of producing active chlorine than that shown in figure 2, involving the oxides of nitrogen.

Reaction (9) is a sink for hydrogen radicals, which are converted to water vapour. Significantly different abundances of OH and HO_2 are calculated in models with and without reaction 9 (Prather 1991; Crutzen *et al.* 1992). Measurements of OH and HO_2 would help to resolve this important question concerning the mechanism of chlorine activation by heterogeneous reactions. Unfortunately, the lack of measurements of hydrogen radicals has long been a barrier to understanding processes in the lower stratosphere.

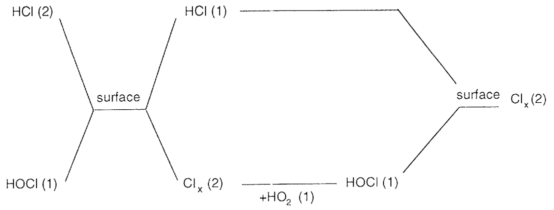

Figure 3. A schematic of the sequence of surface reactions between HOCl and HCl.

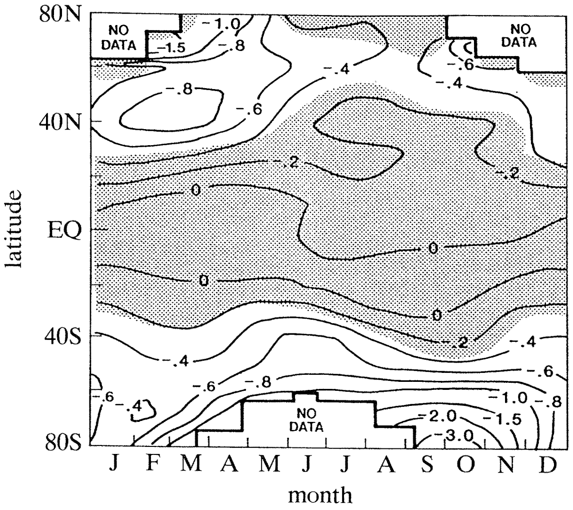

Figure 4. Annual trends in total ozone, as a function of latitude and month, as determined from the Total Ozone Mapping Spectrometer. (From Stolarski *et al.* (1991) and reproduced with permission of *Geophys. Res. Lett.*).

4. GLOBAL IMPLICATIONS

Recently evidence has become available from a variety of sources that the downward trend in ozone is not confined to the Antarctic spring but is instead global in extent. Both ground based measurements (WMO 1990) and satellite data from the Total Ozone Mapping Spectrometer (TOMS) (Stolarski *et al.* 1991) have revealed a statistically significant downward trend in global ozone over the past decade and more. The satellite data, for example, indicate a springtime decrease of about 8% during the 1980s at 50°N with smaller losses elsewhere (see figure 4). Further satellite data, this time from the Stratospheric Aerosol and Gas Experiment, SAGE, have shown that a substantial part of the ozone reduction is in the lower stratosphere, similar to Antarctica (McCormick *et al.* 1992).

Although this decrease in ozone points towards the global influence of chlorine-catalysed ozone destruction, the precise mechanisms remain to be understood. A number of possible causes of the middle latitude ozone loss have been advanced.

1. Ozone could be destroyed in polar latitudes by the mechanisms discussed in § 2. At some later stage the ozone-poor air is then transported to lower latitudes where it mixes and leads, on average, to reduced ozone, a process often called 'dilution'.
2. Chlorine in the active forms Cl and ClO could be produced ('processed') on polar stratospheric clouds in high latitudes. This air could then be transported to lower latitudes where ozone depletion could occur. For example, the production of active chlorine might occur in the dark polar night but the ozone loss would subsequently occur at lower latitudes in sunlight. This mechanism is often called 'processing'.
3. The production of active chlorine could occur in middle latitudes, perhaps on sulphate aerosol, followed by *in situ* ozone loss. Sulphate aerosol is present throughout the lower stratosphere and can be enhanced by volcanic eruptions.

These possibilities have been much debated in the scientific literature (see, for example, Tuck (1989); Murphy *et al.* (1989); Proffitt *et al.* (1989)). The debate, in a subject which has moved rapidly since the discovery of the ozone hole, has perhaps been biased by a southern hemisphere view which may not be appropriate to the northern hemisphere. For example, in debates about the importance of 'processing' it is assumed that the production of active chlorine will happen inside the polar vortex; there is then further debate about the likelihood of this air breaking through the vortex wall to reach lower latitudes. As we will see below, this picture may not be particularly appropriate.

Let us consider the polar hemispheres in turn. Recall from § 2 that to produce high levels of active chlorine (Cl and ClO) we require a number of conditions: (i) the CFCs need to have broken down into other forms of chlorine, like HCl and $ClONO_2$. The smaller the concentration of the CFCs, the higher will be the concentration of HCl and $ClONO_2$; (ii) temperatures need to be sufficiently low for the formation of polar stratospheric clouds, reactions on whose surfaces then turn HCl and $ClONO_2$ into active chlorine. Thus, to produce the largest concentrations of active chlorine, we require very low concentrations of CFCs to be coincident with the coldest temperatures.

As mentioned briefly in § 2, in the south throughout the winter and spring there is a vortex which is basically circumpolar (certainly by comparison with the north). At the centre of the vortex are found both low mixing ratios of the chlorine source gases (and hence, by conservation, high concentrations of the other chlorine compounds like HCl and $ClONO_2$) and low temperatures. Conditions are thus favourable for the production of high concentrations of ClO and hence for large ozone loss in sunlight (see figure 5). The degree to which mixing occurs with lower latitudes is still to be resolved. Simple studies with a numerical model indicates that 'dilution' could certainly explain some of the middle latitudes loss in the south (Chipperfield & Pyle 1988), but this does not rule out a possibly important role for 'processing'.

In the north the situation is different. Measurements during this winter's European Arctic Stratospheric Ozone Experiment (EASOE) (U. Schmidt, private communication) indicate that in the lower stratosphere at the centre of the vortex the concentrations of the CFCs are very low. Thus in the centre of the vortex there is the greatest potential for producing Cl and ClO. However, experience during EASOE also indicated that the coldest temperatures, where polar stratospheric clouds could form, were not always in the centre of the vortex. Indeed very often they were at the vortex edge or even outside the vortex, often associated with the upward extension of tropospheric weather systems. At those locations higher concentrations of CFCs were measured; the potential for producing high Cl and ClO is less here, even though the temperatures are low.

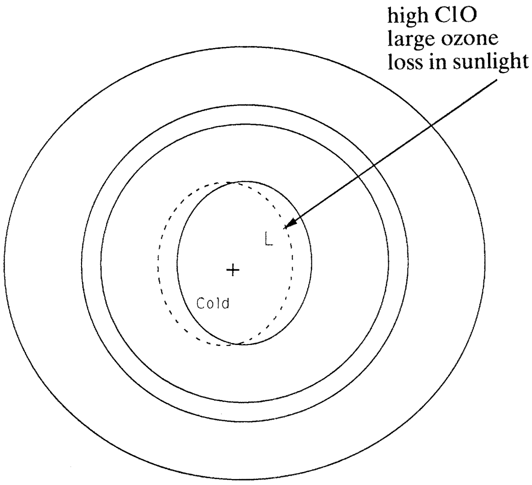

Figure 5. A schematic of the southern hemisphere in polar latitudes during late winter and early spring on a pressure surface in the lower stratosphere. The pole is indicated by +, and the solid lines could be geopotential or potential vorticity isolines, the dotted line contains the region of minimum temperature.

Associated with the variability of the northern hemisphere polar lower stratosphere, the duration of cold temperatures is less than in the south and may stop well before significant sunlight is available to initiate photochemical destruction of ozone. During EASOE coldest temperatures occurred during late December and early January within the polar vortex; calculated ozone loss was much less than if these conditions had obtained in February when solar illumination is much greater. There were also conditions suitable for polar stratospheric cloud formation in late January and early February, although outside the vortex. The consequences of this have still to be investigated.

Two cases, at least, can then be identified in the north, shown schematically in figure 6. Firstly, as happened in early January 1992, the cold temperatures correspond to the centre of the vortex where the concentrations of CFCs are very low and hence high ClO can be produced (see § 5). Some ozone loss must then occur, depending to some extent on the duration of sunlight. In 1992 the vortex warmed, and the ClO levels decreased, by a process not yet properly understood, and massive ozone loss did not happen. Nevertheless, given the natural interannual variability, in other years the cold temperatures might occur later, at times of greater solar isolation, and bigger ozone loss could occur.

Secondly, when the cold temperatures occur outside the vortex, as happened in mid January 1992, somewhat elevated ClO will be produced. Because the CFCS are higher here, the ClO will be less (perhaps less than 1 p.p.b.v.) than within the cold vortex (greater than 1 p.p.b.v.) but much higher than a typical mid latitude value (~ 10 s of p.p.t.v.) (see, for example, Brune *et al.* (1988)). These amounts of ClO are certainly sufficient to produce some ozone loss. Exactly how much ozone loss can be attributed to this mechanism in early 1992 is the subject of active research using data from EASOE.

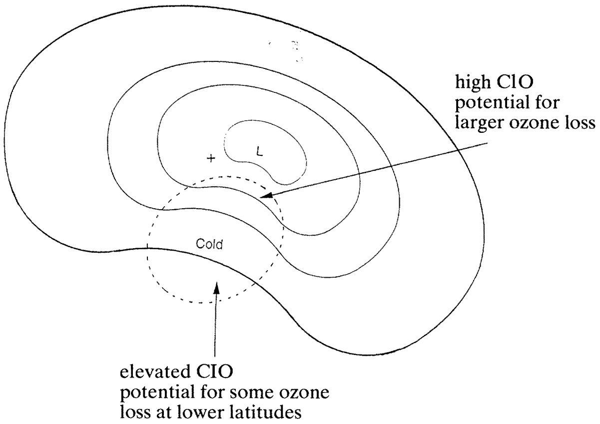

Figure 6. As figure 5, for the northern hemisphere.

The question to be resolved in this case is what the subsequent fate of the ClO may have been; how long did the elevated levels persist before $ClONO_2$ and HCl was reformed? Moreover, did this air remain close to the vortex in high latitudes or is there significant transport to low latitudes? With a wealth of constituent and meteorological data available from EASOE, further progress can confidently be expected.

5. NUMERICAL MODELLING STUDIES

With the development of three-dimensional atmospheric models which include chemical processes, new and powerful tools for the study of combined transport–chemistry problems are becoming increasingly available. In the U.K., the UGAMP (U.K. Universities Global Atmospheric Modelling Programme) is developing a hierarchy of numerical models, one of which, a spectral general circulation model made available by the European Centre for Medium-range Weather Forecasts, has had included a detailed stratospheric chemistry scheme, implemented by the Atmospheric Chemistry Modelling Group at Cambridge University. The model chemistry has been described by Lary (1991) and Lary *et al.* (1993*a*,*b*).

We here show preliminary results from that model to contrast the behaviour of the north and south polar regions. Two short runs are shown, one initialized with the observed meteorological conditions of 5 January 1992, being part of our study for EASOE, and another initialized using conditions appropriate to 1 September of any year. Both runs were integrated for about 21 days. Our future studies will consider the whole winter and spring evolution in both hemispheres. While the gas phase chemistry included in the model is quite detailed only a simple heterogeneous chemistry is included, involving reactions 1, 2, and 4, activated at below 195 K. This is an oversimplification but nevertheless useful for a comparative study of this kind.

Figure 7 shows the southern hemisphere ClO_x ($ClO + 2Cl_2O_2$) at approximately 50 mb for two days during the run corresponding to 10 and 18 September (days 10 and 18). Notice that the active chlorine is

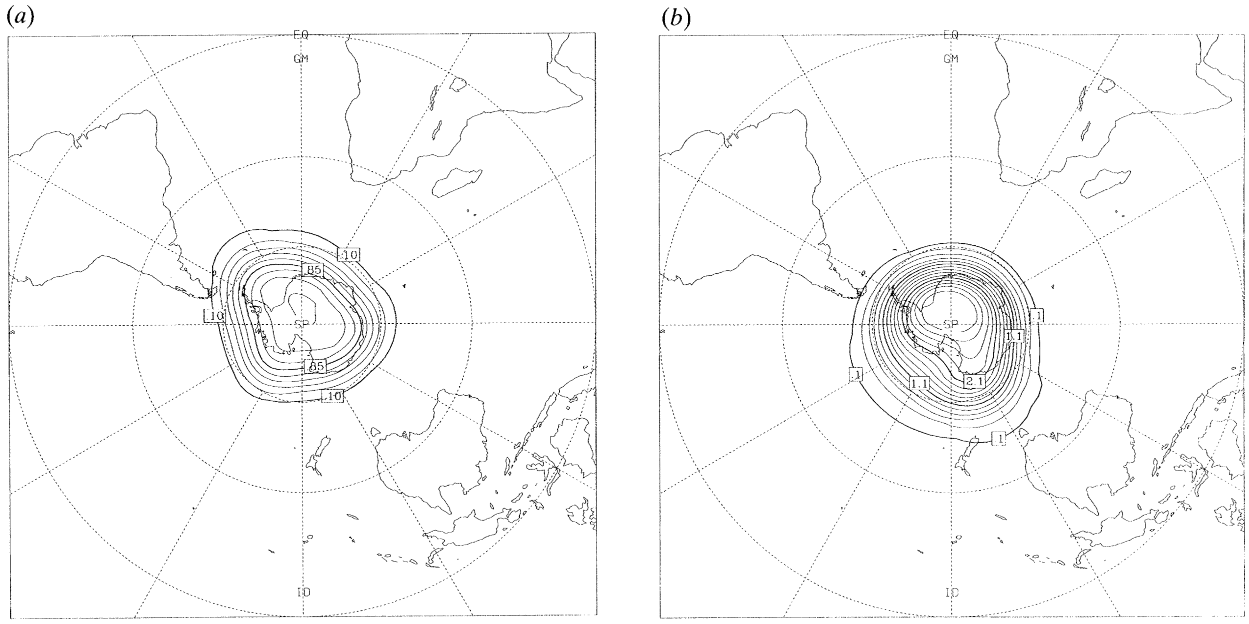

Figure 7. Active chlorine ($Cl + ClO + 2Cl_2O_2$) mixing ratio at a model level of approximately 50 mb in the southern hemisphere on (*a*) 10 September and (*b*) 18 September.

confined to high polar latitudes within the vortex where temperatures are cold enough for the production of polar stratospheric clouds to occur. The cold temperatures are sustained throughout the run. By 18 September, conversion to active chlorine is almost complete in the centre of the vortex, with a mixing ratio of about 2.8 p.p.b.v. With these high levels of active chlorine in sunlight, ozone loss occurs in the model, being about 5% in the vortex during the last ten days of the run.

The situation in the northern hemisphere is shown in figure 8 for 11 January and 22 January. On 11 January, the level of ClO_x is high following several days during which temperatures were below 195 K in the polar vortex. As in the southern hemisphere case the ClO_x has built up from very low initial levels at the start of the run to values greater than 1 p.p.b.v. Results from the EASOE campaign confirm that the polar vortex had high levels of reactive chlorine at this stage in January 1992. Notice that, unlike the southern hemisphere case, the ClO_x shown in figure 8*a* is not centred on the pole; the vortex, filled with active chlorine, was displaced over northern Europe. The higher temperatures in the model between 11 January and 22 January prevented a further increase in active chlorine levels. This, and the fact that the highest ClO_x values were calculated at a time of low solar insulation, means that the O_3 loss calculated in the northern hemisphere in this particular example is much less than in the southern hemisphere case.

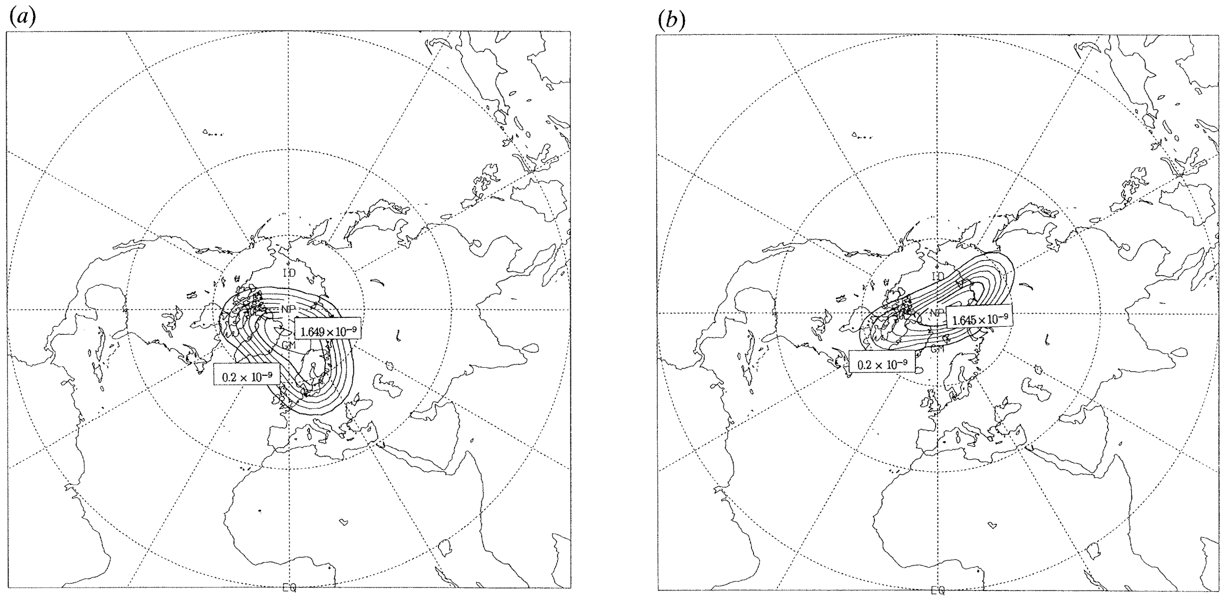

Figure 8. As figure 7 for the northern hemisphere; (*a*) 11 January, (*b*) 22 January.

CONCLUSIONS

Since the discovery of the Antarctic 'ozone hole', many of the basic chemical, microphysical and dynamical processes involved have been elucidated. In a rapidly expanding field there are clearly many areas which require further study: these include the precise details of the heterogenous chemistry; the details of transport processes from high to middle latitudes; the relative roles of chemistry and transport in northern hemisphere ozone changes. Furthermore, the observation of a middle latitude ozone decline has added an important impetus to these studies. It is clear that the complex processes involved, some of which have been discussed here, require a combination of detailed modelling studies with the use of large atmospheric data sets from campaigns like EASOE and from satellite experiments like the Upper Atmosphere Research Satellite.

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Discussion

A. S. McLaren (*Science News, Washington D.C., U.S.A.*). There appears to be a possible correlation between the northern hemisphere location (i.e. Greenland–Iceland–Scandinavia) of high ClO–low ozone in Dr Pyle's presentation and Professor Weller's earlier presentation of 1965–91 observed northern hemisphere temperature changes (towards cooling) in the same general vicinity (particularly Greenland). Does Dr Pyle have any comments on this?

J. A. Pyle. It seems very unlikely that there is a relationship. The stratospheric data I presented referred simply to 1991–92. Other years would be expected to have behaved differently. Furthermore, the build up of chlorine has been must pronounced in the last few years; such large concentrations of ClO would not have been seen in the 1960s or 1970s.

J.-O. Strömberg (*Kristinebergs Marinbiologiska Station, Fiskebäckskil, Sweden*). There have been reports that volcanic eruptions have a major impact on the stratospheric ozone layer. Would Dr Pyle care to comment on this?

J. A. Pyle. Volcanic eruptions can indeed play a major role in stratospheric chemistry. They can possibly emit chlorine directly into the stratosphere. More importantly they emit SO_2 which ultimately forms a sulphate aerosol in the lower stratosphere. It has been suggested that reactions on the aerosol surface can accelerate ozone destruction. During this last winter, many measurements of extremely enhanced sulphate aerosol were made during the EASOE campaign. At the same time, it was clear that the chemistry was highly perturbed with, for example, very low levels of the nitrogen oxides being measured. The full implications of the measurements require further detailed study.