Three dimensional modelling of chlorine activation in the Arctic stratosphere

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Abstract. The UK Universities Global Atmospheric Modelling Programme (UGAMP) General Circulation Model has been used to study the chemical evolution of the northern hemisphere polar vortex. A run that includes a parametrisation of the heterogeneous reactions occurring on polar stratospheric clouds (PSCs) has been initialised with the ECMWF analyses of the 5th of January 1992. This run produces high values of active chlorine within the polar vortex, for example mixing ratios of ClO_x ($=Cl+ClO+2\times Cl_2O_2$) of 1.8ppbv are calculated after six days of integration, with correspondingly low values of HCl and $ClONO_2$. During warm periods of this model run, when the PSC reactions are not active, the ClO_x is converted slowly back into $ClONO_2$. Chemical loss of ozone in January in the model is small.

INTRODUCTION

The conversion of the chlorine reservoirs HCl and $ClONO_2$ into more reactive forms of chlorine on the surfaces of PSCs is an important stage in priming the southern hemisphere winter stratospheric polar vortex for ozone destruction [Anderson et al 1991]. In the northern hemisphere similar processes occur and high levels of active chlorine are observed [Brune et al 1990]. However the considerable ozone loss that occurs in the southern hemisphere has not yet been observed in the northern hemisphere. The root of the difference is the greater amount of wave activity in the boreal hemisphere compared to the austral hemisphere [Schoeberl et al 1992]. Warmer temperatures, a more disturbed, zonally asymmetric vortex, and stratospheric warmings are all related to this wave activity and can affect the chemistry in different ways. For instance if the temperatures are cold early in winter then active chlorine may be produced. Large meridional excursions of the vortex may actually expose this activated air to sunlit conditions even in midwinter and some ozone loss could occur. In contrast to this, enhanced mixing associated with a disturbed northern hemisphere vortex could mean that this ClO_x will be removed into reservoir species before the return of sunlight and so will not destroy ozone.
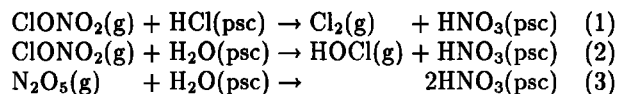
To understand and quantify these effects models that include the full 3-dimensional dynamical, chemical and ra-

diative aspects of the problem are needed. Here we present some results from one such model. After giving an outline of the model, results of a run initialised in early January 1992 are presented. References are made to measurements made during EASOE in order to indicate those results that match the evolution of the real stratosphere. The main emphasis here is on the production and evolution of active chlorine although we also consider the ozone distribution.

MODEL OUTLINE

The UGAMP general circulation model is based on a version of the ECMWF spectral model [Tibaldi et al 1990]. A tracer advection scheme and gas phase chemistry scheme have been added to the model [Lary et al 1993]. This includes the tracers $O_x (=O(^1D)+O(^3P)+O_3)$, $NO_x (=N+NO+NO_2+NO_3)$, HNO_3, $HONO_3$, N_2O_5, N_2O, $ClO_x (=Cl+ClO+2\times Cl_2O_2)$, HCl, HOCl and $ClONO_2$. The partitioning among the family members is achieved by using photochemical steady state expressions. For more details of the reactions included see Lary and Pyle [1991]. Photolysis cross sections and reaction coefficients are taken from DeMore et al [1990]. An enhancement factor lookup table is used to calculate photolysis coefficients [Meier et al 1982; Lary and Pyle 1991]. Integration of the chemical rates of change is by an Euler Backward scheme [Stott and Harwood 1993]. The time step varies from 30 seconds during sunset and sunrise to 15 minutes at nighttime.

As well as the gas phase reactions the model also includes a simple parametrisation of the reactions occurring on the surface of PSCs. This kind of parameterisation has already been employed in studies such as that of Eckman et al [1993]. The reactions

$$ClONO_2(g) + HCl(psc) \rightarrow Cl_2(g) + HNO_3(psc) \quad (1)$$
$$ClONO_2(g) + H_2O(psc) \rightarrow HOCl(g) + HNO_3(psc) \quad (2)$$
$$N_2O_5(g) + H_2O(psc) \rightarrow 2HNO_3(psc) \quad (3)$$

are given a rate of $4.6 \times 10^{-5} s^{-1}$ when the temperature drops below 195K. The Cl_2 produced by the reaction (1) is assumed to dissociate immediately to produce Cl. There are no tracers in the model corresponding to solid phase nitric acid and so the nitric acid produced from the reactions (1), (2), (3) is put straight into the gas phase. This has two consequences. Firstly there is no sedimentation of PSCs, and so no irreversible removal of HNO_3. Secondly all of the nitric acid produced by the heterogeneous reactions will be available for photolysis in the presence of

sunlight. The model run described here does not have a prolonged cold spell and so denitrification is not expected. Furthermore, PSCs are most abundant in early January when photolysis rates are slowest.

The dynamical variables and tracers are advected using a spectral scheme in the horizontal and a finite difference scheme in the vertical [Hoskins and Simmons 1975]. A triangular truncation of 21 wave numbers has been used for the results presented here. This approximates to a 6° × 6° grid. Although the spectral scheme is accurate [Rood 1987], sharp gradients in constituents, such as those associated with a processed polar vortex, can result in numerical errors. These appear in two ways. The first is that the advection scheme appears to be over diffusive [Chipperfield et al 1992]. At low resolutions the sharp gradients in constituents, such as those observed at the edge of the 'chemically perturbed region', cannot be maintained in the model. This smoothing of sharp gradients is also seen in dynamical variables such as PV (figure 1a). However using a spectral method to advect the tracers is consistent with the numerical scheme used for the dynamical variables. The second effect of the numerical errors is that negatives occur in the mixing ratios of some species. Since these are physically unrealistic they are set to zero for the sake of calculating the chemical contribution to the tracer continuity equations, while leaving the tracer values themselves unchanged. This method is conserving and prevents the appearance of any spurious sources and sinks.

The initial meteorological fields have been taken from the ECMWF analysis for January 5th 1992. Tracer fields were generated using a method similar to that of Douglass et al [1991]. The initialisation takes a tracer data set from a 2D model and transforms it into a vortex following coordinate system more appropriate for wave-disturbed flows. For a more detailed discussion of the method see Lary et al (Submitted Manuscript) The resulting fields are then stepped forward for a single day using just the chemistry scheme.

MODEL METEOROLOGY

The model has been run for 30 days. The fields produced are forecast fields and after initialisation are not constrained by the analyses in any way. For the first few days of the run the model dynamical fields compare well with those observed. In a case study of a period later in
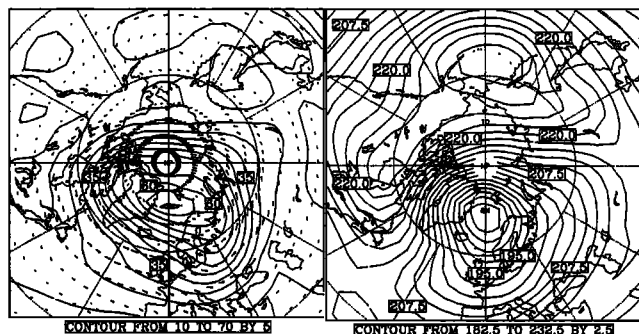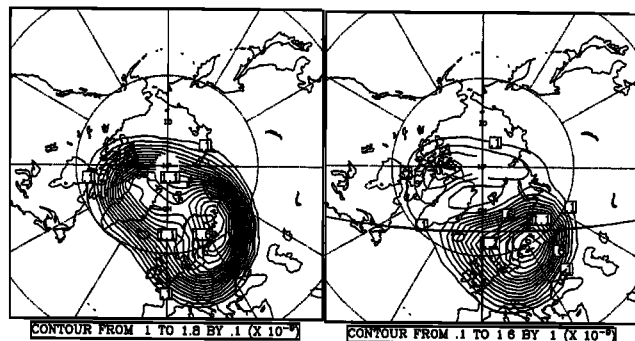

Fig. 2. Modelled distributions of active chlorine mixing ratios on 11th January, 12.00GMT, at 475K. (a) $ClO_x=$ $(Cl + ClO + 2 \times Cl_2O_2)$ (b) ClO, solid line corresponds to 90° zenith angle.

January, Carver et al [this issue] suggest that the model has a good forecast skill for periods of up to about 5 days. Although the model drifts from the observed fields it does reproduce some of the general features of January 1992. For instance in both the real and model atmospheres after a cold period lasting for the first half of January the temperatures warm to above the PSC threshold. The analysed temperatures then drop below the PSC threshold for a short period in late January. The model temperatures also dropped below the PSC threshold towards the end of the run. However the model temperatures are too low, the areal extent of PSCs somewhat too large and the second period when PSCs were present is prolonged compared to the analyses.

The model temperatures for the 11th of January, interpolated onto the 475K surface, are shown in figure 1b. The temperatures at which PSCs form lie over the Norwegian Sea and Northern Scandanavia. Temperatures are much higher over the Aleutians and NE Canada. Model PV and winds are shown in figure 1b. Although the gradients of PV at the vortex edge are not as steep as those in the analyses, there is still a clear polar stratospheric jet. The flow of air, at this time, is through the cold temperatures over Scandanavia, across the pole and through the warm temperatures over NE Canada.

DISTRIBUTION OF CHLORINE

The ClO_x distribution on initialisation of the model reflects the cold temperatures through the PSC parametrisation. The highest mixing ratio of ClO_x is 0.7ppbv. By January 11th, six days into the run, the whole of the model vortex contains high mixing ratios of active forms of chlorine and correspondingly low values of the 'reservoir' species HCl and $ClONO_2$. The total ClO_x peaks at around 1.8ppbv (figure 2a) with about 1.6ppbv of this as ClO (figure 2b). The 0.2ppbv ClO_x contour is contained almost completely within the 30 PVU contour. The tongue of ClO over NE Canada results from thermal decomposition of the dimer in the warm region of air shown in figure 1b. This elevated ClO is in darkness and consequently there should be no associated ozone destruction. The vortex air is depleted in N_2O_5, indicating denoxification. High values

Fig. 1. Model 475K fields at 12.00 GMT on the 11th of January 1992. (a) PV (PVU) and winds (ms⁻¹) (b) Temperature (K)

of HOCl are also seen in the vortex. In the model these are produced by reaction (2). If the reaction of HOCl with HCl on the surfaces of clouds had been included, we expect that such high values would not be present and the ClO mixing ratios would have been further elevated [Crutzen et al 1992; Prather 1992]. These results for early January within the polar vortex agree with the observations of a low HCl column [Bell et al, this issue] and the Microwave Limb Sounder (MLS) measurements of ClO which showed peak mixing ratios of ClO at about 45°E with decreasing values towards 180°E [Waters et al 1993].

As the model run proceeds there is a build up of a collar of $ClONO_2$ around the vortex edge (figure 3a). This is consistent with the observations of Toon et al [1992]. The collar results from the rapid reaction of ClO with NO_2. The cause of the collar could be: in-situ production of ClO in extra-vortical air, or incomplete denoxification of air at the edge of the vortex, or mixing processes across the vortex boundary.

An idea of the temporal evolution of chlorine species in the vortex can be gained by considering the time series for various species at 475K vertically above Heiss Island (58E,80N) (figure 4). The PV values seen at Heiss Island which lie in the range 50-67 PVU, while the values of PV characteristic of vortex air (or at least of activated ClO_x in the model) were greater than about 30 PVU. Heiss Island therefore appears to be representative of vortex air throughout the model run. Of course, the evolution of the mixing ratios at a point on an isentropic surface not only reflects the chemical changes occurring but also has contributions from quasi-horizontal motions and diabatic effects. The PV, O_x and Cl_y (= ClO_x+ HCl + HOCl + $ClONO_2$) give some indication of these motions. The gradual increase in O_x, for example is consistent with diabatic descent.

The temperatures at Heiss Island start off below the threshold for PSC formation but gradually rise. During the period 20th–23rd January the whole vortex became warmer and PSCs were not present. It can be seen that up to this time there is a general increase in ClO_x (figure 4b); in fact values as high as 2.2ppbv are reached. During the warmer period of the run the heterogeneous reactions are not activated anywhere in the vortex and the chemical sink for $ClONO_2$ is reduced. Correspondingly the model shows an increase in $ClONO_2$ during this period while at the same
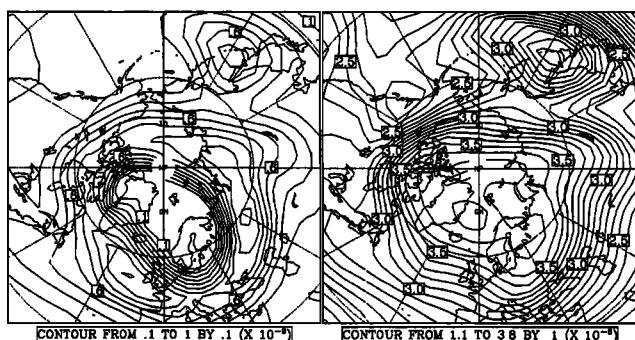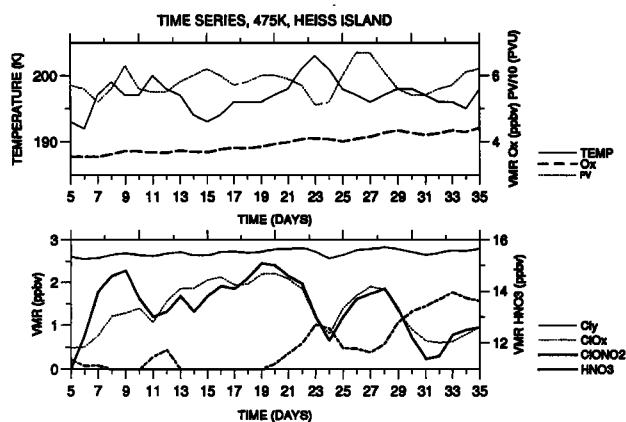

Fig. 4. Time series at 475K above Heiss Island (58E,80N) (a) Temperature (K), O_x (ppbv) and PV (PVU) (b) the mixing ratios of chlorine species.

time the HNO_3 decreases. This is due in part to HNO_3 photolysis, although there is not enough radiation at this time of the year for the 3ppbv loss to be a result of photolysis alone. Horizontal motions of the vortex account for the rest of the change. The NO_2, produced as a result of HNO_3 photolysis, then reacts with the ClO giving $ClONO_2$. However in the GCM the recovery of the activated chlorine may be slightly accelerated due to the diffusivity of the spectral advection scheme. This may enhance NO_2 in the vortex, and the NO_2 will react rapidly with the ClO.

The modelled HNO_3 is high within the vortex for most of the run. Murcray et al [this issue] measured low HNO_3 when PSCs were present at Kiruna on January 9th 1991. In mid January, after temperatures had risen and the PSCs evaporated, as much as 20ppbv HNO_3 were measured. The discrepancy between model and meaurement is due to the model PSC scheme which does not include condensed nitric acid. During EASOE Oelhaf et al [this issue] measured $ClONO_2$ within the polar vortex. In early January the $ClONO_2$ mixing ratio was very low, but rose to about 3ppbv by early March. Although the model has not been run to March there is some evidence for recovery of ClO_x to $ClONO_2$ with mixing ratios of 1.5ppbv at Heiss Island by the beginning of February.

Ozone Distribution

The ozone distribution for the 11th of January is shown in figure 3b. Qualitatively similar features are seen in the MLS observations [Waters et al 1993] with higher mixing ratios of O_3 in the vortex compared to mid-latitudes. There is no obvious signal of the O_3 loss suggested by Waters et al in the region of high ClO_x. Of course, the diabatic descent shown in figure 4a makes the quantification of ozone loss difficult in both the model and the atmosphere, a point we are currently investigating. Comparison of the O_3 fields from this run with those from a run that did not included the parametrisation of PSC reactions indicates only a small amount of photochemical O_3 loss.

Fig. 3. Modelled mixing ratios on 11th January 1992, 12.00 GMT at 475K. (a) $ClONO_2$, (b) O_x (=O_3 + $O(^3P)$ + $O(^1D)$)

Summary

A simple PSC scheme coupled with detailed chemistry implemented in a GCM indicates that high levels of active

chlorine can be present within the northern hemisphere polar vortex. These model results are in broad agreement with observations made during the EASOE winter e.g., the MLS ClO measurements, Waters [1993], and column HCl, Bell et al [this issue]. The detailed gas phase chemistry allows the determination of the subsequent evolution of this chlorine. In periods when the PSC reactions are not activated, $ClONO_2$ becomes the dominant chlorine reservoir. Only a small chemical ozone loss is apparent during January, consistent with the weak illumination at this time of year.

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