A-3.7 Stratospheric denitrification and composition of polar stratospheric clouds inferred from 3D simulations and ILAS data

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Abstract Polar stratospheric clouds (PSCs) form in winter of both hemispheres at an altitude varying between 12 and 30 km. The key role played by these clouds in the Antarctic « ozone hole » phenomenon and in the substantial ozone loss often observed during the Arctic winter is now well recognized. However, the mechanism of formation of PSCs, as well as the physical nature of their particles, is still relatively poorly known. This uncertainty has important implications on our ability to predict their occurrence and their future impact on the ozone layer. This study uses a state-of-the-art three-dimensional model of the stratospheric chemistry to analyse the observations of the ILAS satellite-borne sensor developed by the Environmental Agency of Japan. In particular, vertical profiles of nitric acid (HNO_3) are compared to coincident model calculations in order to derive information on the composition of PSCs and their impact on the vertical distribution of nitrogen species.

Key Words stratosphere, ozone, nitric acid, polar stratospheric cloud (PSC), denitrification

1. Introduction

Polar stratospheric clouds (PSCs) have been recognized to play a key role in the ozone depletion processes which occur in both polar regions in winter and spring. Heterogeneous reactions occurring at their surface convert the main chlorine reservoirs HCl and $ClONO_2$ into active chlorine Cl and ClO which rapidly destroys ozone through catalytic cycles also involving Cl_2O_2 or BrO. PSCs form between 15 and 25 km at low stratospheric temperatures (typically, below 195K). It is therefore expected that the amplitude of the polar ozone loss is closely linked to the particular meteorology of each winter. Reduction of odd nitrogen (NOx = NO + NO_2) concentrations in the gas phase is also an important factor in determining the severity of ozone destruction. The NOx reduction may be either temporary via the conversion of NOx into nitric acid (HNO_3) onto PSC surfaces, or permanent via the irreversible removal of HNO_3 by sedimenting particles. In the Arctic, where temperatures are close to the threshold for sedimentation to occur, denitrification is believed to be potentially important and may play a more and more significant role in the future following the cooling trend identified in these regions. It is therefore important that current models includes a realistic description of denitrification processes, to be able to provide credible predictions of the future evolution of the ozone layer. In this study, we will investigate issues of polar stratospheric cloud composition and denitrification using a global three-dimensional chemistry-transport model. The model includes a simplified but flexible treatment of PSC particles, which allows us to define different scenario of cloud formation, and to test various hypothesis.

In order to validate our approach, we will compare the model results to the observations of the Improved Limb Atmospheric Sounder (ILAS), developed by the Environmental Agency of Japan[1]. This instrument was successfully flown in space on board the polar-orbiting ADEOS platform in August 1996. ADEOS, with ILAS and other sensors on board, performed successfully until June 30, 1997. Among other species (and in particular ozone), ILAS has provided during its 11-month lifetime about 14 daily observations of the HNO_3

vertical profile at high latitudes. The ILAS data were the only source of continuous, high resolution, HNO_3 measurements during this period and offered therefore an invaluable opportunity to test our knowledge of denitrification processes. The algorithm used in this study is version 5.12.

2. Research Objective

The aim of the study is to investigate what can be learned from the ILAS observations about PSC formation and denitrification processes in the stratosphere. For this purpose our strategy will focus on the most relevant species measured by ILAS, i.e. HNO_3 and H_2O, and on the period when denitrification could have the strongest impact on the HNO_3 vertical distribution during the 1996-1997 Arctic winter. This period is well identified and roughly extends from mid-February to mid-March 1997.

Reprobus is a three-dimensional chemistry-transport model that we have been developing since 1992[2),3)]. It describes the chemistry of the stratosphere and the upper troposphere by means of a comprehensive chemical package including 55 chemical species or families. The chemical module computes more than 150 gas phase and photolytic reactions[4)]. Photolysis rates are calculated for each time step and each sunlit grid point using a four-dimensional lookup table expressed as a function of altitude, solar zenith angle, ozone column, and albedo.

Among the 55 species calculated by Reprobus, 40 of them are explicitly transported by a semi-Lagrangian transport code which can be coupled to any three-dimensional wind dataset. The transported tracers include typically long-lived species in the lower stratosphere (such as N_2O or HCl for instance) but also more unstable constituants which have a rather long lifetime in darkness (e.g., OClO, or Cl_2O_2).

The heterogeneous chemistry scheme can handle most of the polar stratospheric cloud particles believed to form : it is therefore possible to define different scenarios of PSC formation, involving either solid particles, like ice or nitric acid trihydrate (NAT) cristals, or liquid particles for which an analytical expression[5)] is used to calculate the equilibrium composition and volume of the H_2SO_4-H_2O binary and HNO_3-H_2SO_4-H_2O ternary droplets, as a function of temperature and the total amounts of H_2O, HNO_3, and H_2SO_4. The routine also computes the aqueous phase concentrations of the soluble species HCl, HBr, HOCl, and HOBr, to calculate the rates of the most important heterogeneous reactions on stratospheric liquid aerosols.

Sedimentation rates are calculated as a function of the size of each type of particles. In general, liquid particles do not grow large enough to reach significant fall off velocities and their sedimentation is therefore neglected. This is not the case for solid particles, which can reach vertical speeds of several kilometers per day when ice cristals are larger than 10 microns. The sedimentation of NAT particles also affects the vertical distribution of HNO_3 in the model, while the sedimentation of ice cristals affects both the HNO_3 and H_2O distribution. The amplitude of denitrification (and dehydration) in the model is therefore strongly dependent on the amount and size of solid particles. Assuming different scenarios for the condensation and evaporation of these particles will have a strong impact on the denitrification of the stratosphere predicted by the model.

For all our experiments Reprobus is coupled to the temperature and wind fields analysed every 6 hours by ECMWF. The version used in this study has 31 levels from the ground up to 10 hPa, and a horizontal resolution of 2 degrees latitude by 2 degrees longitude. An improvement compared to our 1999 study is also the use of the ECMWF water vapor analysis up to a pressure of 110 hPa, in order to have more realistic H_2O fields in the upper stratosphere and tropical tropopause region, where the absence of detailed physical processes in the model (e.g., deep convection, precipitation) may cause problems.

3. Research Method

The method followed in this work is to perform three-dimensional simulations of the

1996-1997 Arctic winter for different scenarios of polar stratospheric cloud formation, and to look at their impact in terms of HNO_3 gas-phase removal and denitrification. Coincident nitric acid measurements performed from ILAS are then compared to the model results to identify the most likely scenario.

Coding and installation of the 3D model

The first step of our work was to complete the setup of the model and to install the code on the NIES NEC/SX-4 supercomputer on which the integrations will take place. The coding of the version of REPROBUS that will be used for the project is now finished and is fully operational on the SX-4. This version includes specific subroutines that will extract during the simulations the model profiles in best spatial and temporal coincidence with the ILAS measurements. The CPU time required by this latest version of the model is about 750 seconds per day of integration.

In order to have more realistic water vapor fields in the troposphere, we have also transferred from the European Centre for Medium range Weather Forecasts (ECMWF) to NIES a new set of 6-hourly global analysis, covering the December 1996-March 1997 period, which now includes the specific humidity together with the wind, temperature, and surface pressure.

Chemical Initialisation

A large part of our EFF work has then been devoted to the improvement of the chemical initialisation of the 3D integrations. In our study the initial values of the nitric acid field are particularly important as the comparison of measured and calculated HNO_3 will be used as a diagnostic of PSC occurrence and denitrification. Two options for the initialisation of the 3D model are currently under study :

The model chemical initialisation is to use the measurements performed from the Microwave Limb Sounder (MLS) on board the UARS satellite. This instrument has the advantage of providing an hemispheric coverage of the earth, allowing a much simpler procedure for the 3D model initialisation. However, due to wear in the antenna scanning mechanism and power sharing with other UARS instruments, very few days of full 3D coverage were available in the early winter 1996-1997. In December 1996 the best coverage was obtained on day 18. We will use the recently released version 5 ozone and nitric acid data, which includes a number of significant improvements compared to the version 4 we employed during our 1999 EF fellowship (i.e., improved treatment of coupled temperature and tangent point retrievals). In particular, various refinements in the forward model and retrieval algorithm have led to a much better precision for version 5 HNO_3 data, despite the fact that the retrievals are now performed on 6 surfaces per decade in pressure, as opposed to 3 in previous MLS data sets.

At the time of the writing (February 14th, 2001) the relevant MLS 3D data of O_3 and HNO_3 for December 18th, 1996 have been received from the Goddard Data Archive Center, and interpolated onto the Reprobus grid. A new 3D simulation is currently under way. Note that the species not initialised from satellite data are initialised from a December 5-year average of a version of Reprobus coupled to Météo-France's Arpège general circulation model. Background concentrations of H_2SO_4 are used, leading to aerosol surface area in general smaller than 1 micrometer^{2}cm^{-3} at temperatures above 200K.

Once the initialisation of our new simulation is validated, a systematic comparison of the ILAS and REPROBUS profiles will be performed over the most interesting period and geographical areas. Several scenarios will be tested. In particular, we will investigate the physical state of the PSC aerosols (liquid vs. solid) through different schemes.

These will include a « NAT scheme » experiment, for which solid particles form when NAT temperature is reached (i.e., around 195 K at 50 hPa), although a supersaturation ratio of 10 is usually taken in account, as suggested by laboratory experiments). This scheme maximizes the occurrence of PSCs and the HNO_3 gas-phase removal since the fomation of

NAT occurs at temperatures 2-3 K higher than the uptake of HNO_3 onto liquid aerosols. It also maximizes the amount of denitrification by favoring the formation of NAT which grows larger than the binary or ternary droplets. The latest version of the Reprobus PSC module includes a high nucleation selectivity, which is the key to the growth of large NAT particles, as recently observed[6] during the 1999-2000 Arctic winter.

The « liquid scheme » ignores the formation of NAT. The PSC particles are supposed to remain liquid as long as the temperature is above the ice frost point. When ice evaporates, all the particles are returned to the liquid phase. This scheme favors the formation of liquid supercooled binary or ternary solutions, and therefore minimizes the amplitude of both the HNO_3 gas phase removal and the denitrification.

4. Result

The new simulations performed at NIES in 2001 have not reached a sufficiently validated stage yet to be presented in this report. However, an illustrative example of the type of analysis we will carry out in the present project in given in Figure 1, which shows a comparison between an ILAS observation of the nitric acid vertical distribution on February 23rd, 1997, and coincident Reprobus profiles. On top is plotted the HNO_3 calculation obtained using the liquid scheme, whereas result from the NAT scheme is shown below. The ILAS measurement exhibits a reduction in the HNO_3 profile around 20 km which suggests a removal from the gas phase due to the formation of polar stratospheric cloud. The temperature at this level, as analyzed by the UKMO, is close to 190K and is therefore below the threshold for NAT formation, but also below the threshold for significant HNO_3 uptake to occur onto liquid aerosol.

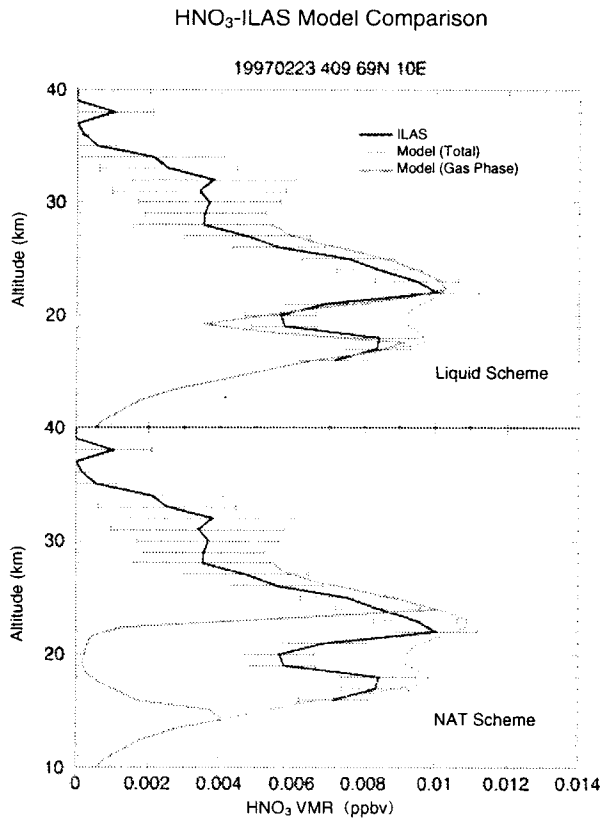

Figure 1. Comparison of nitric acid (HNO_3) measurements by ILAS and three-dimensional model calculations on February 23rd, 1997.
Top : *liquid scheme*
Bottom : *NAT scheme*
Both simulations confirm indeed a significant removal of nitric acid from the gas-phase.

The profile obtained with the liquid scheme appears to be in very good agreement with the observation. Both the vertical extent and the magnitude of the gas phase removal correspond relatively well to the dip observed by ILAS at 20 km altitude. On the other hand, it is clear that the NAT scheme overestimates significantly the vertical extent of the PSC, as well as the gas-phase removal of HNO_3 which is nearly complete at 20 km, in contradiction with the ILAS observation.

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