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Liquid Particle Composition, and Chlorine Activation, in a Lee-Wave Polar Stratospheric Cloud

Introduction

Polar stratospheric clouds (PSCs) can be composed of a number of different types of particle, including solid nitric acid trihydrate (NAT) particles (type Ia), super-cooled ternary solution (STS) droplets (type Ia), and ice particles (type II). We have developed a microphysical box model for the study of these particles. The liquid particle model is fully developed, and is used here to study PSC observations from the EuPLEx campaign.

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The Model

The MADVEC (condensed-mass, advection-based) model is designed for use within mesoscale chemistry and transport models (CTMs). To this end it uses a fixed size discretisation, inside which the aerosol population is described using mass distribution functions for each component (Pilinis, 1990).

The liquid-only model simulates the evolution of STS particles. This is treated as a continuously distributed, internally mixed aerosol, consisting of three components – H_2O, HNO_3 and H_2SO_4. Particle growth is determined using only condensation and evaporation, coagulation is ignored. A detailed description of this model is given in Lowe *et al.* (2003).

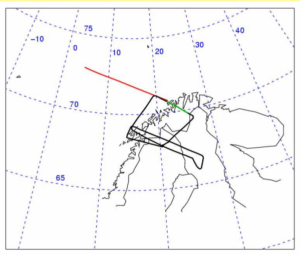


Figure 1. Geophysica flight plan from the 8/2/2003 (black and green line), with the 6hr MM5 back-trajectory used for this study (red line). The green line denotes the section of the flight path used in the generation of the model trajectory.

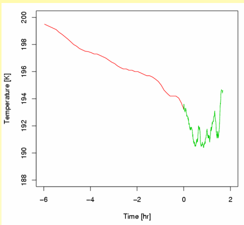


Figure 2. Trajectory used for the MADVEC and equilibrium model runs. The red section is the MM5 trajectory shown in Figure 1, the green section is generated from the section of the Geosphysica flight path indicated in Figure 1.

Lee-wave PSC Event on 8th February 2003

During the 8th February 2003 a series of lee-waves were present over the Scandinavian mountains. Within these the temperature was observed to drop to 190 K (at 51 mbar), sufficiently cold for the formation of liquid PSCs. The Geophysica aircraft made several quasi-lagrangian passes through these lee-wave (Figure 1, black line); here we present a study of the PSC measured during the most northerly of these passes (Figures 1 and 2, green lines).

NO_y data from the SIOUX instrument, and lidar data from the MAS instrument, indicate that the Geophysica passed through a liquid PSC during this event. Mesoscale (Figures 1 and 2, red lines) and global-scale (Figures 3 and 4) back trajectories show that the air-parcels sampled had recently been relatively warm (above 220 K; Figure 4), precluding the seeding of the air parcel by previous PSC events.

To create a trajectory for our model we have combined the MM5 back-trajectory with temperature and pressure measurements from the Geophysica aircraft (Figure 2). The time-scale of the aircraft is multiplied by the ratio of the aircraft to wind speeds to better simulate the passage of the air-parcel through the mountain lee-wave.

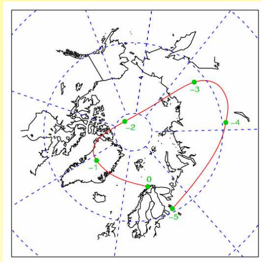


Figure 3. 5-day back trajectory generated using the BADC web-based trajectory model.

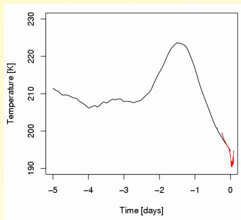


Figure 4. 5-day back trajectory generated using the BADC web-based trajectory model (black line). Our model trajectory (red line) is included for comparision.

Microphysical Simulation of Liquid PSCs

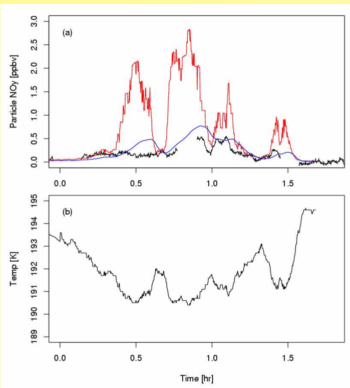
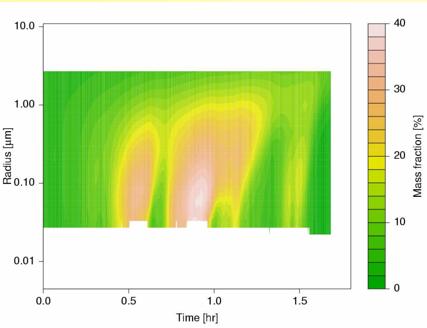


Figure 5. (a) Comparison of the corrected particle NOy data from SIOUX (black line) and our modelled equilibrium and non-equilibrium data (red and blue lines respectively). **(b)** Adapted temperature profile of the lee-wave used for the model trajectory.

To study the evolution of the observed lee-wave PSCs we have used two different microphysical models. The first is our microphysical model, MADVEC, the second is an aerosol model based on the para-meterisation of Carslaw *et al.* (1995), which calculates the properties of a liquid aerosol in equilibrium with its surroundings. These models are initialised with 9 ppbv HNO_3 and 4.5 ppmv H_2O (estimated from SIOUX and FISH data), and 0.5 ppbv H_2SO_4 and a total number concentration of 10 cm^{-3} (taken as standard values for the winter polar stratosphere).

We have compared the particle HNO_3 content of our two models with the particle NO_y content derived from the measurements of the SIOUX instrument (Figure 5a). We see that the equilibrium model (red line) generally over-predicts the NO_y content of the particles, while the output from MADVEC (blue line) is comparable to the measured data (black line). There are, however, steep gradient features of the SIOUX data which are better captured by the equilibrium model, and are due to the only quasi-lagrangian nature of the flight path.



MADVEC shows a size-dependence of the changes in particle composition within the lee-wave event, illustrated in Figure 5 using the liquid-phase HNO_3 mass fractions. The increases seen in the particle phase HNO_3 in Figure 5a are mirrored by the increases in the mass fraction. These compositional changes occur most rapidly around T_{STS} (around 191.5-192 K in this case).

Figure 6. Variation of the liquid phase HNO_3 mass fraction across the particle size range during the lee-wave event shown in Figure 5.

Heterogeneous Chlorine Activation

To model chlorine activation we have added the following heterogeneous reactions to our model

$$ClONO_2 + H_2O(l) \Rightarrow HOCl + HNO_3(aq) \quad (R1)$$

$$ClONO_2 + HCl(aq) \Rightarrow Cl_2 + HNO_3(aq) \quad (R2)$$

$$HOCl + HCl(aq) \Rightarrow Cl_2 + H_2O(l) \quad (R3)$$

No parameterisations of these reactions in ternary solutions exist in the literature, instead we will use the parameterisation of Shi *et al.* (2000) for these reactions on binary sulphate solutions. We must note, however, that Hanson (1998) predicts that such a substitution could lead to over-predictions of the reaction coefficient by 30-50%.

We use the water activity over the STS solution to calculate the composition of the binary solution, and initialise our model runs with 1.5 ppbv HCl and 0.5 ppbv $ClONO_2$. In Figure 7 we show the production of Cl_2 and HOCl, over the full 8 hours of the model run, for both MADVEC (blue line) and the equilibrium model (red line). The equilibrium model produces approximately 20% more Cl_2 than MADVEC; the difference is mostly due to the larger particle surface areas produced by the equilibrium model.

The HALOX instrument measured ClO_x ($ClO + 2Cl_2O_2$) concentrations of around 300 pptv within the lee-wave, however the solar zenith angle at this time was around 110°. Because of this it is not straightforward to relate the measured ClO_x with the modeled Cl_2 production.

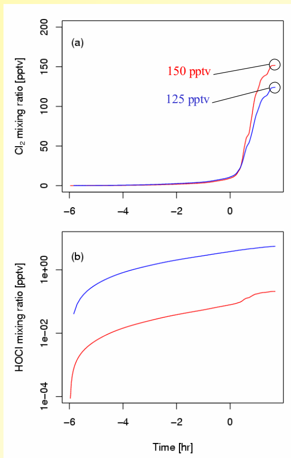


Figure 7. Total production of **(a)** Cl_2 and **(b)** HOCl for the equilibrium model (red line) and MADVEC (blue line) over the trajectory shown in Figure 2.

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