

# Effects of heterogeneous chemistry on the composition of the stratosphere.

---

CEC Environment Programme Contract EV5V-CT93-0349

Contribution to the final report from the  
Danish Meteorological Institute

This CEC-project has been accomplished in collaboration with  
Universita degli Studi - L'Aquila (coordinator)  
University of Oslo  
Service d'Aerosomie du CNRS  
Norwegian Institute for Air Research  
Belgian Institute for Space Aeronomy

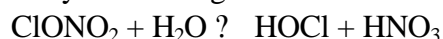
Period: 1 January 1994 - 31 December 1995

---

## Introduction.

Strong evidences point to the role of heterogeneous chemical reactions, taking place on stratospheric aerosol particles of volcanic origin, depleting  $\text{NO}_x$  and activating chlorine species into a potentially ozone destructing forms. Similar processes take place inside the circumpolar vortex during winter on polar stratospheric clouds (PSC), resulting in severe ozone depletions in polar regions. Recent field observations, laboratory experiments, and theoretical studies have revealed a large uncertainty in our knowledge of the composition, physical phase, and formation processes of the stratospheric particles.

Hydrolysis of chlorine nitrate by the heterogeneous reaction



on sulfate aerosols could be an important path way for activation of stratospheric reservoir chlorine into HOCl. This species would photolyse in the presence of sun light to release chlorine atoms and OH radicals which destroy ozone catalytically.

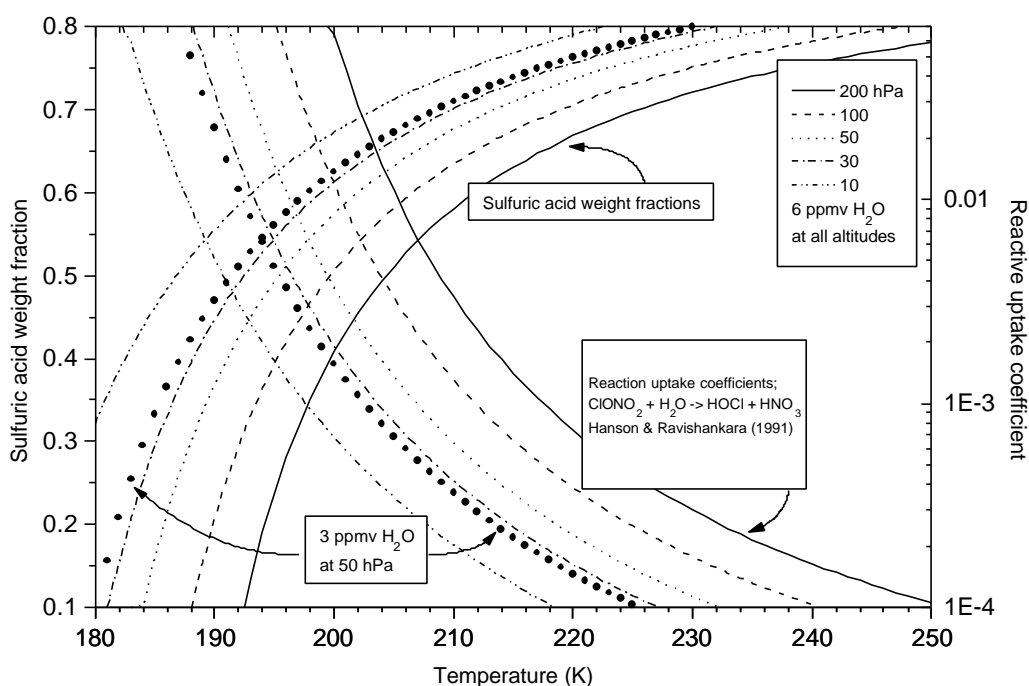
Although the heterogeneous reaction  $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$  on sulfate aerosols dominates at lower stratospheric temperatures the hydrolysis of  $\text{ClONO}_2$  could be efficient for chlorine activation when most of the HCl is activated, and also at higher stratospheric temperatures above 200 -210 K where the solubility of HCl in sulfate aerosols decreases. In the polar winter stratosphere the hydrolysis reaction is most efficient on the surfaces of type 2 polar stratospheric clouds (PSC), composed of water ice, whereas the efficiency on the surfaces of solid type 1a PSCs, composed of nitric acid trihydrate (NAT), and frozen sulphuric acid tetrahydrate (SAT) aerosol particles is low, compared to the liquid aerosols<sup>1</sup>

The first-order loss-rate coefficient for gas-phase  $\text{ClONO}_2$  in the hydrolysis reaction on liquid sulfate aerosols is given by  $k = (\gamma v A) / 4$ , where  $\gamma$  is the reactive uptake

---

<sup>1</sup>Ravishankara and Hanson, J. Geophys. Res. 101, 3885, 1996

coefficient ("sticking coefficient"),  $v$  is the average molecular velocity, and  $A$  is the aerosol surface area per unit volume of air, available for the heterogeneous reactions. The reactive uptake coefficient depends strongly on the aerosol composition<sup>2</sup> as given by the expression  $\log_{10}(\gamma) = 1.86 - 7.47 W$ , where  $W$  is the  $\text{H}_2\text{SO}_4$  weight fraction of the liquid aerosol particles. The sulfate aerosols are assumed to be in equilibrium with the ambient water vapor. The  $\text{H}_2\text{O}$  vapor pressure over sulfuric acid solution decreases with decreasing temperature and water content. Therefore the aerosols, in order to maintain the equilibrium, will take up water and become more dilute at low temperatures or at low altitudes where the partial pressure of water vapor is high<sup>3</sup>. Under these conditions the acid weight fraction decreases and hydrolysis becomes more efficient. This is illustrated in Figure 1 showing the  $\text{H}_2\text{SO}_4$  weight fractions and  $\gamma$ -values at different pressure altitudes as functions of temperature, assuming 6 part per million by volume (ppmv) of water vapor at all altitudes. For comparison is also shown (dotted) the same quantities at 50 hPa, assuming 3 ppmv  $\text{H}_2\text{O}$ . Notice the strong increase in the reactive uptake coefficient with decreasing temperatures at constant pressure altitudes, and also the strong increase with decreasing pressure altitudes at a constant temperature. However, changing the water vapor mixing ratio by a factor of 2, as illustrated for the 50 hPa pressure altitude, has a smaller effect on the efficiency of the reactive uptake coefficient.



**Figure 1.** Sulphuric acid weight fractions and reactive uptake coefficients at different pressure altitudes (cf. legend), calculated as functions of temperature, assuming 6 ppmv  $\text{H}_2\text{O}$  at all altitudes. For comparison the calculations are also shown for 3 ppmv  $\text{H}_2\text{O}$  at 50 hPa (dots).

In addition to the increase of  $\gamma$ -values at low temperatures the surface area density  $A$  of the aerosol particles will also increase due to the water uptake, enhancing the

<sup>2</sup>D. Hanson & A.R Ravishankara, *J. Geophys. Res.* 96, 17307-17314, 1991.

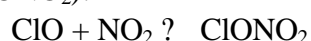
<sup>3</sup>H.M. Steele & P. Hamill, *J. Aerosol Sci.* 12, 517-528, 1981.

heterogeneous reaction rate. Furthermore, at very low polar winter temperatures the aerosol particles are expected also to take up significant amounts of nitric acid (HNO<sub>3</sub>) and grow appreciably into type 1b PSC liquid ternary solution (HNO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O) particles. The uptake of HNO<sub>3</sub> by this process is not expected to affect the hydrolysis rate significantly.

The most important heterogeneous chemical reaction at midlatitudes on sulfate aerosol surfaces is the hydrolysis of N<sub>2</sub>O<sub>5</sub>:



which deplete the gas phase of reactive nitrogen NO<sub>x</sub> (denoxification). Thereby the levels of reactive chlorine would increase due to less efficiency of the reaction to convert ClO back into the reservoir form (ClONO<sub>2</sub>):



Current atmospheric chemistry models seem to overestimate the denoxification through the heterogeneous N<sub>2</sub>O<sub>5</sub> -hydrolysis reaction, involving the sulfate aerosol particles and using the temperature independent reactive uptake coefficient<sup>2</sup> of  $\gamma = 0.1$ .

Growing evidences have emerged during the past few years that previous concepts for our understanding of the processes for the formation of polar stratospheric clouds have been too simplified. Prior to the onset of the project it was generally believed that PSCs formed according to a 3-stage concept, namely that liquid stratospheric sulfate aerosols would freeze above the ice frost point, thereby serving as nucleation centres for type 1 PSCs. These particles would grow by co-condensation of nitric acid and water vapor into nitric acid trihydrate (NAT) at decreasing temperatures and finally serve as nucleation centres for water ice type 2 PSC below the frost point. This concept was generally in good agreement with various measurements from Antarctica performed in the late part of the previous decade and built into many microphysical models, including the first version of the DMI model, developed during the predecessor of this project "Modelling of changes in stratospheric ozone and other trace gases due to the emission changes" (contracts EV4V-0203 and EV5V-CT)2-0079)<sup>4</sup>.

Results from the first American and European Arctic campaigns (AASE, EASOE) showed that this picture of formation was too simplified. Two types (1a and 1b) of PSC 1 particles were identified<sup>5</sup>, showing different optical properties and probably reflecting differences in particle shape and size distribution. Measurements indicated that the stratospheric aerosol particles could stay in the liquid phase without freezing at temperatures close to the ice frost point<sup>6</sup>, and high partial pressures of HNO<sub>3</sub> indicated that some of the PSC particles could not be composed of NAT<sup>7</sup>. Occasionally denitrification was observed without accompanying dehydration<sup>8</sup>, as seen over Antarctica, and it became difficult to explain the formation of large solid type 1 PSC particles, responsible for the nitric acid removal of by particle sedimentation. Laboratory experiments and new thermodynamical models, developed by European and US research groups, indicated that the spherical type 1b PSC particles are probably composed of liquid ternary solution particles (HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O) of relative high HNO<sub>3</sub> vapor

---

<sup>4</sup>Larsen, DMI Sc. report 91-2; Larsen, Geophys. Res. Lett. 21, 425, 1994.

<sup>5</sup>Browell et al., Geophys. Res. Lett. 17, 385, 1990; Toon et al., Geophys. Res. Lett. 17, 393, 1990.

<sup>6</sup>Dye et al., J. Geophys Res. 97, 8015, 1992

<sup>7</sup>Rosen et al. Geophys. Res. Lett. 16, 791, 1989; Schlager et al., Geophys. Res. Lett. 17, 1275, 1990

<sup>8</sup>Fahey et al., Nature 344, 321, 1990; Arnold et al., Geophys. Res. Lett. 19, 677, 1992

pressure, compared to NAT<sup>9</sup>. At low temperatures these particles take up significant amounts of nitric acid and water and grow to considerable particle sizes.

### **Objectives and the role of DMI in the project.**

The PSC formation depend strongly on the temperature history of the air parcels where the particles form. By using a 3-D forecast model a realistic development of the temperature fields can be used as input to the microphysical calculations. Simulations of PSC formation has been intended to be performed for situations where observations of PSC characteristics exist, e.g. measurements of particle size distributions and optical depth. Effects of denitrification and dehydration due to particle sedimentation could be studied by comparison of model calculated and observed concentrations of nitric acid and water vapor. Investigations could be performed for situations before and after the eruption of volcano Mt. Pinatubo in both hemispheres in order to clarify possible changes in the PSC characteristics due to the enhanced sulfate aerosol loading.

This aim was intended to be accomplished by the in close corporation with Institut d'Aeronomi Spatiale de Belgique, in a series of case studies of the formation of Polar Stratospheric Clouds. It was intended to use the microphysical simulation model for PSC formation from the DMI, coupled to a 3-D atmospheric forecast model from the European Centre for Medium-range Weather Forecast (ECMWF). The investigations would aim at a better description of details of the microphysical processes. An investigation of the influence of a partial freezing among the background sulfate aerosol on the PSC formation would be attempted.

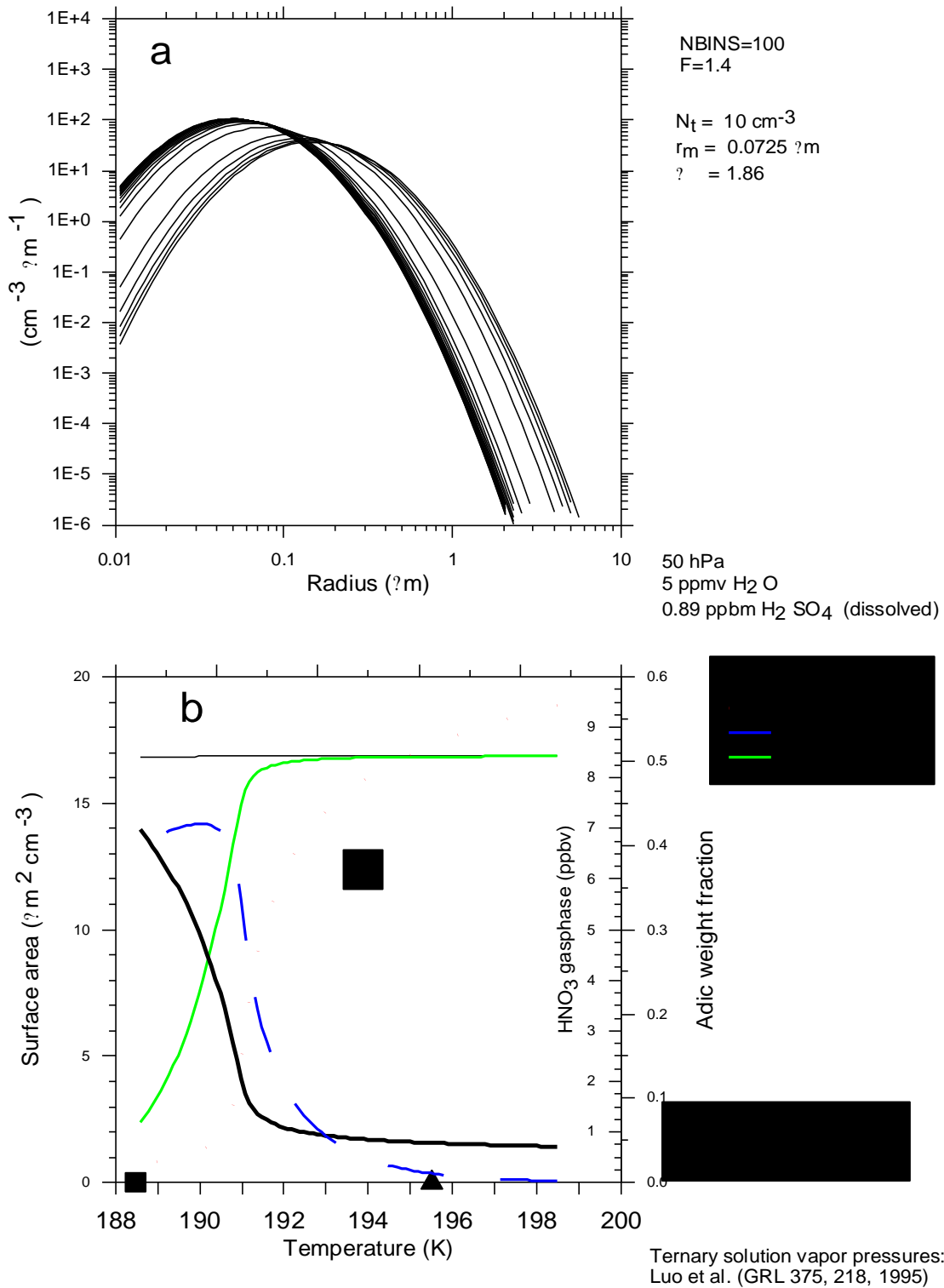
The main tasks of the DMI within the project have thus been **1)** to improve and implement a microphysical code of stratospheric aerosols and polar stratospheric clouds in existing atmospheric chemistry models in collaboration with the other project partners, and **2)** to analyse data from recent field campaigns.

### **Microphysical modelling and coupling to existing models.**

The DMI microphysical model has been improved to describe the equilibrium growth and composition of type 1b particles as shown in Figure 2 below. The model has also been improved include the sedimentation of the liquid particles.

---

<sup>9</sup>Zhang et al., J. Phys. Chem. 97, 8541,1993; Tabazadeh et al., Geophys Res. Lett. 21, 1619, 1994; Carslaw et al., Geophys Res. Lett. 21, 2479, 1994.



**Figure 2.** Changes in differential size distribution (a) and composition (b) of an ensemble of stratospheric aerosol particles upon equilibrium cooling of the particles from 200 K to the ice frost point at 50 hPa pressure altitude, calculated by the DMI microphysical model. The lower panel b shows the increasing uptake of  $\text{HNO}_3$  in the particles and depletion in the gas phase together with the sharp increase in the particle surface area at temperatures between the NAT condensation and the ice frost point. At higher temperatures the particles would be classified as stratospheric sulfate aerosols which, at decreasing temperatures, continuously turn into type 1b PSCs, composed of liquid ( $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ) ternary solutions with increasing  $\text{HNO}_3$  and decreasing  $\text{H}_2\text{SO}_4$  weight fractions.

The winter stratosphere temperatures in the Arctic are higher and more variable than over Antarctica, mainly due to stronger planetary wave activity. Therefore the PSC formation in the northern hemisphere is often sporadic, occurring in connection with tropospheric high pressure systems of synoptic scale or in connection with lee waves where the air in both cases is adiabatically cooled, leading to short-lived PSC formation. Hence, PSCs in the Arctic are often observed in their initial formation phase, and a detailed knowledge of the formation process is needed to explain the observations. Over Antarctica zonal mean temperatures are low enough for the formation of PSCs over large areas in a continuous period from June through September. Therefore "old" PSC particles are often observed, and the initial detailed processes of the PSC formation appear to be of less importance. This also means that the conventional 3-state formation concept is adequate to describe the southern hemisphere PSC observations, since the sulfate aerosols, once frozen, will stay in the solid phase for long periods throughout the winter, in contrast to the conditions in the Arctic where repeated freezing/melting cycles of the aerosol make the interpretations much more difficult.

The DMI microphysical model, using the 3-stage concept, has been built into the 2D atmospheric chemistry model at NCAR-CNRS (De Rudder *et al.*, 1996, Tie *et al.*, 1996). Calculations by the model give a good representation of PSC occurrences in both hemispheres, illustrating the effects of heterogeneous chemistry on PSCs as the likely causes of the observed increasing ozone depletions in the 1980s. The model represents the enhanced PSC occurrence due to increased concentrations of stratospheric sulfate aerosols after Mt. Pinatubo, and point to the fact that larger areal coverage by PSCs could be more important for future ozone depletions than increases in surface area densities of PSC particles. Effects of increased concentrations of water vapor and nitrogen species due to high altitude aircraft are discussed from the model calculations.

The DMI microphysical model has also been coupled to the 2D atmospheric chemistry model at BISA (Fonteyn and Larsen, 1996). The model gives a good representation of PSC formation over Antarctica using monthly zonal averaged temperatures without imposing any special temperature evolution. Calculations by the model illustrate the importance of including a detailed treatment of PSC sedimentation in order to represent more accurately the observed  $\text{NO}_y/\text{N}_2\text{O}$  relationship, and illustrates the important influence of particle sedimentation and thereby denitrification on the chlorine-catalytic ozone destruction.

The DMI model has been coupled to the Oslo 2D-model, and also to the photochemical trajectory model at NILU (Fløisand *et al.*, 1996) which is based on the chemistry package of the Oslo 2D-model. Finally, the microphysical model has been coupled to the 3D-advection model at BISA which is based on analysed temperature- and wind fields from the ECMWF.

### **Analysis of data from field measurements.**

As mentioned above it has been difficult to explain the formation of large solid type 1 PSC particles which could be responsible for the occasionally observed denitrification in the Arctic areas by particle sedimentation without dehydration (i.e. without forming type 2 PSC ice particles). According to classical nucleation theory (and the old 3-stage

concept for PSC formation) large NAT particles would form in air parcels when the cooling rate is low ( $< 1$  K/day)<sup>10</sup>. However this condition may indeed not be very common in the Arctic due to prevailing wave activity. The important finding that type 1b PSC may be composed of liquid ternary solution particles, growing at temperatures below the NAT condensation temperature, meant that the available nitric acid vapor would be taken up in all particles whereby the individual particles would not grow to sizes large enough for an appreciable sedimentation. Therefore, it seems necessary that the available nitric acid has to condense on a small fraction (i.e. a few) of the available particles in order to explain denitrification, and a new theory for the formation of solid type 1 PSC is needed. Furthermore, an intensive scientific debate currently concerns the freezing of the ternary solution particles, where some laboratory experiments indicate that the freezing can take place above the ice frost point<sup>11</sup>, while other experiments only see freezing below<sup>12</sup>.

Based on field measurements of the large abundance of sulfate aerosols from the Mt. Pinatubo and the DMI microphysical aerosol model, using temperature histories from air parcel trajectories from the ECMWF meteorological fields, inferences were made about the freezing behaviour of the stratospheric aerosol (Larsen *et al.*, 1995). This analysis showed the expected behaviour of growth by water vapor uptake at decreasing temperatures. Furthermore, the analysis indicated a hysteresis in the freezing-melting cycle where the particles melt at temperatures around 215 K (in good agreement with laboratory measurement<sup>13</sup>) and freeze at temperature less than 5 K above the ice frost point.

These findings were consistent with analysis of particle measurements performed by the ER-2 during the AASE campaign<sup>14</sup> which indicated that sulfate aerosols might freeze upon an increase in temperature after previously being cooled to temperatures close to the ice frost point. This freezing concept was further investigated by the DMI group, using balloonborne backscatter measurements of PSC formation from previous European and US campaigns (Larsen *et al.*, 1996). This analysis indicated that particles, classified as liquid according to the freezing scenario of Tabazadeh *et al.*<sup>11</sup>, show the expected behaviour of particle growth at 3-4 K below the NAT condensation temperature (cf. the DMI model calculations in Figure 2). The behaviour of the solid particles is more complicated, showing that newly formed solid particles are generally of small sizes, whereas particles which have existed in the solid state for more than 30 hours appear to possess larger particle sizes. Furthermore, the aged solid particles retain their large sizes during evaporation up to the NAT condensation temperatures during evaporation, indicating the composition to be NAT. These observations may indicate that solid particles form in a metastable solid phase (dilute solid HNO<sub>3</sub> solutions or nitric acid dihydrate, NAD) and turn into stable NAT crystals after a while. This finding is consistent with laboratory experiments of the freezing process<sup>15</sup> which also show that solid particles initially may form in a metastable phase. This process may provide a mechanism for the formation of a few large solid particles since the first particles,

---

<sup>10</sup>Larsen, DMI Sc. report 91-2.

<sup>11</sup>Molina *et al.*, *Science* 251,1418, 1993; Iraci *et al.*, *Geophys. Res. Lett.* 21,867 1994; Fox *et al.*, *Science* 267, 351, 1995.

<sup>12</sup>Koop *et al.*, *Geophys. Res. Lett.* 22, 917, 1995.

<sup>13</sup>Middlebrook *et al.*, *J. Geophys. Res.* 98, 20473, 1993.

<sup>14</sup>Tabazadeh *et al.*, *Geophys. Res. Lett.* 22, 1725, 1995.

<sup>15</sup>Marti and Mauersberger, *Geophys. Res. Lett.* 20, 359, 1993; Fox *et al.*, *Science* 267, 351, 1995.

transformed into the stable NAT of relatively low vapor pressure compared to the metastable phase, may take up all available HNO<sub>3</sub> by gasphase condensation. Thereby any remaining metastable phase particles will start evaporating, and a transfer of HNO<sub>3</sub> will take place to the few first formed stable NAT particles. Hence, the available HNO<sub>3</sub> will thereby condense on a small number of particles which will grow large and possess an appreciable fall velocity. Alternatively, large particles may form if type 2 PSC ice particles fall in from above to a region with supersaturated conditions with respect to NAT<sup>16</sup>. Thereby the particles may obtain a NAT coating preventing the ice from evaporating, and the particles could grow to large sizes.

Although many details are unknown in the above suggested freezing scenario for the formation of large NAT particles by metastable phases it has been attempted to describe the freezing in the DMI microphysical model. This model version has been coupled to the 3D-advection scheme at BISA, which is based on analysed winds and temperature fields from the ECMWF, aiming at an analysis of the measurements of PSC particle volumes, obtained during the AASE campaign by the ER-2 aircraft<sup>6</sup>. Preliminary results indicate that not all the measured particles can be assumed to be liquid particles in equilibrium with the ambient HNO<sub>3</sub> vapor<sup>17</sup>, but rather that the observed particles in individual flights could be a mixture of liquid and solid particles, pointing to the fact that the particles have experienced different temperature histories where also sedimentation plays an important role in the interpretation of the measurements. It appears that only by analysing the measurements using 3-dimensional transport (including sedimentation) can the measurements from all the flights be understood. A paper on this analysis is being prepared.

Finally, the DMI microphysical model has been coupled to the photochemical trajectory model at NILU which also uses the chemical package of the Oslo 2D model. This model configuration has been used to analyse the ozone depletions, observed by ozone sondes during the SESAME campaign (Fløisand *et al.*, 1996). The calculated ozone depletions, due to heterogeneous chlorine activation on PSC surfaces, are generally in agreement with the timing of the observed ozone destruction. The model shows the expected large ozone depletions when PSCs appear in late winter and sunlight is present in the Arctic regions, indicating depletion rates larger than 1.5 %/day in March 1994. The analysis illustrates the differences in the ozone depletions inside and outside the polar vortex and vertical differences in the ozone depletions in the two SESAME winters due to different vertical temperature structures.

### **Participation in the intercomparison of the model results.**

The DMI has contributed to the intercomparison of the 2D model results, mainly on interpretation of the heterogeneous ClONO<sub>2</sub> + H<sub>2</sub>O → HOCl + HNO<sub>3</sub> activation on sulfate aerosols and the dependence of this reaction on temperature and humidity as described in the introduction.

### **Conclusions.**

---

<sup>16</sup>Wofsy *et al.*, *Geophys. Res. Lett.* 13, 1284, 1990.

<sup>17</sup>Carlaw *et al.*, *Geophys. Res. Lett.* 21, 2479, 1994.

Work within this project has revealed the importance of a detailed modelling of the formation and evolution of the stratospheric particles. Parameterisations of PSC occurrence could in some cases be adequate for calculation of heterogeneous processing since saturation effects of heterogeneous activation of chlorine species will show up even at relatively low particle surface areas. However, for a detailed treatment of denitrification and dehydration a more detailed modelling of particle behaviour is needed as it has been demonstrated in this project. Obviously there are still many questions regarding the detailed PSC formation which could be important for the description of freezing and formation of large particles, in particular in the Arctic where temperature conditions for the particle formation are highly variable. A more detailed treatment of PSC formation could also be important for the heterogeneous chemical processing. Liquid particles may turn out to be the dominant type of PSC in the Arctic compared to NAT particles. Although the liquid particles start growing at lower temperatures than NAT the reactive uptake coefficients for most of the heterogeneous reactions are much larger for the liquid particles compared to solid particles<sup>1</sup>, further emphasising a more accurate treatment of particle behaviour in atmospheric chemistry models, describing the heterogeneous processes in the stratosphere.

## Publications:

- A. De Rudder, N. Larsen, X. X. Tie, G. P. Brasseur and C. Granier, Model study of polar stratospheric clouds and their effects on stratospheric ozone: Part I -Model description, *Journal of Geophysical Research*, 101, 12567-12574, 1996.
- I. Fløisand, F. Stordal, N. Larsen, S.J. Reid, G.O. Braathen, H. Gernandt, V. Dorokhov, B. M. Knudsen, B. Rognerud, and I.S.A. Isaksen, Trajectory model calculations compared with ozonesonde data from 1994 and 1995, *Journal of Atmospheric Chemistry*, submitted 1996.
- D. Fonteyn and N. Larsen, Detailed PSC Formation in a Two Dimensional Chemical Transport Model of the Stratosphere, *Ann. Geophysicae*, 14, 315-328, 1996.
- N. Larsen, J.M. Rosen, N.T. Kjome and B. Knudsen, Deliquescence and freezing of stratospheric aerosol observed by balloonborne backscattersondes, *Geophysical Research Letters*, 22, 1233-1236, 1995.
- N. Larsen, B. Knudsen, J.M. Rosen, N.T. Kjome, and E. Kyrö, Balloonborne backscatter observations of type 1 PSC formation: Inference about physical state from trajectory analysis, *Geophysical Research Letters* 23, 1091-1994, 1996.
- N. Larsen, B. Knudsen, J.M. Rosen, and N.T. Kjome, PSC formation in the Arctic observed by balloonborne backscattersondes, in J.A Pyle and N.R.P. Harris, and G.T. Amanatidis (ed), *Polar stratospheric ozone, Proceedings of the third European workshop, Schliersee, 18-22 September 1995, Air Pollution Research Report no. 56, European Commission, p. 105-108, 1996* .
- E.R. Lutman, J.A. Pyle, M.P. Chipperfield, D.J. Lary, I. Kilbane-Dawe, J.W. Waters, and N.Larsen, Three Dimensional Studies of the 1991/92 Northern Hemisphere Winter Using Domain-Filling Trajectories with Chemistry, *J. Geophys. Res.*, submitted 1995.
- X. X. Tie, G. P. Brasseur, C. Granier, A. De Rudder, N. Larsen, Model study of polar stratospheric clouds and their effects on stratospheric ozone: Part II -Model results, *Journal of Geophysical Research*, 101, 12575-12584, 1996

## Presentations:

- N. Larsen, B. Knudsen, J. Rosen og N.T. Kjome, Deliquescence and freezing of stratospheric sulfate aerosol observed by balloonborne backscattersondes, *International Conference on Ozone in the Lower Stratosphere, Halkidiki, May 1995, (poster)*.
- N. Larsen, B. Knudsen, J.M. Rosen, and N.T. Kjome, PSC formation in the Arctic observed by balloonborne backscattersondes, *Third European Symposium on Polar Stratospheric Ozone Research, Schliersee, September 1995, (poster)*.
- N. Larsen, B.M. Knudsen, T.S. Jørgensen, J.M Rosen, N.T Kjome og E. Kyrö, Balloonborne Backscatter Observations of PSC formation: Inference about physical state from trajectory analysis, *AGU fall meeting, San Francisco, December 1995*.