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Vertical distribution of nighttime stratospheric NO₂ from balloon measurements: comparison with models

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Abstract. Vertical distributions of NO₂ and O₃ mixing ratios and the aerosol extinction coefficient were measured by night between 18 and 32 km altitude (9-80 hPa) at mid latitudes using the balloon-borne instrument AMON on March 24, 1994. The NO₂ profile is compared with results of simulations involving the REPROBUS 3D Chemical-Transport Model and a Lagrangian model in which the ozone mixing ratio and the aerosol surface area are initialized using AMON measurements (other mixing ratios are initialized with REPROBUS). As confirmed by Lidar observations, the surface areas were larger than the monthly and zonally averaged SAGE 2 data available for March 1994 at 45° N. The Lagrangian model shows relatively good agreement with AMON results for pressure higher than 40 hPa and smaller than 15 hPa, but the computed NO₂ value is too high between 15 and 40 hPa. This seems to indicate that heterogeneous reactions involving the NO_y species in the aerosol layer are still incompletely understood.

Introduction

Previous work [e.g. Hofmann and Solomon, 1989; Brasseur and Granier, 1992] has shown that the vertical NO₂ distribution is very dependent upon the sulfate aerosol content in the lower stratosphere. This dependence is based on the high probability of heterogeneous hydrolysis of N₂O₅ in these aerosols and its conversion to HNO₃. Several measurements of the nitrogen species partitioning have shown that best agreement with the models is achieved when this reaction is taken into account [McElroy *et al.*, 1992; Rinsland *et al.*, 1994; Webster *et al.*, 1994]. However, the assumed probability coefficient ($\gamma = 0.1$) has been found in some cases to be too high [McElroy *et al.*, 1992; Toumi *et al.*, 1993] and, recently, Renard *et al.* [1996] have shown that discrepancies exist between the results of a box model and vertical NO₂ distribution measured in the aerosol layer on October 1993 at mid-latitude, even when assuming hydrolysis of N₂O₅.

Here we present new measurements of NO₂ concentration in the aerosol layer that were made at mid latitude by night using the balloon-borne instrument AMON during the Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME) in March 1994. Ozone and aerosol extinction coefficient profiles were also obtained by AMON. Measurements are compared with simulations of a Lagrangian model initialized with outputs of a 3D Chemical-Transport Model and constrained with the ozone concentrations and aerosol surface area derived from AMON data.

Observational method and vertical profiles

AMON (French acronym for "Absorption par Minoritaires Ozone et Nox") is composed of a 20-cm Cassegrain telescope, a grating spectrometer designed for continuous coverage of the UV and visible wavelength domains, and a CCD detector [Naudet *et al.*, 1994]. Spectra are sampled at 0.14 nm per pixel. During the stratospheric flight, the instrument was mounted onboard the stabilized platform of the Geneva Observatory. Observations were made using the stellar occultation method, which allows retrieval of the slant column density of atmospheric species for different lines of sight below the balloon horizon.

The flight took place on March 24, 1994, from the launch site at Aire-sur-l'Adour, France (43.7° N, 0.3° W). Useful observations were made from 22:37 UT to 22:58 UT at a balloon altitude of 34.1±0.1 km, using the star Rigel (β Orionis). NO₂ absorption was observed around 440 nm, where its spectral signature is easily detectable. The slant columns were retrieved by applying a differential method, which allows the Rayleigh, aerosols and ozone contributions to be removed by a high-pass filter, and by using the NO₂ cross-sections measured by Coquart *et al.* [1995]. The contribution of aerosols was retrieved in the residuum of this spectral domain, and the ozone contribution was extracted in the Chappuis band (around 590 nm). A detailed description of the data processing is given by Renard *et al.* [1996].

The vertical profiles were obtained by applying a tangent ray-inversion technique. The O₃ and NO₂ concentrations were retrieved for the 18-32 km altitude range, together with the aerosol extinction coefficient at 440 nm (Table 1), the measured profiles being obtained at approximately 22:30 local time. NO₂ and ozone mixing ratios versus pressure were derived by using pressure and temperature measurements made during the balloon's ascent (see also Table 1). The measured aerosol extinction coefficient was converted to an aerosol surface area by using the conversion factor computations given by Jaeger *et al.* [1995] and available for March, 1994, at mid-

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latitudes (Jaeger, personal communication). The resulting aerosol surface area profile is shown in Figure 1, together with the profile derived from Lidar backscatter coefficients [Chazette *et al.*, 1995] measured at the Observatoire de Haute Provence (OHP, 43.9° N, 5.7° E) on March 23, 1994, at 20:30 UT (David, personal communication) and converted by using Jaeger factors: very good agreement is obtained between the two profiles. SAGE 2 data are available close to Aire-sur-l'Adour only on March 11 and April 5, nevertheless good agreement is obtained between the SAGE 2 extinction coefficient profile at 453 nm on April 5 (not shown here) and the AMON profile. The SAGE 2 profile on March 11 is significantly lower, indicating an increase in the aerosol content at Aire-sur-l'Adour on March 24 relative to the beginning of the month. Such an increase was also observed at OHP from March 13. The monthly and zonally averaged profile (Lenoble, personal communication) available for March 1994 at 45° N, is shown in Figure 1. It is mainly representative of the conditions prevailing at the beginning of March.

Modeling calculations

Two models have been used to establish a comparison with the AMON NO₂ profile:

- The 3D CTM REPROBUS, in which wind and temperature fields are prescribed every six hours by ECMWF analysis. Description of the REPROBUS chemical package, which covers 42 species, is given by Lefevre *et al.* [1994]. For simulation, the model was constrained by the monthly and zonally averaged aerosol surface area derived from SAGE 2 data (Figure 1); aerosols were not transported in this version of REPROBUS.

- A Lagrangian model, in which 47 species, 135 reactions in gas phase and 2 heterogeneous reactions are included [Lateltin *et al.*, 1994]. For our calculations the more important heterogeneous reaction is the hydrolysis of N₂O₅ for which the probability coefficient is assumed to be $\gamma = 0.1$. Hydrolysis of ClONO₂ is also included. With this model it is possible to compute the evolution of

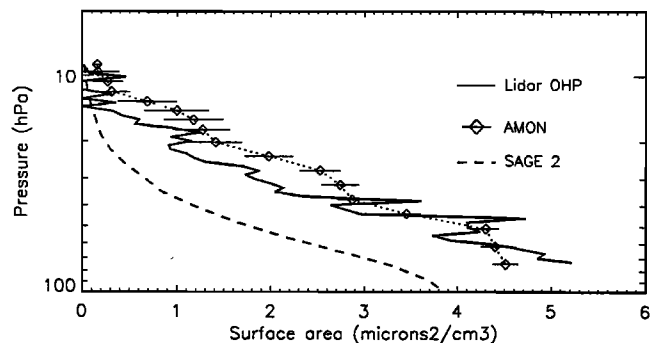


Figure 1. Aerosol surface areas derived from AMON measurements of the extinction coefficients compared with results derived from Lidar observations at OHP and from SAGE 2 (zonally and monthly averaged) available for 45°N in March 1994. Error bars on the aerosol surface areas derived from AMON observations are also shown.

species along trajectories of air-parcels that end at the exact location and time of the AMON measurements. Mixing ratios of the chemical species are initialized by REPROBUS outputs at the start of the trajectories, except for ozone for which the AMON mixing ratio is used (it is in fact very similar to the REPROBUS mixing ratio between 15 and 50 hPa). Aerosols are transported as passive tracers by maintaining their surface area, which is derived from AMON, constant along the trajectory. The trajectories (not shown here) follow the external edge of the polar vortex above about 20 km. They reach latitudes as high as 70°N about 4 days before their arrival at Aire-sur-l'Adour.

Ten-day trajectories have been computed; this is sufficient for the partitioning in the nitrogen family to adjust to the large aerosol surface areas used in the Lagrangian model compared with those used in the REPROBUS model. With these large aerosol surface areas, the reaction rates for the hydrolysis of N₂O₅ ranges from half-a-day to two days. To estimate the uncertainties in NO₂ concentrations due to possible errors on the trajectories followed by the air parcels, computations were

Table 1 . AMON measurements

Altitude (km)	Pressure (hPa)	Temperature (K)	NO ₂ concentration (10 ⁹ cm ⁻³)	O ₃ concentration (10 ¹² cm ⁻³)	Aerosol extinction coefficient (10 ⁻³ km ⁻¹)
32.0	8.90	220.5	1.760 ± 0.193	1.492 ± 0.178	0.018 ± 0.004
31.5	9.60	217.8	2.107 ± 0.318	1.561 ± 0.234	0.019 ± 0.056
30.8	10.64	217.1	2.425 ± 0.309	1.712 ± 0.246	0.040 ± 0.039
30.1	11.84	214.4	2.120 ± 0.302	1.845 ± 0.258	0.052 ± 0.052
29.4	13.13	212.5	2.275 ± 0.306	2.121 ± 0.238	0.125 ± 0.097
28.8	14.43	211.2	2.401 ± 0.381	2.521 ± 0.239	0.177 ± 0.113
28.1	15.89	210.4	3.121 ± 0.380	2.917 ± 0.261	0.229 ± 0.111
27.4	17.64	210.5	3.203 ± 0.390	3.294 ± 0.270	0.240 ± 0.109
26.5	20.22	211.0	2.590 ± 0.362	3.449 ± 0.274	0.328 ± 0.115
25.5	23.54	211.0	1.834 ± 0.334	3.710 ± 0.258	0.530 ± 0.122
24.5	27.43	210.5	1.765 ± 0.344	3.955 ± 0.244	0.744 ± 0.115
23.6	31.95	210.5	1.502 ± 0.314	4.340 ± 0.259	0.925 ± 0.122
22.5	37.46	211.0	0.873 ± 0.311	5.004 ± 0.287	1.150 ± 0.114
21.6	43.54	211.0	0.320 ± 0.254	5.167 ± 0.312	1.473 ± 0.119
20.5	51.29	210.3	0.136 ± 0.305	4.519 ± 0.281	1.970 ± 0.111
19.3	61.93	209.1	0.022 ± 0.370	4.202 ± 0.269	2.151 ± 0.133
18.1	74.66	210.8	0.015 ± 0.450	4.444 ± 0.299	2.359 ± 0.124

also made of eight trajectories that end close to the location of AMON measurements, respectively at ± 50 km in east-west and north-south directions, and ± 250 m on the vertical. The locations at the beginning of these trajectories were found to be very different, but the Lagrangian calculations have shown that the differences between the various computed NO₂ mixing ratios at the end of each trajectory are less than 10 per cent. This is because all the trajectories were very close to each other during the last three days.

Discussion

For the comparison between model results and NO₂ measurements to make sense, it is necessary that the total NO_y concentration be well simulated in the REPROBUS model, the outputs of which are used to initialize the Lagrangian calculations. Measurements of the total column of the major NO_y species, HNO₃ and ClONO₂, were made at Jungfraujoch (46.5° N, 8.0° E) in the Swiss Alps, not too far from Aire-sur-l'Adour (43.7° N, 0.3° W), on March 20, 21 and 22, 1994, with Fourier-transform-spectrometers [Rinsland *et al.*, 1996]. Figure 2 shows very good agreement between the REPROBUS results and a) HNO₃ column measurements on March 20/21, b) ClONO₂ column measurements on March 21/22. Model outputs are just slightly above the measured values of the HNO₃ column on March 22 and of the ClONO₂ column on March 20. Moreover, the day-to-day variation of the columns is well reproduced. Although no definitive conclusions can be drawn from this very partial comparison, the good agreement of measured and modeled values bolsters our confidence in the NO_y behavior simulated by REPROBUS for this period.

Figure 3 gives a comparison between the NO₂ AMON profile and the results of the Lagrangian simulation. It is seen that:

- Between 10 and 15 hPa, there is a good agreement between the AMON measurements and the Lagrangian model results. In this pressure range, the aerosol content of the atmosphere is very low (Figure 1) and the results are close to those that would be obtained when assuming only reactions in the gas phase. This good agreement is another

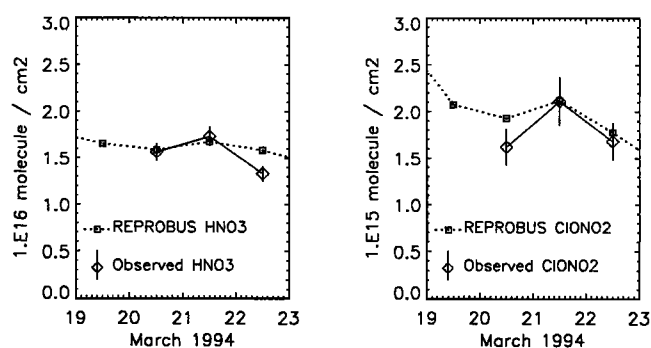


Figure 2. Comparison between REPROBUS outputs and measurements of HNO₃ and ClONO₂ columns measured at Jungfraujoch (46.5° N, 8.0° E). Both sets of data are diurnal averaged values. Error bars on measurements are shown.

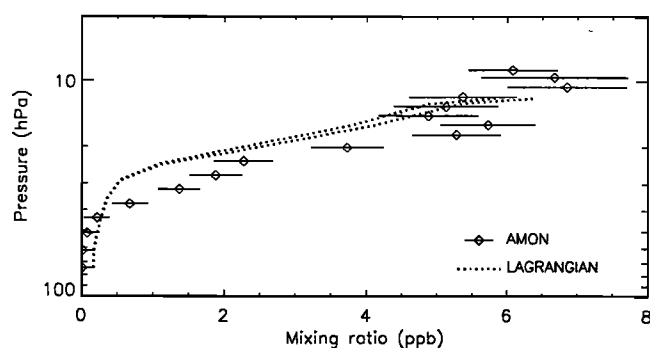


Figure 3. Comparison between AMON NO₂ measurements and results from Lagrangian simulations. Uncertainties on model results due to uncertainties on the trajectories of the air parcels (as discussed in the text) are not shown here. The two dotted curves represent the minimum and maximum NO₂ mixing ratios computed in assuming uncertainties on the aerosol surface areas derived from AMON measurements shown in Figure 1.

clear indication that NO_y behavior and photochemistry in the gas phase are probably well simulated in the model.

- Between 15 and 40 hPa, some discrepancies appear between the AMON measurements and the Lagrangian results. The maximum disagreement is observed from 35 to 25 hPa (23-25 km), where the measured NO₂ mixing ratio is 2.8 ± 0.6 times the computed mixing ratio. In this pressure range, the aerosol surface area is relatively large (between 1.0 and 3.5 $\mu\text{m}^2 \cdot \text{cm}^{-3}$).

- At 42 hPa, assuming the large relative uncertainty on the measurement, there is good agreement between the AMON and Lagrangian results. For pressures higher than 50 hPa, AMON gives only upper limits for the mixing ratio. Model results are not in disagreement with these values. In this pressure range, the aerosol surface area is large (more than 4 $\mu\text{m}^2 \cdot \text{cm}^{-3}$).

Three explanations can be proposed for the observed disagreement in the 15-40 hPa range. The first of these relates to the computed NO_y mixing ratios; assuming larger mixing ratios in the Lagrangian model could explain the disagreement. We nevertheless think that this is unlikely. Figure 4 shows the NO_y mixing ratio profile

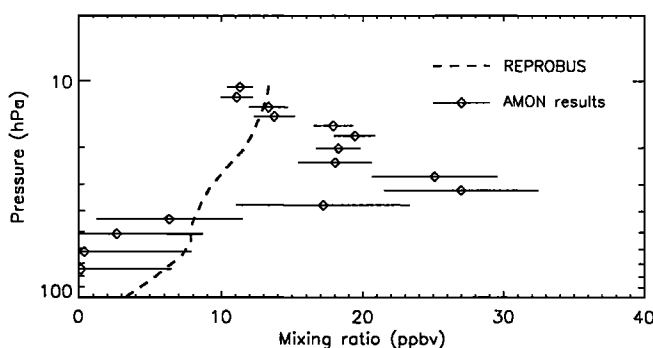


Figure 4. NO_y mixing ratios computed by REPROBUS and used to constrain the Lagrangian calculations (dashed line) and NO_y profile necessary to explain the AMON measurements of NO₂ mixing ratios shown on Figure 3 (full line). Calculation of the error bars takes into account the uncertainties on the measured NO₂ mixing ratios.

computed by REPROBUS at the start of the trajectories, as well as the profile needed to explain the measured NO₂ profile: it appears that the mixing ratios needed in the 35-25 hPa range (more than 20 ppbv) are quite unrealistic.

Errors in the assumed aerosol surface areas could also explain the disagreement. Figure 3 shows negligible uncertainties on the NO₂ profile due to uncertainties on the measured extinction coefficients by AMON, but larger errors could result from uncertainties on the assumed aerosol size distribution to convert aerosol extinction to surface area. Such errors are inherent to all remote optical techniques. Nevertheless, calculations show that errors would have to be large; between 35 hPa and 25 hPa, a surface area as low as $0.7 \mu\text{m}^2 \cdot \text{cm}^{-3}$ would be needed instead of $2.6 \pm 0.3 \mu\text{m}^2 \cdot \text{cm}^{-3}$.

We think it more likely that the disagreement is due to a still incomplete understanding of the heterogeneous reactions which take place on sulfate aerosols or, as suggested by Lary *et al.* [1996], to the presence in the stratosphere of soot from commercial air traffic. Soot particles have the ability to convert HNO₃ to NO [Thlibi and Petit, 1994] and have been measured by aircraft flying at 20 km [Blake and Kato, 1995]. They could be present at higher altitude, up to 25 km, where the maximum disagreement between model results and measurements of NO₂ is observed.

Finally, it should be pointed out that the maximum disagreement observed between measurements and model for March 24, 1994, is located in the same altitude range (23-25 km) as the disagreement observed on October 1993 at the same location [Renard *et al.*, 1996]. It is clear that other studies are needed to understand this phenomenon more clearly.

Conclusion

Measurement of the NO₂ mixing ratios at mid-latitudes by night in March 1994 have shown these values to be higher than the model mixing ratios in the 15-40 hPa pressure range. The discrepancy is maximum in the 23-25 km altitude range. This result is consistent with previous measurements made at the same location in October 1993 and could be due to a still incomplete understanding of the heterogeneous reactions on sulfate aerosols. It could also support, at least qualitatively, the hypothesis of the influence of soot particles on the partitioning of species in the NO_x family. Other studies are necessary to resolve this problem.

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