

MODELLING POLAR STRATOSPHERIC CLOUDS AND THEIR INFLUENCE ON OZONE

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It has long been recognized that chlorine can destroy stratospheric ozone, and the use of halocarbons has led to a pronounced increase in the stratospheric chlorine content. By the early 1990s the chlorine content of the Earth's stratosphere had risen to about 3 parts per 10⁹ by volume (ppbv) compared to the natural level of about 0.6 ppbv. The discovery of the Antarctic Ozone Hole in 1985¹ (Farman J.C., Gardiner B.G., Shanklin J.D., 1985) was met with a certain amount of arguably justifiable scepticism, motivated in part by the belief that the lower Antarctic stratosphere would not be the location where ozone depletion would first be manifested. Rather, it was thought that ozone near 40 km in mid-latitudes would show the first signs of change. The atomic chlorine produced by the destruction of chlorine containing trace gases, emitted at the Earth's surface like the halocarbons (CFC), destroys by a catalytic cycle ozone very effectively near 35-45 km. But because most of the total stratospheric ozone content resides at much lower altitudes, this and other ozone-destroying chemical cycles involving chlorine were predicted to lead to column-integrated ozone changes of perhaps 5% sometime near the middle of the twenty-first century using models considering the detailed *gas-phase chemistry* of the atmosphere. Such theoretical predictions stood in stark contrast to remarkable 50% column change reported for the Antarctic in 1985.

The ozone hole is a seasonal phenomenon that is tied to the dynamic meteorology of the Antarctic atmosphere. During winter an early spring, the Antarctic has the coldest temperatures found in the Earth's stratosphere, some 10-15 K colder than those of the Arctic in the same seasons. This interhemispheric temperature difference is believed to be due largely to differences in the surface topography of the two hemispheres. These cold polar temperatures, in turn, result in a strong temperature contrast between the Antarctic and the mid-latitudes of the Southern Hemisphere. It has long been known that the steep temperature gradient is accompanied by rapid circumpolar flow and a relatively isolated polar vortex.

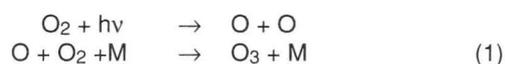
Just after the discovery of the Antarctic Ozone Hole, several distinct, and in some ways quite opposing theories were advanced. Currently, only the halocarbon theory has been retained on the basis of observations of the

chemistry taking place in the Antarctic polar vortex. This theory began with the recognition that important chemical reactions might be taking place on cloud surfaces in Antarctica. This changed a long-standing emphasis on gas-phase stratospheric chemistry to include perturbations by *heterogenous processes*. It has long been recognized that the extreme cold temperatures of the Antarctic stratosphere lead to the formation of polar stratospheric clouds (PSC) there, in much greater frequency and thickness than found elsewhere on Earth, even in the Arctic. For many years, these clouds were considered little more than a scientific curiosity. These PSCs allow conversion of inactive chlorine into reactive chlorine. Heterogeneous reactions would be expected to take place in the coldest part of the Antarctic stratosphere, where clouds form (at 10-25 km altitude). Such processes have the important effect of altering the altitude range over which chlorine compounds are capable of ozone destruction from ozone-poor altitudes near 35 to 45 km to lower, ozone-rich altitudes, thus yielding far larger total column ozone depletion than anticipated based on standard gas-phase photochemistry alone.

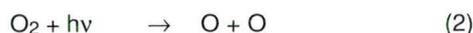
In this paper, we will first address the basics of ozone destruction and the importance of heterogenous chemical processes, taking place on aerosols (PSCs). In the second part, we will focus on the properties of polar stratospheric cloud particles and their integration into numerical chemical transport models of the stratosphere. The remaining sections will cover the discussion of results obtained by modelling studies in a two and three dimensional framework.

1. Ozone chemistry

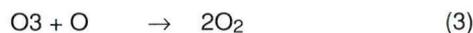
Since a complete description of stratospheric chemistry is beyond the scope of this paper, only the most important features will be discussed. Stratospheric ozone is produced as a result of the photolysis of molecular oxygen by solar radiation at wavelengths less than 242.4 nm :



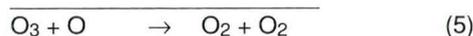
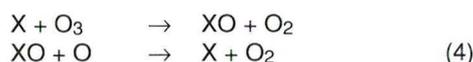
During daytime, ozone is photodissociated :



but the net destruction of "odd oxygen" ($\text{O} + \text{O}_3$) results from the reaction :



and, more importantly, from catalytic cycles of the form :

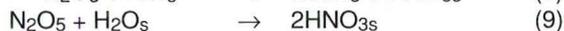
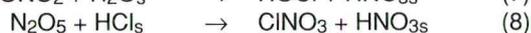


where X is a radical which can be H, OH, NO, Cl, or Br.

The atmospheric concentration of these radicals is determined by the photolysis or oxidation of so-called source gas released in the troposphere at the earth's surface as a result of biogenic, oceanic or anthropogenic processes and transported into the stratosphere by atmospheric circulation. Important source gases include H_2O , CH_4 , H_2 , N_2O and a large number of halocarbons (for example, CFC-11, CFC-12 and HCFCs).

Since gas-phase chemistry does not lead to high enough concentrations of the chlorine radicals to account for the catalytic ozone destruction, found in the Antarctic Ozone Hole, reactions on the surface of particles composing polar stratospheric clouds were invoked to provide additional sources of halogen radicals².

The reactions proposed included :

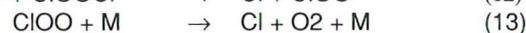
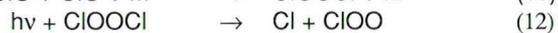


where the suffix *s* denotes a species present in the solid phase. The detailed processes taking place in or on these particles are not known. The heterogeneous reaction rates are often specified by a "sticking" coefficient, which gives the probability that a reaction occurs when a molecule collides with a particle. The reaction rate is then estimated by multiplying the sticking coefficient with the molecule-particle collision rate. The collision rate depends on the particle surface area density, i.e. the available particle surface area per unit volume, which can be calculated from the particle size distributions. According to present views, reaction 6 followed by :

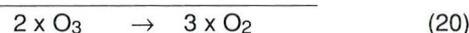
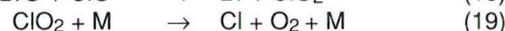
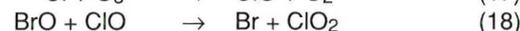
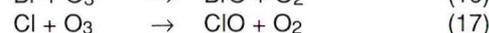
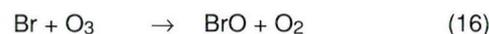


provides the dominant source of chlorine radicals in the polar stratosphere. Subsequent loss of O_3 occurs primar-

ly by a sequence involving production and photolysis of the ClO^3 (ClO dimer : ClOOCI) :



and reactions involving the coupling between chlorine and bromine, which also contribute to the ozone destruction rate through the reaction cycle⁴ :



Results obtained from different Antarctic and Arctic measuring campaigns provided evidence that changes in O_3 in spring are the result from high concentrations of ClO and BrO within the polar vortex (isolated cold region, chemically perturbed region). To account for the observed level of ClO it is essential that a large fraction of the available inorganic chlorine be converted to reactive species such as ClO, Cl and ClOOCI by heterogeneous processes on PSCs. Measurements indicate a fractional conversion of available inorganic chlorine to reactive chlorine as high as 80%. The large loss of O_3 observed in recent years over Antarctica, lowering the column concentration to as low as 110 Dobson Units⁵, requires that the concentrations of chlorine and bromine radicals remain high until at least the end of september. To maintain the required high concentrations of ClO and BrO it is essential that the abundance of HNO_3 be exceptionally low; otherwise, photolysis of HNO_3 would provide a source of NO_2 sufficient to convert a major fraction of the available radicals to unreactive forms such as ClONO_2 by the reaction :



In order to account for a low abundance of HNO_3 , and consequently NO_2 , at the beginning of the spring, it is necessary that HNO_3 be physically removed from the stratosphere.

It is thus clear, to perform consistent model studies, simulating catalytic polar ozone destruction, a detailed coupling with microphysical PSC formation is necessary in the stratospheric chemical models.



Figure 1 : Polar Stratospheric Clouds during an Arctic Winter

2. Polar Stratospheric Clouds

Because the formation of polar stratospheric clouds requires cold temperatures, PSCs are found predominantly in the polar winters. They are subclassified as type 1 or type 2, depending on their formation temperature. Type 1 PSCs (PSC-I) are composed of a mixture of nitric acid and water, they are formed when the polar stratospheric temperatures fall below about 195 K. Type 2 PSCs (PSC-II) are composed of crystalline water ice and appear only when stratospheric temperatures drop below 188 K.

Basically, four microphysical processes must be considered when modelling the evolution of an ensemble of PSC particles : nucleation, growth or shrink of the particles by condensation or evaporation of vapor, and sedimentation. The microphysical model used in these studies has been first constructed to simulate the microphysical processes in a single grid point⁶, a box model or 0-D model. During a temperature decline the model describes a sequential transformation from a background of sulfuric acid aerosols with a given particle size distribution, through the heterogeneous nucleation process to the formation of nitric acid trihydrate PSC-I particles, and further growth of these particles by vapor diffusion and condensation. Finally the PSC-I particles can be nucleated to form pure ice PSC-II particles upon further temperature decrease. The particle size distributions, particle surface area densities, and sedimentation flux of each particle type are calculated together with the exchange of vapor due to condensation/evaporation. Since "large" particles are removed from the stratosphere by gravitational settling, the sedimentation of PSC particles lead to loss of condensed HNO_3 , denitrification, and of condensed H_2O , dehydration.

In the model, for a good representation of the polar stratospheric cloud particles, each type is decomposed

into 50 bins of different sizes (this number of bins was decided from box model calculations). The particle volumes (V_i , for $i = 1, \dots, 50$) are related by $V_{i+1} = fV_i$, f being a constant ratio ($f > 1$). Taking $f = 2$ and a minimum particle radius $r_1 = 0.001 \mu\text{m}$ for the first bin, the radius of the last bin is $r_{50} = 82.6 \mu\text{m}$. This size range covers the typical radius values of sulfate aerosols and PSCs of both types. The microphysical model calculates for each time step and for each bin the changes in particle number density and volume of condensed matter per particle due to nucleation, condensation, evaporation and sedimentation. The PSCs also induce loss and production terms for the gas phase nitric acid and water vapor. Since the time constants encountered in the microphysical processes can be smaller than the time constants used in the Chemical Transport Models (either two or three dimensional) special care has been taken on the integration of the microphysical model in CTMs. In this framework, the variables that are calculated are the nitric acid and water vapor mixing ratios, the number of particles per unit air mass for each PSC type and bin, and the total volume of condensed material per unit air mass for each PSC type and bin.

This highly detailed microphysical PSC model has been coupled with :

- A zonally monthly averaged 2-D chemical transport model of the stratosphere with an elaborate chemical package, to study the influence of PSCs on the stratospheric chemistry.
- A global three dimensional chemical transport model of the atmosphere, with imposed initial water and nitric acid vapor, to study the detailed evolution of PSC characteristics on a short time scale (weeks).

3. Model Results

3.1. 2-D Model Calculations

The 2-D model (altitude versus latitude) allows climatological studies to be performed. This model is based on a zonally and monthly averaged temperature climatology of the atmosphere, in an isentropic framework. The model includes all relevant chemical reactions. The source gases have surface concentrations to reflect the conditions for a 1990 atmosphere. This model with PSCs coupled represents very well the PSC climatology as observed by SAM-II⁷. First, we show the calculated PSC evolution during the Southern Hemisphere winter, followed with the consequences on polar chemistry.

Formation of PSC-I particles starts when the saturation ratio of HNO_3 vapor is larger than 1 (condensation), for stratospheric HNO_3 values this happens at about 195 K.

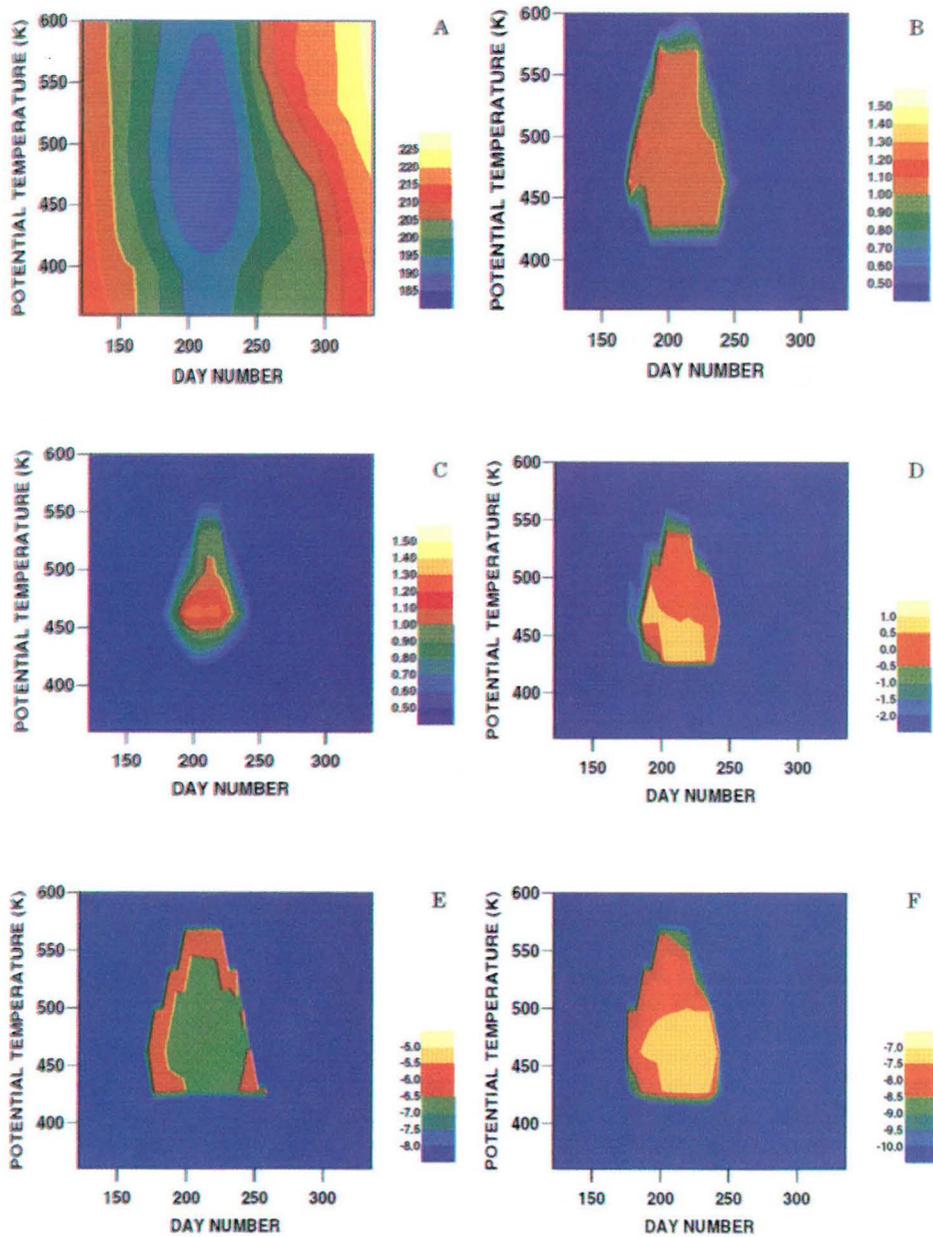


Figure 2 : Time altitude distribution for : A : Temperature (K), B : nitric acid saturation ratio, C : water saturation ratio, D : PSC-I total number density (cm^{-3}) on \log_{10} scale, E : PSC-I mean radius (m) on \log_{10} scale, F : PSC-I total surface area density ($\text{cm}^2\text{cm}^{-3}$) on \log_{10} scale

When the saturation ratio of water vapor is greater than 1, PSC-II particles start forming. For stratospheric conditions, this occurs at about 188 K. When the cooling, 1 K/day, is slow enough, equilibrium conditions are easily satisfied and a small number of larger particles are formed. When the temperature decreases rapidly, 50 K/day, a large number of small particles are formed. Figure 2

shows the evolution of the different PSC characteristics as a function of time and altitude. Although the low temperature region, favourable for PSC formation, is not extended as far as into spring as compared with observations, the PSC region in latitude, altitude, and, to a lesser extent in time agrees well with observations. The PSC characteristics, particle size distribution, number

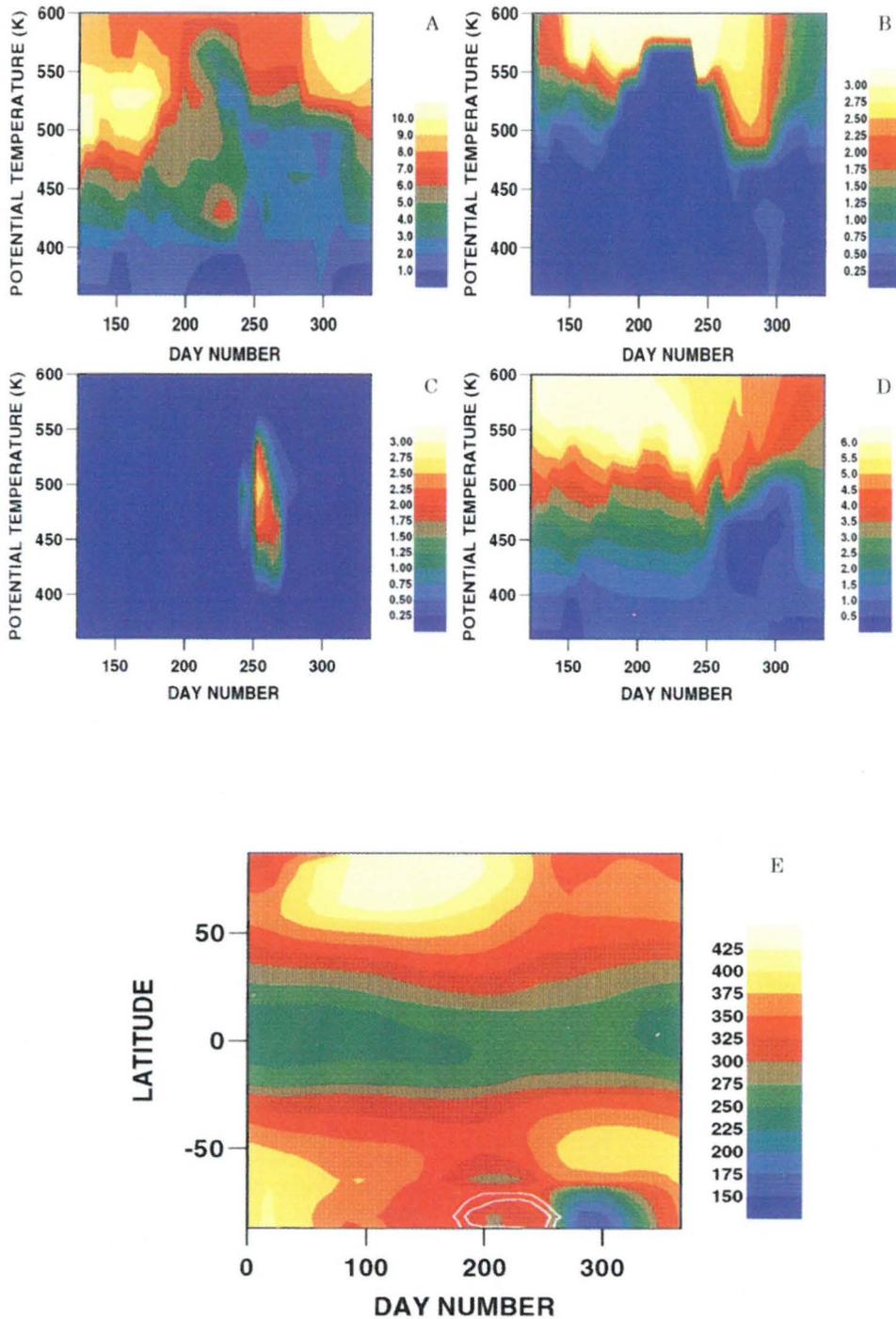


Figure 3 : Time altitude distribution for (the altitude range in km for these potential temperatures is 15-25 km) : A : total nitric acid (ppbv), B : ClONO₂ (ppbv), C : ClO + 2 x ClOOCl (ppbv), D : O₃ (ppmv). Figure F represents the time latitude distribution for total ozone in Dobson units (shaded), full lines represent the extent of the PSC-I

density, and surface area density agree also with experimental data.

With the presence of PSCs the polar heterogenous processes can take place. Schematically, the following evolution can be expected :

- removal of gas phase HNO_3 and H_2O by condensation,
- definitive removal of condensed HNO_3 and H_2O by sedimentation,
- uptake of HCl by PSCs, taking place during polar night,
- conversion of ClONO_2 and N_2O_5 into more reactive chlorine, also taking place during polar night,
- with return of sunlight, conversion of reactive chlorine into ClO and its dimer,
- catalytic ozone destruction,
- recovery of ClONO_2 ,
- slower recovery of HCl .

In our model calculations, the PSCs only persist during the Southern Hemisphere polar winter. In this darkness, the conversion of unreactive chlorine into the ClO precursors takes place. When sunlight returns, high levels of ClO are formed and ozone is destroyed catalytically after the disappearance of the PSCs.

These different features are shown in the model calculations as presented in figure 3. The total nitric acid (gas phase + condensed phase) is depleted by sedimentation, see figure 3.A, reaching values of about 2 ppbv as in agreement with observations⁸. In figures 3C to D, the conversion of HCl and ClONO_2 into finally ClO and its dimer is shown, where ClO peaks at values of about 1.2 ppbv in agreement with Antarctic measurements⁹. In figure 3.D and figure 3.E, the simulated ozone hole is presented. Very low ozone values are found from mid-September until mid-October in the lower stratosphere, from 15 to 25 km. The ozone column content has values as low as 150 Dobson units. This simulation of the ozone hole is in very good agreement with observations.

The influence of the ozone destruction during late winter and early spring in Antarctica is not limited to the polar regions. The Antarctic Ozone Hole does affect the ozone distribution over much of the Southern Hemisphere through a dilution process associated with the break-up of the polar vortex. This is confirmed by Satellite observations¹⁰. The influence of heterogenous processes on PSC particles is very important on the polar ozone chemistry. With the eruption Mt. Pinatubo, other heterogeneous processes have been studied and found to be important as well. These heterogenous processes on sulfate aerosol particles have a less efficient ozone-destruction capacity, but due to volcanic eruptions their effect can be enhanced. The low ozone values in the Northern Hemisphere 1992 and 1993 winter can be attributed to

heterogenous processes on sulfate particles as a result from the 1991 Mt. Pinatubo volcanic eruption.

Taking all these effects into account, our model studies simulate the observed global ozone decline for the last decade¹¹ very well.

Since the model is a 2-D climatological model, observed interannual differences, longitudinal effects and thus polar stratospheric cloud during Northern Hemisphere winters can not be simulated. In the Northern Hemisphere, there is evidence for a 5-8% decrease for the last decade in total ozone, with the largest depletion at the highest latitudes

during winter and spring. There is abundant direct evidence for perturbed chemistry in the Arctic similar to that of Antarctica¹², but the required cold temperatures, necessary for polar stratospheric cloud formation, are generally neither as widespread nor as longlasting as in the spring season in Antarctica. This greater meteorological variability has important consequences for the PSC formation, and 2-D model study is not adequate for simulating PSC and consequently a 2-D model study of Northern Hemisphere polar chemistry is very difficult to interpret.

4.2. 3-D Model Calculations

The 2-D model calculations simulate well the chemical climatology of the Antarctic Ozone Hole. Unfortunately, the Arctic polar winter exhibits a much greater dynamical variability, making 2-D model chemical climatology studies more difficult. The polar vortex, in the case of the Antarctic winter, is characterized by its symmetry over the South Pole, stability, and, long duration (beginning of winter until beginning of spring). During the Northern Hemisphere winter period, the polar vortex is characterized by a great variability. Also, differences exist in the behaviour of PSCs, where the Arctic PSCs are more localized in space and time. To address a detailed study of these mechanisms, the 2-D models are not satisfactory anymore and the use of highly sophisticated 3-D models is necessary. Therefore we developed a global 3-D Chemical Transport Model extending from the Earth's surface up to about 30 km. This model retrieves its dynamical fields (winds, temperature) from the Numerical Weather Prediction model of the European Centre for Medium Range Weather Forecasts¹³, used in a lower resolution for the time period of interest. Thus the real meteorological conditions for a certain time and location are satisfied. These 3-D model calculations allow a comparison with detailed experimental observations of PSCs taken during polar campaigns.

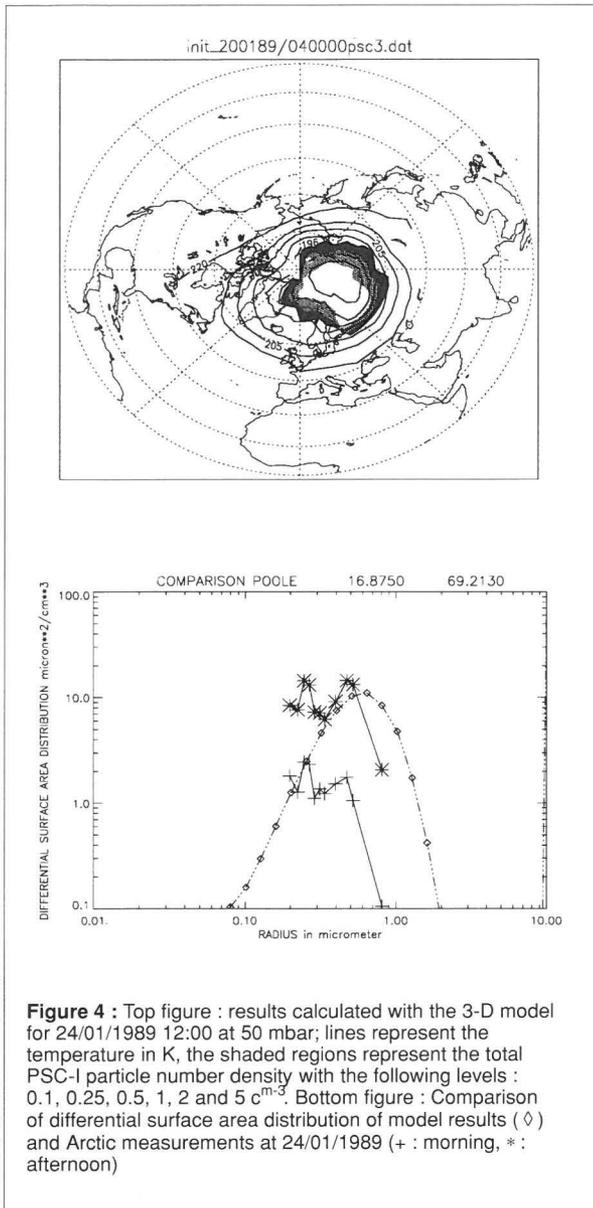


Figure 4 : Top figure : results calculated with the 3-D model for 24/01/1989 12:00 at 50 mbar; lines represent the temperature in K, the shaded regions represent the total PSC-I particle number density with the following levels : 0.1, 0.25, 0.5, 1, 2 and 5 cm^{-3} . Bottom figure : Comparison of differential surface area distribution of model results (\diamond) and Arctic measurements at 24/01/1989 (+: morning, *: afternoon)

In this stage the 3-D model is used in the validation of the PSC microphysical model and a chemical package is not yet included in the model. Of special interest is the period of January 1989 when data were collected during the Airborne Arctic Stratospheric Expedition. On 24 January 1989, data were taken of a well formed polar stratospheric cloud. In the morning the edge of the PSC extended from 82°N over Greenland down to 70°N over Scandinavia, in the afternoon the edge moved south to about 65°N over Scandinavia. The top figure 4 shows the calculated total PSC-I particle number density at 50 mbar for noon 24 January 1989. These calculations show that PSC presence is well correlated to the low temperature region which centered well of the North Pole. For this

situation, this air parcels had circumpolar trajectories exhibiting large temperature coolings when entering the low temperature region. According to theory, this should lead to a great number of small PSC particles which quickly disappear when leaving this cold region by evaporation. This calculations shows clearly the difference of PSC-events during the Arctic winter compared to the Antarctic winter where generally the PSCs cover the whole polar region.

The fine structure of size distribution of the PSC-I particles, using these model calculations, can be compared with observations. In the bottom figure 4, the calculated differential surface area distribution for different sized particles is compared with experimental data. The model results are taken at local noon. It is clear that the overall calculated distribution is in very good agreement with observations. Nevertheless, the fine structure does not agree, the observed bimodal distribution is not simulated. This discrepancy between model and observations is consistent with unexplained features observed during the Arctic winter. With the current understanding of PSCs, the denitrification in the Arctic winter is poorly understood.

Also, the results from these calculations allow to quantify the heterogeneous processing on PSCs and estimate their influence on ozone behaviour.

Conclusion

In this paper some results on modelling of polar stratospheric clouds were presented. In short, these models summarize the current understanding of the chemical behaviour of the chemical composition of the stratosphere. Since the appearance of the Antarctic Ozone Hole, it has become clear that heterogenous processes play an important role in the stratospheric chemistry. Due to the public awareness, great efforts were undertaken in the search for the understanding of this phenomenon and this has lead to numerous experimental campaigns. This understanding has lead to the development of our 2-D and 3-D models.

The inclusion of an elaborate microphysical model for PSC formation in the 2-D model, allows a good representation of the Antarctic climatology in the sense of polar stratospheric clouds, heterogenous processes and ozone destruction. Although the model is aimed to represent a stratospheric *chemical* climatology, the total ozone decline over the last decade can be simulated by this coupled PSC-chemistry transport model.

The 3-D PSC formation model allows us to focus on a specific winter and study in great detail the the evolution of the characteristics of PSCs. In the future, this model

will be complemented with an elaborate chemistry package to study specific detailed ozone behaviour.

Both models can add great value to the analysis of on-going measuring campaigns in which B.I.S.A. is involved.

Acknowledgements

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We are grateful to the European Centre for Medium Range Weather Forecasts, the director and its staff for granting us the possibility of using their NWP and computer resources. Especially, we would like to thank A. Simmons and D.Dent for their personal and valuable assistance.

Notes

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