Arctic profiles of HCl, HNO$_3$ and NO$_2$ measured during THESEO 2000 by the LPMA/DOAS balloon payload

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Introduction

The LPMA (Limb Profile Monitor of the Atmosphere) experiment is a remote sensing infrared Fourier transform instrument operating in absorption against the sun [1]. Its high spectral resolution and sensitivity allow the retrieval of vertical profiles of trace species having stratospheric mixing ratios as small as 0.1 ppbv. This is particularly important for chlorine reservoir species (like HCl and ClONO$_2$ [2]) and tracer species (like HF) for which such measurements are very difficult with *in situ* techniques.

We report here results derived from spectra recorded during the balloon flight LPMA16 within the THESEO 2000 campaign. As scheduled in the work programme, the balloon flight of the payload LPMA/DOAS took place on 18 Feb. 2000 from ESRANGE (68 N, 21 E) near Kiruna (Sweden).

The results obtained from the Differential Optical Absorption Spectroscopy (DOAS) instrument are covered in a parallel poster from the Institut für Umwelt Physik (UIP) of the University of Heidelberg (PI: K. Pfeilsticker).

The LPMA/DOAS flight of 18/02/2000

The launch time was 12:15 UT on 18 Feb. 2000 from the ESRANGE balloon launch pad. The balloon reached float at 14:15 UT for an altitude of about 30 km at a pressure level around 9 hPa. All the equipment operated in a nominal manner with the sun-tracker feeding both the FTIR (parallel beam) and the UV-vis (fibre optics) spectrometers with a reasonably stable solar beam. Slightly more perturbed conditions were observed, however, as compared to other Arctic flights of the same LPMA/DOAS payload. This translates into slightly noisier spectra for the FTIR instrument. It was the first time that the LPMA/DOAS was operating with a smaller

mechanical structure (for reducing weight) with a mass of 460 kg (i.e. below the 500 km limit recommended by CNES).

Measurements were possible from an altitude of about 2.5 km during the ascent with only a small number of loss of sun periods in the dense troposphere and around the tropopause when the stability of the pointing (azimuth control of the gondola in the direction of the sun) is always difficult. Measurements were continued at float until loss of sun just above the horizon for a tangent altitude of about 13 km. Separation and recovery occurred in Finland.

The measurements allowed to sample air masses inside the Arctic vortex. As an illustration, figure 1 presents a PV map from ECWF for the 475 K level. However, the LPMA/DOAS line of sight geometry was sampling the vortex in the vicinity of its inner edge, leading to a rather strong sensitivity of the retrieved profiles to the actual position of this boundary. The 10 day back-trajectory analysis from ECWF (figure 2) indicates that air masses sampled by LPMA circulated in the polar vortex for many days before the flight. This analysis indicates that PSC events where possible from 2 to 10 hours before the flight between 380 and 475 K levels.
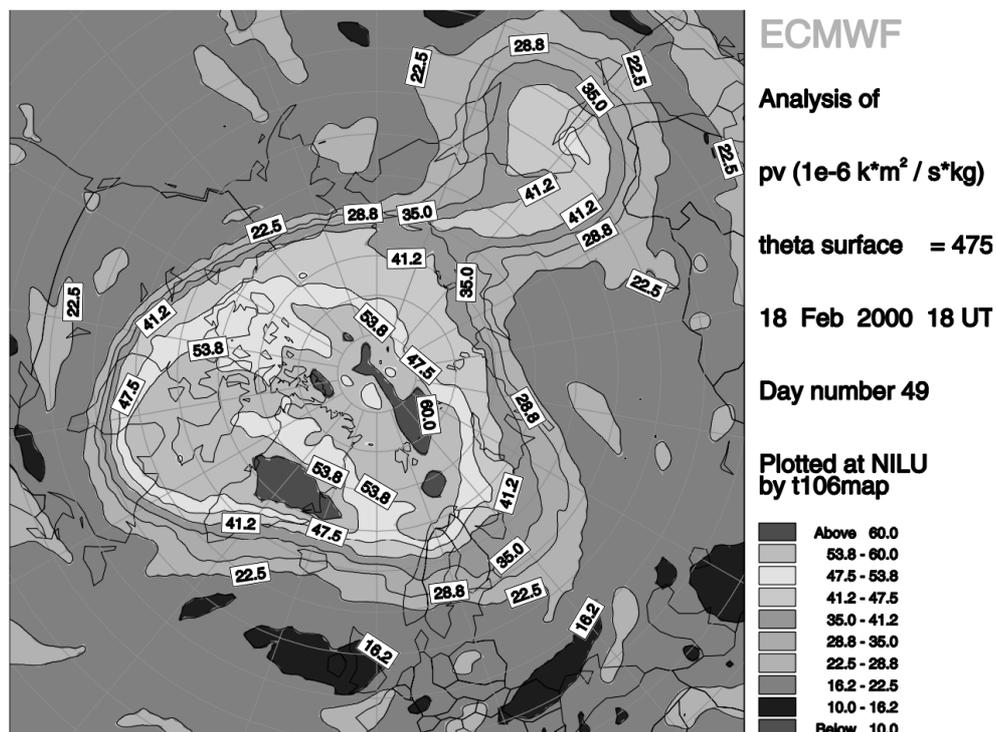

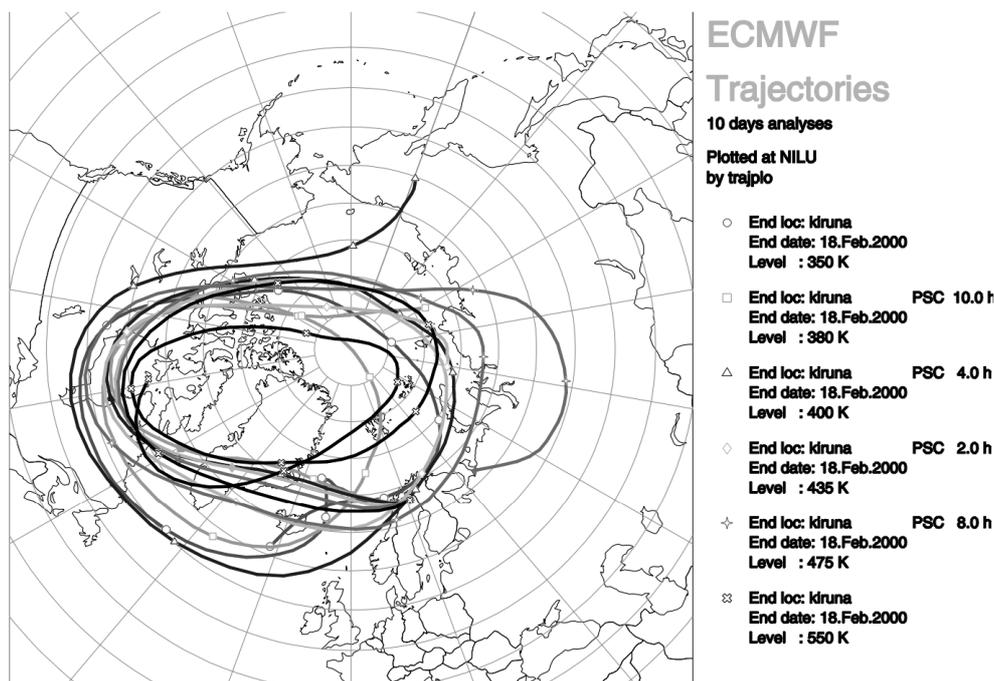**Figure 1.** PV map at 475 K level from ECMWF corresponding to LPMA flight.

Figure 2. Back-trajectories from ECMWF for 6 theta levels (ending location over Kiruna).

Results obtained by LPMA

Retrievals of vertical concentration profiles have been performed using ascent spectra (occultation spectra are more difficult to process because of the increased angular jitter mentioned above; they will be processed later on). The vertical resolution for ascent is about 2 km, even though the vertical sampling is 1 km. The flight was performed inside the vortex and chlorine activation is clearly apparent when comparing the HCl profile measured by LPMA in Feb. 2000 and the HCl profile measured the preceding winter (10 Feb. 1999) when the vortex was warmer and not so deep (see Figure 3).

Activation of chlorine results in a depletion of HCl, as compared to normal conditions, and this rather inactive reservoir species has been converted into more active chlorine species like ClO, $(ClO)_2$ or HOCl resulting in large ozone destruction episodes.

The tracers N_2O and CH_4 have also been retrieved to detect air intrusion and to test the diabatic descent modelling within the CTM (figure 4).

As for the previous ILAS validation campaign, the profile of the two NO_y species NO_2 [3] and HNO_3 [4] have been obtained (figure 5 and 6) allowing studies of the NO_y chemistry in the Arctic in winter.

The ozone profile retrieved from LPMA spectra is showing lower mixing ratio values above 23 km than the Sodankyla soundings performed the same day (figure

7), but the location of the 2 measurements (LPMA/DOAS and ozone sondes) are differing by 300 km, which can explain some of the observed differences in a region where the vortex boundary was moving rapidly (see figure 1 and 2).
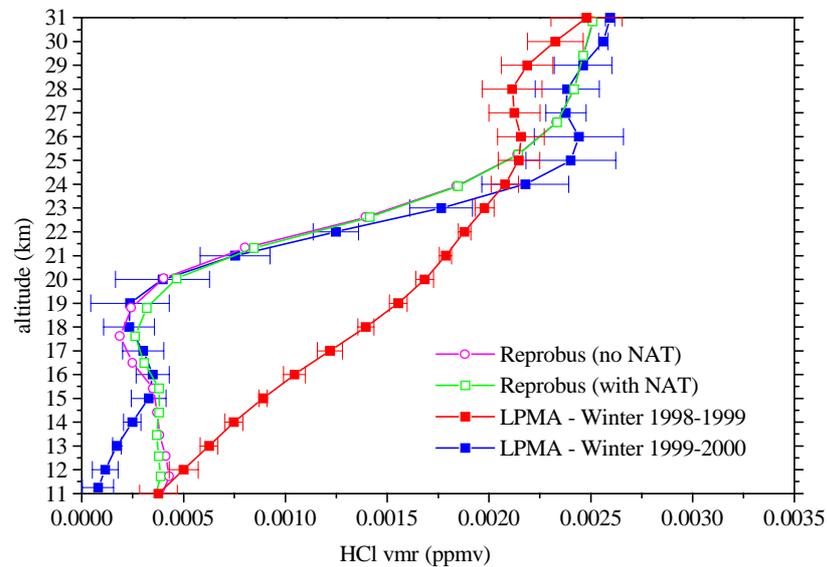

Figure 3. Observed HCl profiles in the Arctic vortex in February 1999 and February 2000. This latter profile is compared with the Reprobus simulation with and without NAT.
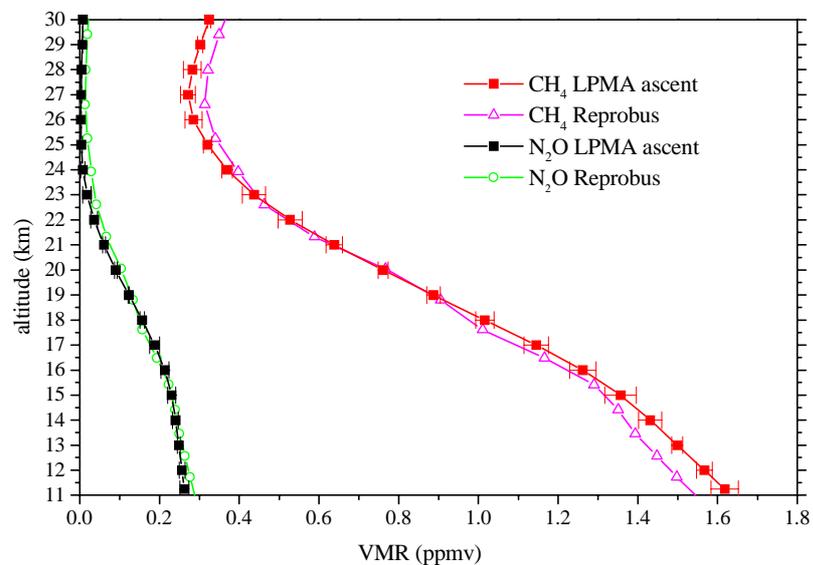

Figure 4. N_2O and CH_4 vertical profiles measured by LPMA and compared with the Reprobus simulation.
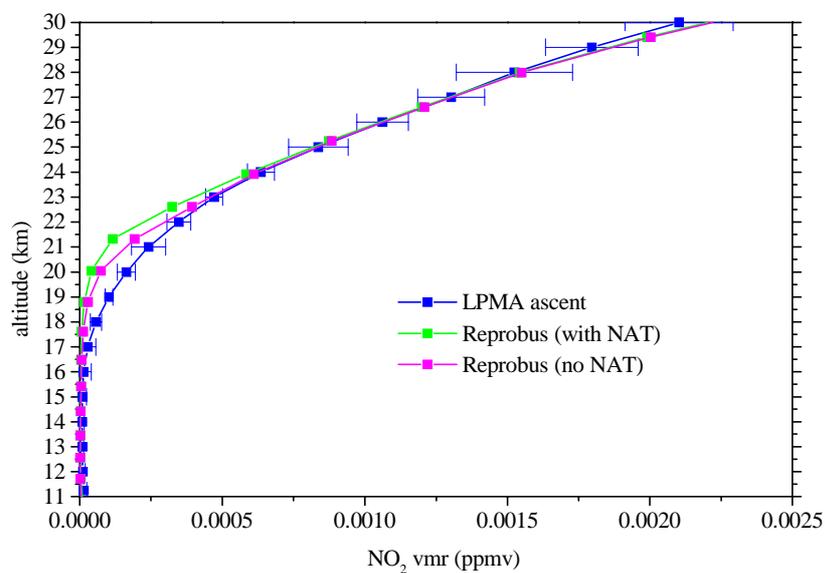
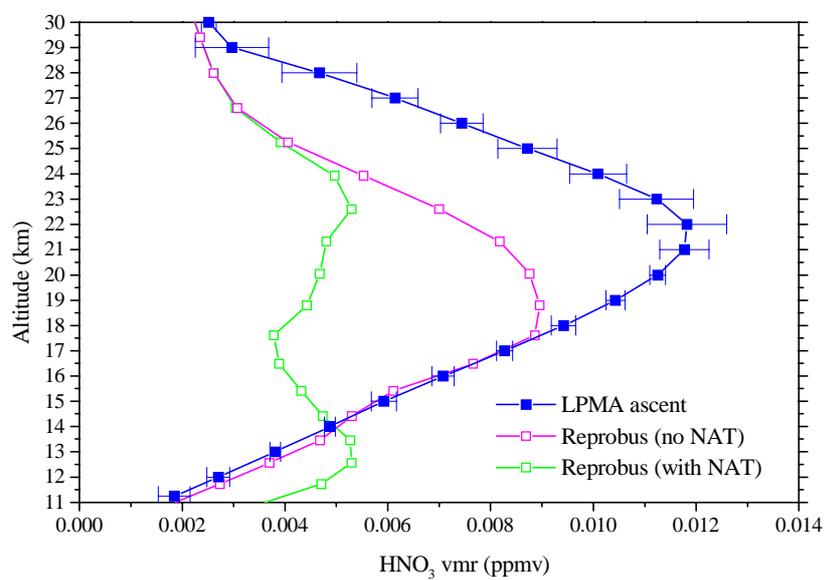**Figure 5.** NO$_2$ vertical profiles measured by LPMA and compared with the Reprobus simulation.

Figure 6. HNO$_3$ vertical profiles measured by LPMA and compared with the Reprobus simulation.
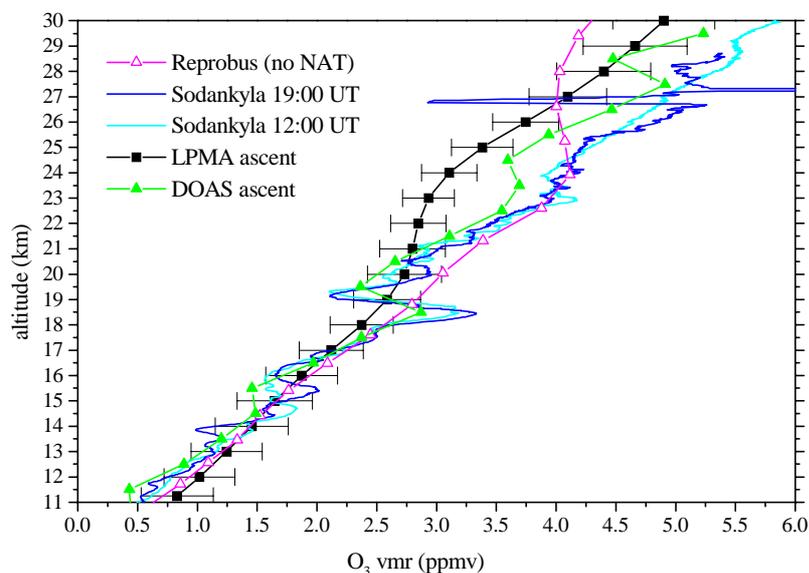
Figure 7. O_3 vertical profiles measured by LPMA and by DOAS compared with a sounding performed from Sodankyla and with the Reprobus simulation.

Comparison with 3D CTM

The Reprobus model is a three-dimensional chemistry transport model which computes the time evolution of 55 stratospheric species [5, 6]. The chemical package includes a comprehensive treatment of gas-phase chemistry (147 reactions and photolysis rates), as well as heterogeneous reactions taking place at the surface of liquid polar stratospheric clouds. The model was initialized at the beginning of the winter. The wind and temperature fields used to drive the transport of chemical species and to compute the chemical rates have been prescribed every 6 hours by the ECMWF analysis and interpolated in time and space to match the Reprobus grid points. In this configuration Reprobus extends on 42 vertical levels from the ground up to 1 hPa, with a horizontal resolution of 2×2 degrees, and a chemical time step of 15 minutes.

The HCl profile measured by LPMA (figure 3) is compared with two simulation performed by F. Lefèvre using the 3D chemical transport model Reprobus. These two simulations differ by the PSC scheme included in the model. The agreement of CTM with HCl observations of LPMA is good for these two simulations, but we will see below that the agreement for NO_y species is significantly improved when no NAT are considered in the model. HCl is overestimated by the model below 15 km, which can be explained by an improper initialisation of chlorine species at the lower levels.

The N_2O and CH_4 tracer profiles are consistent with the ones calculated by Reprobus (figure 4) confirming that the diabatic descent is well represented in the model.
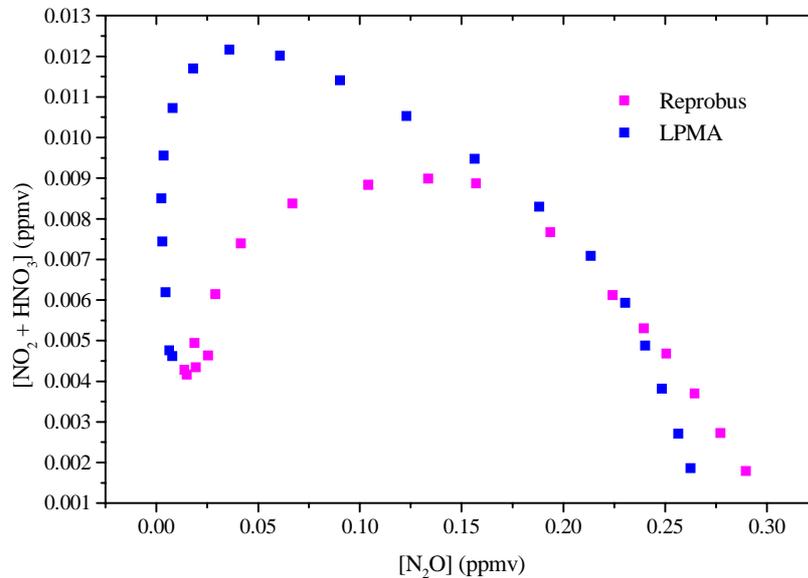

Figure 8. Correlation of $[N_2O]$ versus $[HNO_3+NO_2]$ for LPMA observations and for the corresponding Reprobus simulation.

The NO_y species NO_2 and HNO_3 have also been retrieved and their observed profiles (figure 5 and 6), when compared to Reprobus, confirm again that the NO_y chemistry in the Arctic in winter is not yet fully reproduced by the best 3D CTM models: HNO_3 is underestimated around the peak of the profile and NO_2 is largely converted to other NO_y species and/or into PSCs by the model, whereas its observed mixing ratio is not negligible (~ 0.2 ppbv) in the altitude range 23-18 km. Figure 8 presents the correlation between N_2O and the sum $NO_2 + HNO_3$. This figure shows clearly that the NO_y amount in the model is underestimated above 18 km. In addition, when NAT are considered, the simulation shows a large depletion in the HNO_3 profiles due to sedimentation, increasing the disagreement with LPMA observations.

The large disagreement between measured and simulated HNO_3 could be explained for a part by a problem of initialisation of NO_y species. This initialisation (at the to beginning of the Arctic winter) is performed by correlation knowing N_2O. This correlation had been determined at mid latitude [7] but may be inaccurate at high latitude before the vortex formation.

Anyhow, a better initialisation would not explain the NO_y underestimation (also existing in other CTM models). A possible descent of NO_y species from high altitude (mesospheric NO_y) has to be examined more systematically [8]. This would improve the agreement between models and observations if this leads to an increase of HNO_3 without increasing significantly NO_2.

The ozone profile retrieved from LPMA spectra is showing lower mixing ratio values above 23 km than the Sodankyla soundings performed the same day, but the location of the 2 measurements (LPMA/DOAS and ozone sondes) are differing by 300 km, which can explain some of the observed differences in a region where the vortex boundary was moving rapidly.

Conclusion

Overall the agreement between balloon observations and model is satisfying especially for HCl, the tracers CH_4/N_2O and O_3, even when large destruction occurs. There is, however, a pending problem of CTMs to reproduce precisely the profiles of HNO_3 and (to a lesser extent) NO_2 in cold Arctic vortex conditions.

References

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