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On the ability of chemical transport models to simulate the vertical structure of the N_2O, NO_2 and HNO_3 species in the mid-latitude stratosphere

G. Berthet[1,2], N. Huret[2], F. Lefèvre[1], G. Moreau[2], C. Robert[2], M. Chartier[2], L. Pomathiod[2], M. Pirre[2], and V. Catoire[2]

[1]Service d'Aéronomie, Institut Pierre-Simon Laplace, F-75252 Paris, France
[2]Laboratoire de Physique et Chimie de l'Environnement, F-45071 Orléans, France

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Correspondence to: G. Berthet (g.berthet@damtp.cam.ac.uk)

Abstract

In this paper we study the impact of the modelling of N_2O on the simulation of NO_2 and HNO_3 by comparing in situ vertical profiles measured at mid-latitudes with the results of the Reprobus 3-D CTM (Three-dimensional Chemical Transport Model) computed with the kinetic parameters from the JPL recommendation in 2002. The analysis of the measured in situ profile of N_2O shows particular features indicating different air mass origins. The measured N_2O, NO_2 and HNO_3 profiles are not satisfyingly reproduced by the CTM when computed using the current 6-hourly ECMWF operational analysis. Improving the simulation of N_2O transport allows us to calculate quantities of NO_2 and HNO_3 in reasonable agreement with observations. This is achieved using 3-hourly winds obtained from ECMWF forecasts. The best agreement is obtained by constraining a one-dimensional version of the model with the observed N_2O. This study shows that modelling the NO_y partitioning with better accuracy relies at least on a correct simulation of N_2O and thus of total NO_y.

1. Introduction

The partitioning of individual nitrogen species within reactive nitrogen family (NO_y) is a very important factor in the stratospheric chemistry of ozone. The photolysis and the photo-oxidation of N_2O is the main source of NO_y species in the stratosphere:

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \quad (1)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \quad (2a)$$

$$\rightarrow 2NO \quad (2b)$$

Reaction (2b) is the dominant path for the production of NO_x species (e.g. McElroy and McConnell, 1971). NO_x ($NO + NO_2$), the most reactive form of the NO_y compounds,

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are involved in the main processes controlling the ozone budget. They both account for a major part of ozone reduction in the middle and upper stratosphere through rapid catalytic cycles (e.g. McElroy et al., 1992; Osterman et al., 1997; Brühl et al., 1998) and moderate the ozone-destroying catalytic cycles involving halogen and hydrogen radicals (e.g. Salawitch et al., 1994; Wennberg et al., 1994). NO_x are chemically linked to nitric acid HNO_3 which is the main reservoir of the NO_y family below ~30 km and are primarily produced by photolysis of HNO_3. The partitioning of NO_y species, and in particular NO_2 and HNO_3, is also affected by heterogeneous reactions on sulphate aerosols that convert active nitrogen to HNO_3 (e.g. McElroy et al., 1992; Fahey et al., 1993).

Nevertheless the quantitative understanding of the partitioning of the NO_y species in the models remains limited. Several studies have shown significant discrepancies between computed and observed partitioning of NO_y species depending on the location (mid- or high latitudes) and time (day or night, period of the year) (e.g. Sen et al., 1998; Gao et al., 1999; Payan et al., 1999; Wetzel et al., 2002; Stowasser et al., 2002, 2003). Observations of the various NO_y species such as HNO_3 and NO_2 are not satisfyingly reproduced by chemistry-transport models at mid-latitudes with in particular recurrent underestimations of NO_2 mixing ratios (Wetzel et al., 2002; Stowasser et al., 2003). The different compounds among the NO_y family are also represented as ratios to separate dynamical from chemical effects on the NO_y partitioning and to reduce the influence of missing amounts of total NO_y in the models. Simulations of these ratios generally appear to be more satisfactory (e.g. Kondo et al., 2000; Wetzel et al., 2002) even though Stowasser et al. (2003) have presented NO_2/NO_y ratios strongly underestimated by model results in the lower stratosphere. This seems to demonstrate that dynamical effects constitute the major part of the discrepancies with observations in the middle-stratosphere.

The SPIRALE (French acronym for "Spectroscopie InFrarouge par Absorption de Lasers Embarqués") balloon-borne instrument is able to measure in situ profiles of NO_2 and HNO_3 and of their precursor N_2O with a high vertical resolution. Such in situ

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measurements appear to be more able to characterize local processes than remote sensing observations using lines of sight of a few hundred of kilometres. We report here measurements of these species at mid-latitudes on 2 October 2002 in the frame of the first validation campaign of the ENVISAT satellite. In this paper we try to balance the dynamical and chemical effects on the modelling of the NO_y partitioning. First we assess the influence of the 3-D winds used in the Reprobus CTM on its ability to reproduce the NO_y partitioning. Then a one-dimensional (1-D) version of the model is used to test the impact of a correct initialisation of N_2O on the simulation of the chemistry controlling the NO_y partitioning. It is the first modelling study of the in situ simultaneous observations by SPIRALE of NO_2 and HNO_3 with a CTM.

2. The SPIRALE balloon-borne instrument

A detailed description of the instrumental characteristics of SPIRALE and of its operating mode can be found in Moreau et al. (2005). To summarize, the SPIRALE balloon-borne instrument performs in situ simultaneous measurements of several long-lived and short-lived chemical species from the tropopause up to 40 km. It uses six tunable salt laser diodes in the mid-infrared domain (3 μm to 10 μm). The six laser diodes are cooled and the beams are injected into a multipass Heriott cell located under the gondola. The cell (3.5 m) is deployed during the flight above the tropopause. Eighty six reflections occur, giving a 300 m optical path. Species concentrations are retrieved from direct absorption, by fitting experimental spectra with spectra calculated using HITRAN 2001 database (Rothman et al., 2003). The instrument provides measurements with a vertical resolution of a few meters.

SPIRALE is used routinely, in particular as part of European and satellite validation campaigns. On 2 October 2002, during the ENVISAT validation campaign, the SPIRALE flight was conducted during the morning at mid-latitude from the Aire sur l'Adour launch base (France, 43.7° N, 0.3° W). In our study we analyse the measurements of N_2O, HNO_3 and NO_2 profiles obtained during the ascent of the balloon around

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08:00 UT. The data used in this study are averaged over a vertical range of 250 m. Relative uncertainties on concentrations are then 3% for N_2O, and 7% for HNO_3 and NO_2.

3. Model calculations

The Reprobus chemical-transport model (Lefèvre et al., 1994, 1998) has been widely used in previous studies of the stratospheric chemistry (e.g. Lefèvre et al., 1994; Deniel et al., 1998; Hoppel et al., 2002). The model is designed to perform annual simulations as well as detailed process studies. It computes the evolution of 55 species by means of about 160 photolytic gas-phase and heterogeneous reactions, with a time step of 15 minutes in this study. A semi-lagrangian code transports 40 species or chemical families, typically long-lived tracers but also more unstable compounds which may have a long lifetime in darkness. Kinetics parameters used in the present study are based on the most recent data in general taken from Sander et al. (2003). The new laboratory measurements of photodissociation cross-sections of HO_2NO_2 both in the UV (Knight et al., 2002) and in the near IR (Roehl et al., 2002) have been included in the photodissociation calculations. The heterogeneous chemistry module includes reactions on liquid aerosols. Their surface area densities are inferred from SAGE II measurements (Thomason et al., 1997).

Reprobus was integrated from 1 April 2002 to 15 October 2002. The model extends from the surface up to 0.1 hPa on 42 levels, resulting in a vertical resolution of about 1.3 km in the lower stratosphere. The horizontal resolution is 2° latitude by 2° longitude. Temperature, winds and ground pressure are specified from the three-dimensional (3-D) European Centre for Medium-Range Weather Forecast (ECMWF) meteorological data. The ozone field was initialized on 1 April 2002 from the ECMWF ozone analysis. Other species were initialized from an April zonal mean computed from a long-term simulation of Reprobus.

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4. Comparisons between SPIRALE measurements and 3-D calculations

4.1. N_2O profile

4.1.1. Measurement

The in situ profile of N_2O measured by SPIRALE (Fig. 1) presents different features which suggest that the instrument observed air masses of different origins. In particular a 5 km layer with a minimum value of 50 ppbv at 27 km is clearly present between 23 and 29 km.

A detailed study based on the SPIRALE observations of N_2O and CH_4 has been made to investigate the dynamical state of the stratosphere during this flight (Huret et al., 2005[1]). Using a combination of $[CH_4]$:$[N_2O]$ correlations and potential vorticity maps calculated by the MIMOSA contour advection model (Hauchecorne et al., 2002) this study shows a perturbed situation probably due to the vertical wind shear occurring during the first stage of the polar vortex formation. From the $[CH_4]$:$[N_2O]$ correlations, mid-latitude air was diagnosed between about 16 and 23 km whereas the air masses sampled above 29 km mainly originated from tropical latitudes. This is consistent with the location of the instrument with respect to the dynamical barrier existing in this region: the MIMOSA model calculates potential vorticity values in the 43–50 pvu range at 550 K (about 22.5 km) and close to 149 pvu at 810 K (about 30 km) at the location of the measurement at 06:00 UT (Fig. 2a and b). Between 23 and 29 km the N_2O profile is clearly non-monotonic (Fig. 1) and the vertical profiles of both tracers are associated with a significantly different $[CH_4]$:$[N_2O]$ correlation with respect to Michelsen et al. (1998) correlation curves (Huret et al., 2005[1]). This gives an indication that mixing processes have probably occurred, similarly to the mixing event processes occurring

[1]Huret, N., et al.: On the vertical structure of the stratosphere at mid-latitude during the first stage of the polar vortex formation and in polar region in presence of a large mesospheric descent, J. Geophys. Res., in preparation, 2005.

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inside the Arctic vortex and across the vortex edge (Plumb et al., 2003; Konopka et al., 2004) or to the mixing of polar vortex air into middle latitudes detected from tracer-tracer scatter plots (Waugh et al., 1997). The analysis of such a mixing event is out of the scope of our paper.

Similar conclusions can be derived from the comparisons performed by Urban et al. (2004) between SPIRALE measurements and the observations of the SMR instrument onboard the Odin satellite (e.g. Murtagh et al., 2002). This study shows that averaging Odin/SMR measurements over 27.5–42.5° N (mostly tropical air) and 42.5–55° N (mostly mid-latitude air) gives N_2O amounts similar to those observed by SPIRALE above 29 km and below 23 km, respectively. Between 23 and 29 km the N_2O profile measured by SPIRALE is located between the two averaged profiles observed by Odin/SMR, suggesting a mixing event.

4.1.2. Model calculations

CTM calculations were driven using the 3-D 6-hourly ECMWF operational analysis for winds, temperature and ground pressure recurrently employed in modelling studies (e.g. Lefèvre et al., 1998; Wetzel et al., 2002; Stowasser et al., 2003; Ricaud et al., 2005). Figure 1 compares the observed profile of N_2O to the model result obtained at the grid point closest to the measurement position. The model slightly underestimates the observations below 20 km but discrepancies are mainly observed above 25 km: Reprobus overestimates SPIRALE measurements of N_2O above 30 km, and does not reproduce the structure at 27 km. Other measurements-model comparisons have revealed overestimations of the calculated amounts of N_2O. N_2O mixing ratios measured by the MIPAS-B balloon-borne instrument at mid-latitudes during summer time are overestimated by the KASIMA 3-D CTM below 30 km (Wetzel et al., 2002). Comparisons between Reprobus and the Odin satellite measurements have shown that the model overestimated the N_2O amounts observed by Odin/SMR at mid-latitudes in mid-September 2002 (Ricaud et al., 2005). Similar disagreements are observed with preliminary measurements of the MIPAS instrument on board the ENVISAT satellite

for the same period (R. Runhke, personal communication). This notorious problem appears to be related to a too strong vertical transport above the Equator when using ECMWF operational analysis winds which provide too large quantities of N_2O in the tropical middle stratosphere (Ricaud et al., 2005). Then these amounts reach mid-latitudes by the Brewer-Dobson circulation and quasi-horizontal transport from the tropical latitudes (Holton et al., 1995).

4.2. NO_y partitioning

We do not consider the diurnal variation of NO_2 since it appears to be weak between the half time of SPIRALE measurements during the ascent of the balloon (08:00 UT at about 24 km) and the last measurement (08:30 UT at float altitude). Figure 3 shows the comparisons between the observed profiles of NO_2 and HNO_3 and the model calculations for a solar zenith angle of 70° at 08:00 UT. Significant underestimation is visible on the simulated profile of NO_2 above 22 km (33, 40 and 22% lower than the observation at 23, 27 and 31 km, respectively) where N_2O is overestimated by the model. The model underestimates the measured mixing ratios of HNO_3 above 27 km (12, 19 and 26% lower than the observation at 27, 28 and 31 km, respectively). Simulated HNO_3 is overestimated below 22 km (51 and 23% higher than the observation at 18 and 20 km, respectively) where N_2O is underestimated by the model. For other altitudes Reprobus results stay within the error bars of the SPIRALE measurements.

One must examine whether such underestimation of the mixing ratios of these two major species among the NO_y family is related to the ability of the model to calculate the total amounts of NO_y. Indeed 3-D CTMs may underestimate the total amount of NO_y at mid-latitudes, as shown by the comparison between the KASIMA CTM and observations by the MIPAS-B instrument (Wetzel et al., 2002), which affects the simulation of the various NO_y species. This result is supported by recent comparisons between different European models with preliminary MIPAS observations (R. Ruhnke, personal communication). Since SPIRALE does not measure all of the NO_y species (N_2O_5, $ClONO_2$, NO_3 and HO_2NO_2 are missing), we have reconstructed the in situ

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profile of total NO_y (hereafter NO_y*) using the compact N_2O-NO_y relations measured in different latitude bands. Figure 4 presents the NO_y* profile inferred from the 28–46° N correlation given by Michelsen et al. (1998). The profile from the 3–10° N latitude band correlation is also represented above 29 km where air masses appear to mainly originate from low latitudes (see Sect. 4.1.1). N_2O and NO_y are anticorrelated for N_2O mixing ratios larger than about 50 ppbv. Subsequently, the comparison between the reconstructed and simulated profiles of NO_y (Fig. 4) reveals a significant underestimation by Reprobus above 25 km where N_2O is overestimated by the model. Above 30 km the model particularly underestimates the NO_y* profile inferred from the 3–10° N N_2O-NO_y correlation. A slight overestimation is observed at some altitudes below 20 km where N_2O is underestimated by the model. These two behaviours are the result of the discrepancies observed in Fig. 1. Any problem in the modelling of N_2O has a direct impact on the calculated quantities of total NO_y. The transport of too large quantities of the N_2O precursor species at mid-latitudes stated above can result in a too weak production of NO_y after its transport from tropical latitudes (e.g. Ricaud et al., 2005) which explains the low values for the upper part of the profile in Fig. 4.

To minimize the effect of the uncertainty in the total NO_y modelling we have compared the NO_2/HNO_3 ratios rather than individual profiles (Fig. 5). In that case better results are obtained: the NO_2/HNO_3 ratio is well reproduced by Reprobus above 27 km and between 17 and 22 km. However an underestimation can be seen between 22 and 27 km (34 and 31% lower than the observation at 23 and 27 km, respectively) as a result of NO_2 underestimation. From the NO_2/HNO_3 ratio we can see in this altitude range that the particular structure attributed to a mixing event affects our ability to reproduce the observed NO_y partitioning. We conclude from Fig. 5 that the NO_y partitioning seems to be correctly reproduced by the CTM at all altitudes except at those of the particular vertical structure. Note that the strong peaks of the NO_2/HNO_3 ratio at 15 and 16.5 km cannot be reproduced by the model which could be due to its too low vertical resolution.

From this result it is worth trying to improve the simulation of the total NO_y profile.

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The modelling of N_2O relies mostly on transport. Thus, one can expect that a better simulation of the transport of N_2O can improve the agreement between measurements and calculations of the NO_2 and HNO_3 quantities.

5. Sensitivity to the wind fields

5.1. 6-hourly and 3-hourly ECMWF winds

In the work of Legras et al. (2005) in situ measurements of N_2O performed from the ER-2 aircraft are compared both to Reprobus 3-D outputs (computed at the time/positions of the flight track) and to reconstructed trajectories. Significant discrepancies are observed between the CTM and the reconstructed trajectories when computed with 6-hourly ECMWF operational analysis. These are characterized by strong variations and unrealistic structures apparently as a result of high-frequency fluctuations in the winds. A dramatic improvement is obtained by Legras et al. (2005) when using 3-hourly analysis to compute air mass trajectories and the resulting N_2O distribution. We have tested this result by performing a second simulation using 3-hourly wind fields obtained by interleaving 3H and 9H forecasts between the ECMWF 6-hourly operational analysis. Figure 6 compares N_2O zonal means calculated by Reprobus when driven by 6-hourly and 3-hourly winds on 2 October 2002, at the time of SPIRALE observations. It can be seen that using 3-hourly winds clearly leads to more realistic N_2O values in the upper stratosphere, as a result of a slower circulation and reduced vertical diffusion. This result is consistent with the analysis of Legras et al. (2005). It also supports the work of Stohl et al. (2004) who show that forecast winds are less diffusive than operational analysis.

5.2. 3-D CTM calculations using 3-hourly winds

SPIRALE observations are now compared to two additional Reprobus 3-D CTM simulations using different wind sources: 1) a simulation considering 3-hourly wind fields,

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interleaving operational analysis at 00:00, 06:00, 12:00, and 18:00 UT with forecasts valid at 03:00, 09:00, 15:00 and 21:00 UT, as in the work of Legras et al. (2005) (hereafter named Reprobus-3h-ope-for). 2) a simulation only considering forecasts at 3-h interval, based on the analysis at 00:00 and 12:00 UT (hereafter Reprobus-3h-for). The "baseline" simulation using 6-hourly operational analysis is referred as Reprobus-ope in the following. Initialising the transport every 3 h has clearly allowed us to model more accurately the vertical profile of N_2O tracer species at the time of the SPIRALE measurement (Fig. 7). Below 20 km the new N_2O profile is characterized by slightly higher values with a better agreement with Reprobus-3h-for. Above 20 km the N_2O quantities are decreased towards the profile obtained from the operational analysis. A slight underestimation of the measurements is observed for the upper part of the profile but the decrease of N_2O amounts as altitude increases appears to be more consistent than the Reprobus-ope simulation results. However, the vertical structure observed by SPIRALE around 27 km cannot be reproduced with the new simulations.

The Reprobus-3h-ope-for and Reprobus-3h-for simulations result in enhanced total mixing ratios of NO_y above 20 km where N_2O calculated values are lower in comparison with the typical Reprobus-ope simulation (Fig. 8). Below these altitudes, the increased simulated amounts of N_2O give lower NO_y mixing ratios in better agreement with the NO_y* in situ profile deduced from Michelsen et al. (1998)'s correlation. Above 30 km however, the modelled total amounts of NO_y from the two additional simulations do not appear to be sufficient when compared to the two NO_y* profiles (cf. Sect. 4.2). This could be considered as a limitation of the use of the Michelsen et al. (1998)'s correlation curve between N_2O and NO_y.

NO_2 and HNO_3 profiles calculated by the 3-hourly wind simulations have increased mixing ratios which are in better quantitative agreement with SPIRALE observations (Fig. 9). For example, NO_2 quantities calculated with the Reprobus-3h-for simulation above 22 km are increased by 31, 22 and 12% at 23, 27 and 31 km, respectively, in comparison with the Reprobus-ope simulation (Fig. 9a). Nevertheless, underestimation is still visible around the 27-km structure and also above 30 km as a result of the

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apparent underestimation of total NO_y* quantities (27 and 12% lower than the observation at 27 and 31 km, respectively). Below 22 km the disagreement remain roughly similar between the three model experiments. For HNO_3, most of the Reprobus-3h-for simulation values are located within the error bars of the SPIRALE profile (Fig. 9b), even though some fine specific structures cannot be reproduced, such as at 21 km (36% higher than the observation). Slight improvement is obtained in comparison with the Reprobus-3h-ope-for experiment below 22 km where Reprobus-3h-for simulation gives the best agreement with the NO_y* in situ profile. The results of the two 3-hourly simulations of the NO_2/HNO_3 ratio fall now within the error bars of the in situ observation (Fig. 9c) which shows that the mid-latitude partitioning between these two species can be modelled correctly provided that the simulated NO_y total amounts are well taken into account.

Ignoring the specific problem of mixing, the Reprobus 3-D CTM underestimates the NO_2 and HNO_3 amounts at mid-latitudes due to the underestimation of total NO_y which is in turn the result of transport uncertainties in the model that affect the simulation of N_2O. ECMWF 6-hourly operational analysis seem to be characterized by some noisy and unrealistic features which are not present in the forecasts (Legras et al., 2005) and apparently affecting the transport calculations in Reprobus and in other CTMs. The strict reasons for the significant improvements of the NO_y comparisons using the 3-hourly winds are still unclear. Nevertheless it is thought that using 3-hourly wind data gives a better sampling for the interpolation of the positions between two consecutive wind records in Reprobus.

However discrepancies between the SPIRALE measurements and the model results in Fig. 9 still remain especially for NO_2 above 30 km as a result of the underestimation of the total amounts of NO_y* at these altitudes. Recent studies have shown that satisfying comparisons can be obtained between observations and model calculations when those are constrained by observations of total NO_y (e.g. Küll et al., 2002). This points out the necessity of an adequate simulation of total amounts of NO_y to reproduce the partitioning of the individual species.

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6. 1-D calculations

To get rid of the influence of the problem of transport and hence of the missing quantities of total NO_y, we have used the Reprobus model in its one-dimensional form. Constraining 1-D-Reprobus calculations by observed total NO_y has significantly improved the modelled partitioning of NO_y species compared to balloon measurements in the summer polar stratosphere (Dufour et al., 2005). Similar conclusions have been obtained from comparisons between balloon observations and lagrangian simulations in January 1999 inside a warm Arctic vortex (Stefan Bausch, private communication). In the present study the 1-D-Reprobus initialisation is constrained by the N_2O profile measured by SPIRALE and by the corresponding NO_y* profiles. However the N_2O-NO_y correlation curves from Michelsen et al. (1998) have been determined on given latitude bands and it is not straightforward to choose the adequate correlation values that have to be considered above 29 km where air seems to originate from low latitudes. Two simulations are performed in our study. The first one (referred as Reprobus-1D-midlat) is constrained with the NO_y* profile inferred from the N_2O-NO_y correlations in the 28–46° N latitude band. In the second simulation (hereafter Reprobus-1D-midlat-trop) the computed NO_y* profile is defined by the N_2O-NO_y correlation values in the 28–46° N and 3–10° N latitude ranges below and above 29 km, respectively (cf. Sect. 4.2). These two model experiments allow us to test the sensitivity of the choice of the N_2O-NO_y correlation law on the modelled partitioning of NO_2 and HNO_3. The other species are initialised from the 3-D-Reprobus simulation as in the work of Dufour et al. (2005).

For both experiments the calculated mixing ratios of NO_2 and HNO_3 are close to the measurements (Fig. 10). For NO_2 significant improvement is obtained above 22 km: the Reprobus-1D-midlat experiment provides values that are only 17% and 3% lower than the SPIRALE profile at 23 and 27 km, respectively. Above 29 km the measured quantities lie between the results of the two simulations. An average of the results of both simulations is in perfect agreement with the observation of NO_2 at these altitudes. Similar conclusions can be derived from the HNO_3 profile which is satisfyingly

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simulated for the whole altitude range (24% and 10% lower than the observation at 18 and 20 km, respectively, 6% and 24% higher than the observation at 23 km and 28 km, respectively) except in the layer around 27 km (41% higher than the observation at 27 km). The calculation of the NO_2/HNO_3 ratio is not significantly improved between 22 and 27 km (22% and 31% lower than the observation at 23 km and 27 km, respectively), the computed ratio being underestimated at 27 and 28 km as a result of HNO_3 overestimation. Taking into account the N_2O-NO_y correlation uncertainty of Michelsen et al. (1998) the 1-D-simulation cannot reproduce simultaneously NO_2 and HNO_3 in the particular layer of a possible previous mixing event. Actually the correlation curves of Michelsen et al. (1998) determined on given latitude bands cannot account for a full description a N_2O-NO_y correlation within a layer containing mixed air from tropical and mid- latitudes.

7. Conclusions

We have used in situ observations of N_2O, NO_2 and HNO_3 by the SPIRALE balloon-borne instrument to test our ability to reproduce the observed NO_y partitioning at mid-latitudes. In a first part we have used the Reprobus 3-D CTM computed with the most recent kinetics data from the JPL recommendation and driven by the meteorological parameters from ECMWF. Discrepancies appear between the simulation and the measurement of N_2O when transport calculations are conducted with the ECMWF 6-hourly operational analysis widely used in the scientific community. This affects the modelling of NO_2 and HNO_3 with in particular an underestimation of the NO_2/HNO_3 ratio. The comparisons for N_2O are improved at all altitudes when transport calculations are driven by 3-hourly wind data. This result is consistent with the analysis of Legras et al. (2005) who shows much better agreement between ER-2 in situ observations and distributions of N_2O calculated using such 3-hourly wind fields. From this improved simulation, more realistic N_2O, NO_2, and HNO_3 profiles are calculated by Reprobus. However, the vertical feature observed by SPIRALE around 27 km in the N_2O profile

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cannot be reproduced by the 3-D CTM. This feature is attributed to a previous mixing event which is beyond the capabilities of the model at its current horizontal and vertical resolution.

The best results regarding the partitioning of NO_y are obtained by constraining the 1-D version of model with the observed profile of N_2O and the corresponding total NO_y deduced from established N_2O-NO_y correlations. In these conditions, our model simulations show that the observed mid-latitude NO_2/HNO_3 ratio can be reproduced with excellent agreement at all stratospheric altitudes. Modelling the NO_y partitioning with the best accuracy relies at least on a satisfying simulation of N_2O and thus of total NO_y. This result is consistent with the conclusions of Dufour et al. (2005) who constrained their model for the Arctic summer period with the sum of the measured NO_y species. It also suggests that discrepancies found between observations and modelling of the NO_y partitioning at mid-latitudes mainly originate from transport effects rather than general knowledge of the stratospheric chemistry.

The problem of transport calculation may also affect the modelling of diabatic descent inside the polar vortex where disagreements appear when comparisons are performed between models and satellite observations (e.g. Ricaud et al., 2005). A next step of our work is to make comparisons at a global scale and for long time series using satellite data such as those of ODIN and ENVISAT.

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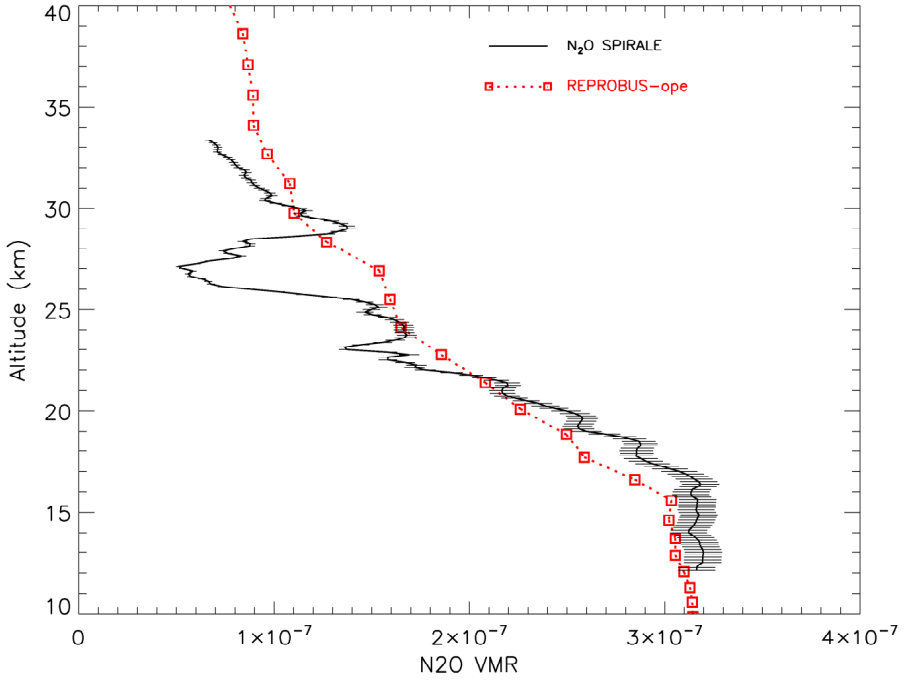

Fig. 1. In situ volume mixing ratios (VMRs) of N_2O measured by the SPIRALE instrument on 2 October 2002 at mid-latitudes (black line) and compared to the VMRs simulated by the Reprobus 3-D CTM at the time of SPIRALE observations (08:00 UT) and obtained at the grid point closest to the measurement position (red line). The model is computed using ECMWF operational analysis data. For more clarity the measurement error bars are represented every 100 m.

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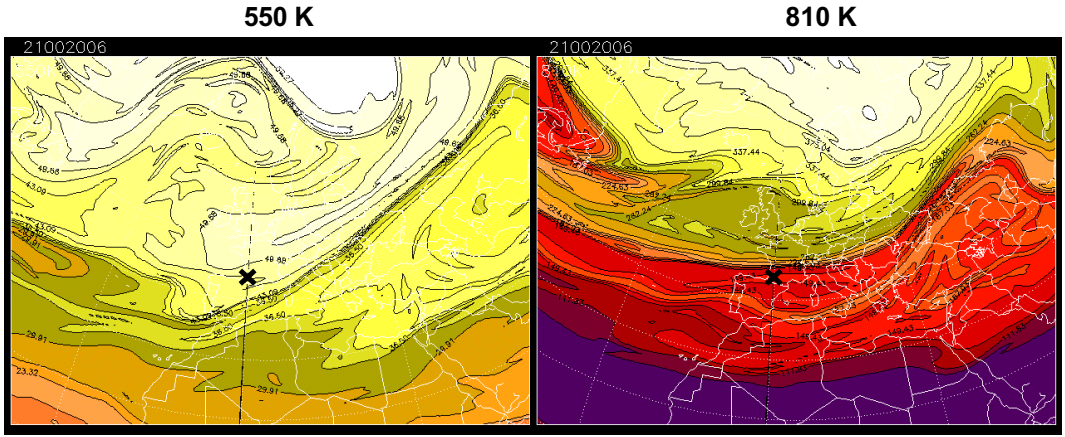

Fig. 2. Potential Vorticity (PV) isocontours calculated by the MIMOSA high-resolution advection model at 06:00 UT on 2 October 2002 at: **(a)** 550 K (about 22.5 km); and **(b)** 810 K (about 30 km). The red regions denote air masses from tropical latitudes. The black cross denotes the SPIRALE instrument location.

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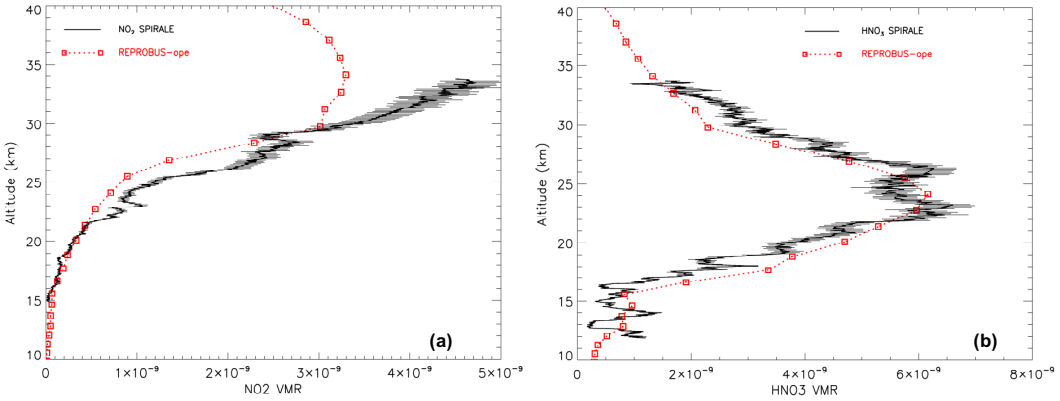

Fig. 3. Comparison between measured vertical profiles of NO_2 **(a)** and HNO_3 **(b)** on 2 October 2002 at mid-latitudes (black lines) and profiles simulated by the Reprobus 3-D CTM at 08:00 UT and a solar zenith angle of about 70° (red lines). The model is computed using ECMWF operational analysis data.

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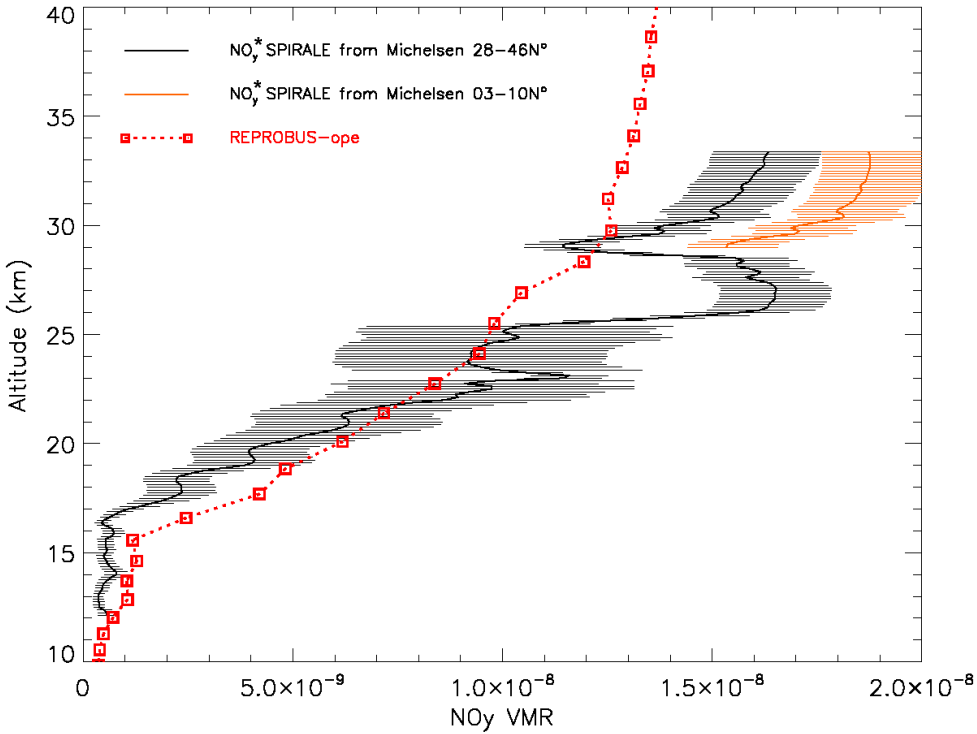

Fig. 4. Vertical profiles of reconstructed NO_y* compared to the Reprobus model output on 2 October 2002 (red line). Black curve: NO_y* profile inferred from the N_2O-NO_y correlation determined by Michelsen et al. (1998) in the 28–46° N latitude band. Orange curve: NO_y* profile inferred from the correlation valid in the 3–10° N latitude band (only represented above 29 km where the air seems to mostly originate from low latitudes).

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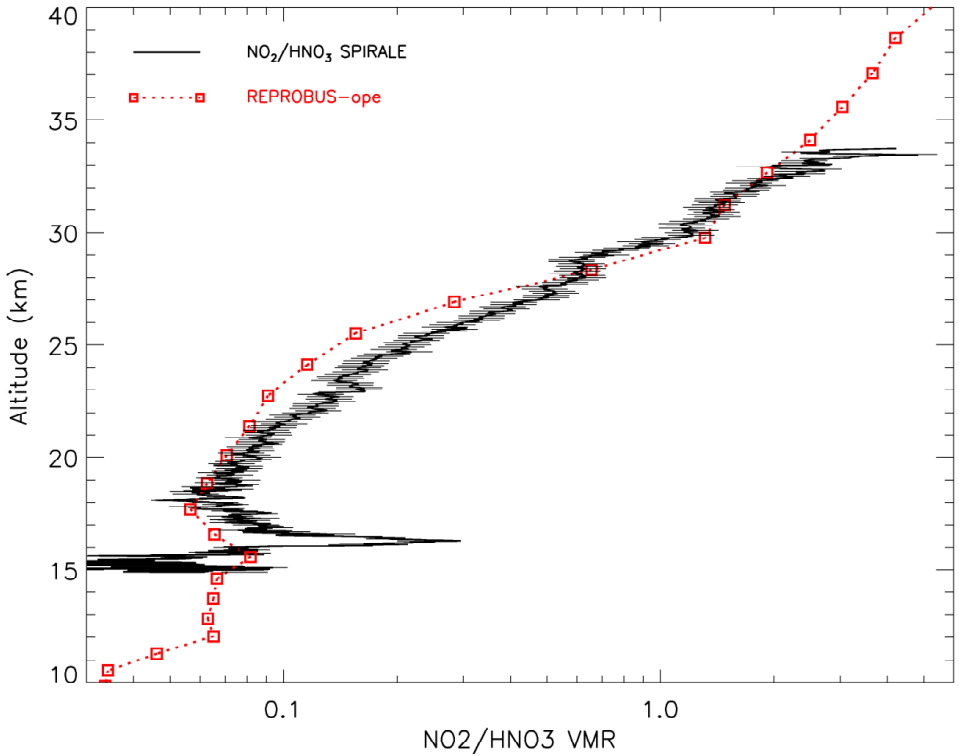

Fig. 5. NO_2/HNO_3 ratio measured by SPIRALE (black line) and calculated by Reprobus 3-D CTM at 08:00 UT (red line). The model is driven by ECMWF 6-hourly operational analysis.

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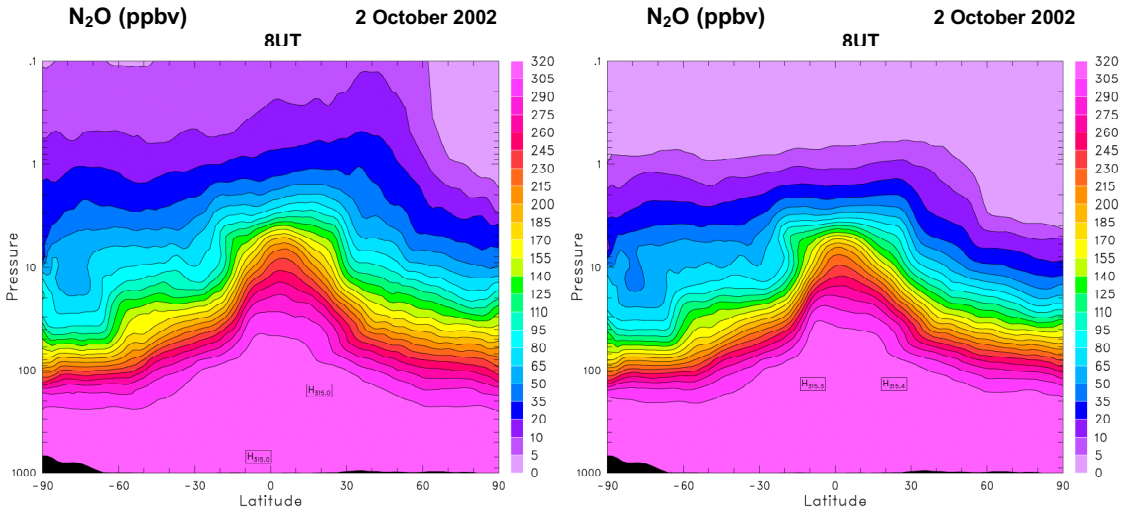

Fig. 6. N_2O zonal means simulated by Reprobus on 2 October 2002 at 08:00 UT. **(a)** Results obtained using 6-hourly ECMWF operational analysis data; **(b)** Results obtained using 3-hourly analysed and forecast data (see text).

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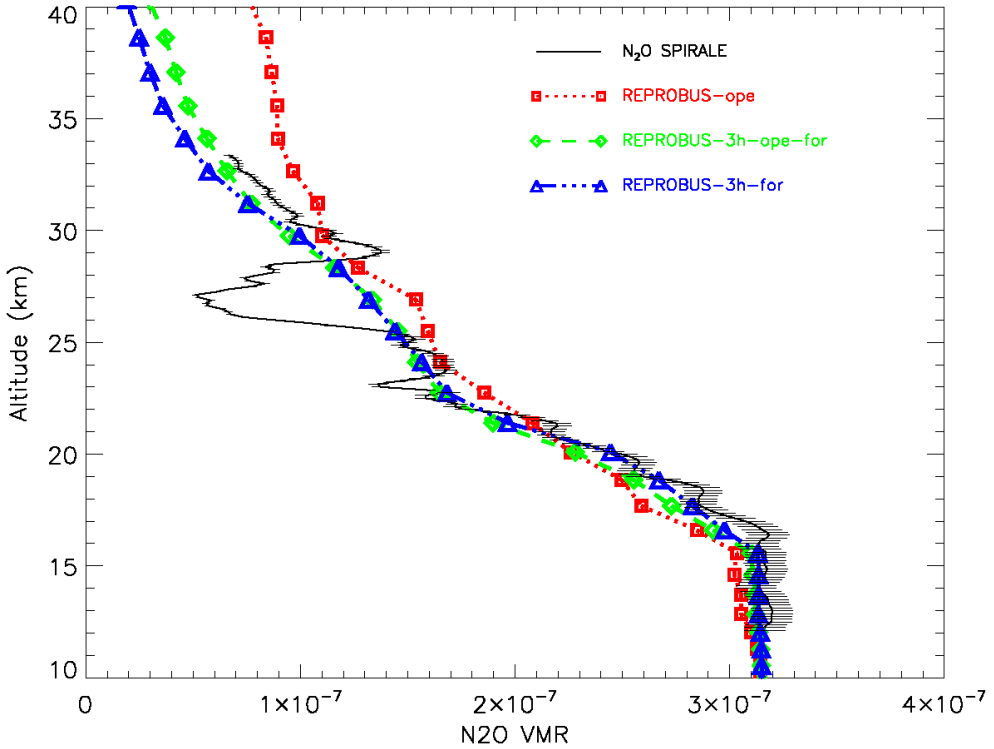

Fig. 7. Same as Fig. 1 but the comparison is made with the results of three model simulations. Red line: 6-hourly operational analysis (Reprobus-ope); green line: 3-hourly data obtained by interleaving operational analysis with forecasts (Reprobus-3h-ope-for, see text); blue line: 3-hourly forecasts available since 2002 (Reprobus-3h-for).

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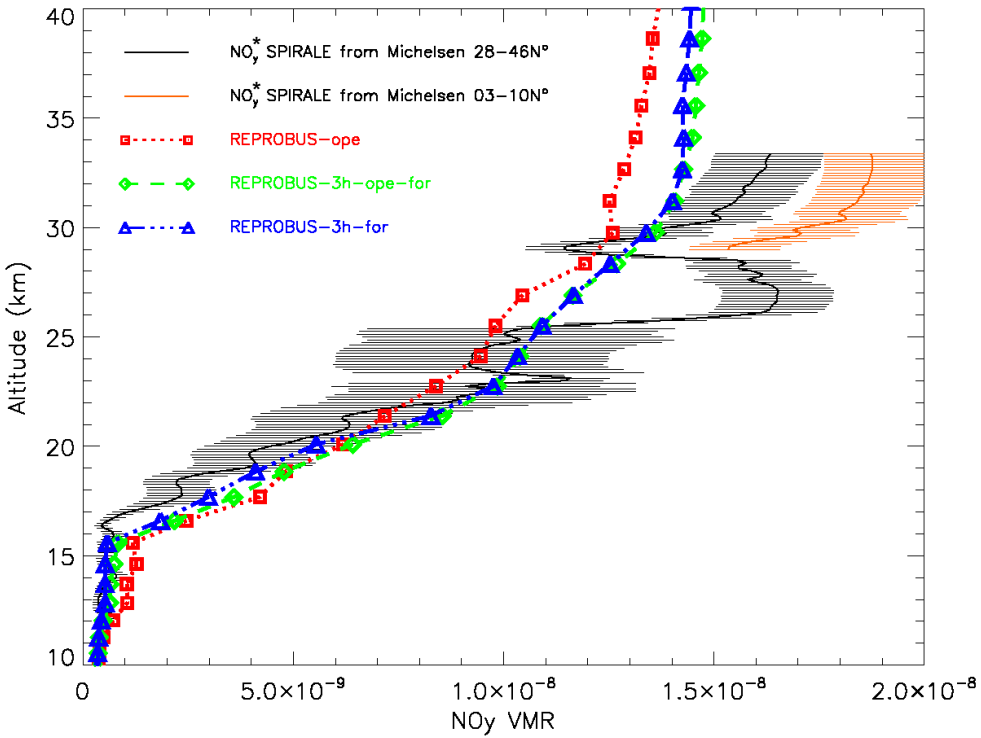

Fig. 8. Same as Fig. 4 but the comparison is made with the results of the three model simulations. Red line: 6-hourly operational analysis (Reprobus-ope); green line: 3-hourly data from operational analysis and forecasts (Reprobus-3h-ope-for, see text); blue line: 3-hourly forecasts (Reprobus-3h-for).

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Simulation of the vertical structure of N_2O, NO_2 and HNO_3

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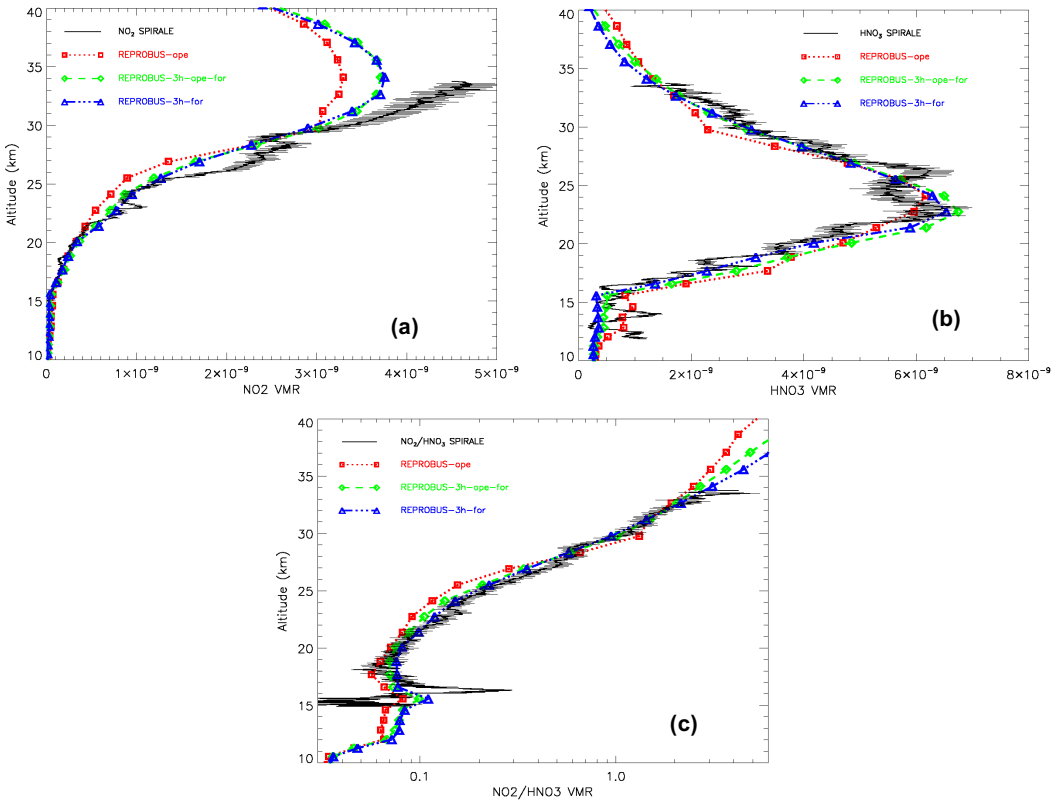

Fig. 9. NO_2 **(a)** and HNO_3 **(b)**: same as Fig. 3 but the comparison is made with the results of the three model simulations (Reprobus-ope, Reprobus-3h-ope-for and Reprobus-3h-for). NO_2/HNO_3 ratio **(c)**: same as Fig. 5 but the comparison is made with the results of the three model simulations.

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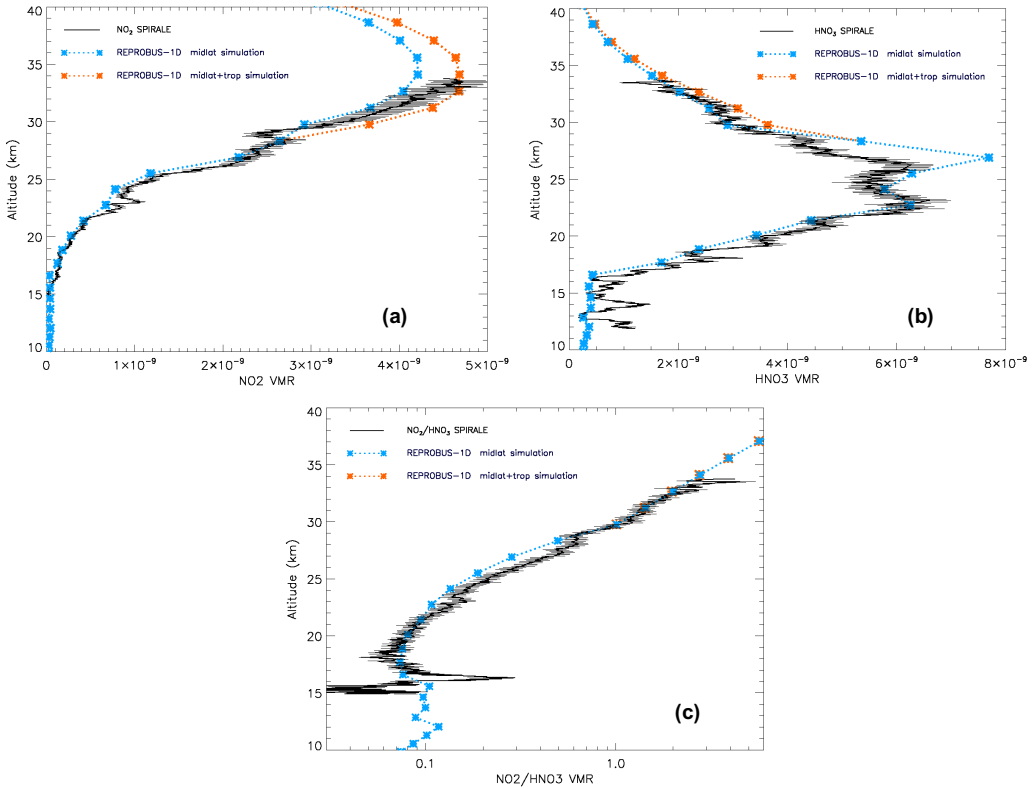

Fig. 10. NO_2 **(a)**, HNO_3 **(b)** and NO_2/HNO_3 ratio **(c)** measured by SPIRALE (black curve) and simulated by Reprobus. The model is here constrained by the measured profile of N_2O and the NO_y* deduced from the N_2O-NO_y correlation. Blue curve: Reprobus-1D-midlat experiment, NO_y* profile inferred from the correlation valid in the 28–46° N latitude band. Orange curve: Reprobus-1D-midlat-trop experiment, NO_y* profile inferred from the correlation valid in the 3–10° N latitude band, only shown above 29 km where the air seems to mostly originate from low latitudes.

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Simulation of the vertical structure of N_2O, NO_2 and HNO_3

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