Origin of the January–April 2004 increase in stratospheric NO2 observed in the northern polar latitudes

Jean-Baptiste Renard, Pierre-Louis Blelly, Quentin Bourgeois, Michel Chartier, Florence Goutail, Y.J. Orsolini

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Jean-Baptiste Renard,[1] Pierre-Louis Blelly,[1] Quentin Bourgeois,[1] Michel Chartier,[1] Florence Goutail,[2] and Y. J. Orsolini[3]

Received 10 December 2005; revised 13 April 2006; accepted 1 May 2006; published 1 June 2006.

[1] Large increase in stratospheric NO_2 content has been observed during the 2003–2004 Arctic winter. The first one, in early November 2003 is well documented and is due to a strong solar protons event. A second event occurred on January 22, 2004, leading to a large amount of NO_2 in the lower mesosphere. This second event can be analyzed using data from nighttime satellite measurements performed by the GOMOS and MIPAS instruments onboard Envisat, and by ground based column measurements performed by SAOZ. It seems that in-situ production of NO_2 is located at an altitude of around 60 km associated with the precipitation of electrons with energy of a few hundred keV. These electrons originated from the high latitudes magnetosphere, and are associated with a solar coronal mass ejection. Therefore, a particular nighttime chemistry in the lower mesosphere is proposed to explain the measurements.
Citation: Renard, J.-B., P.-L. Blelly, Q. Bourgeois, M. Chartier, F. Goutail, and Y. J. Orsolini (2006), Origin of the January–April 2004 increase in stratospheric NO_2 observed in the northern polar latitudes, *Geophys. Res. Lett.*, *33*, L11801, doi:10.1029/2005GL025450.

1. Introduction

[2] Many satellite instruments have observed abnormal strong increases in NO_2 content in the middle and upper northern polar stratosphere during winter 2003–2004 and the beginning of spring 2004. These observations, with maximum concentration at altitudes of around 45 km, were obtained at night using the GOMOS (Global Ozone Monitoring by Occultation of Stars) instrument [*Seppälä et al.*, 2004] and MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) instrument onboard the Envisat satellite [*Orsolini et al.*, 2005], and at sunset/sunrise using POAM (Polar Ozone and Aerosol Measurements) III and SAGE (Stratospheric Aerosol and Gas Experiment) III [*Randall et al.*, 2005], ACE [*Rinsland et al.*, 2005], and HALOE [*Natarajan et al.*, 2004]. The increases were attributed to solar flare events, and associated with proton events that occurred at the end of October and the beginning of November 2003; these events were some of the strongest ever recorded. The effect of high-energy solar proton on chemistry of the middle atmosphere, leading in particular to production of NO_2, is discussed by *Jackman and McPeters* [2004].

[3] The October/November 2003 event is well documented and interpreted. On the other hand, the persistence of NO_2 in the middle stratosphere (above 40 km) during the first months of 2004, detected using satellite instruments during sunset/sunrise, is not clearly understood. Because of the variability of the latitude coverage of POAM III, SAGE III and HALOE, resulting in gaps in the temporal coverage at the beginning of 2004, and the lack of data for altitudes above 50 km, the link between this persistence and the 2003 event is not established. These instruments could have missed another event that could have occurred at the beginning of 2004.

[4] Fortunately, MIPAS and GOMOS instruments onboard Envisat allow continuous observations of the polar stratosphere. Moreover, these instruments have enabled retrieval of vertical profiles of NO_2 during night in the upper stratosphere and lower mesosphere since 2002. We propose here to use these data in order to estimate the content of this species throughout the 2003–2004 winter, and to search for a possible second event.

2. GOMOS and MIPAS Measurements

[5] GOMOS is an UV-visible spectrometer using stars as light source; the vertical sampling interval is around 1 km, from altitudes of 135 km down to the lower stratosphere. The data are available for the 2003 and 2004 period, although data are missing from 1st January 2004 to end of March 2004, with little data available at the beginning of March. It should be noted that all the GOMOS measurements are being reprocessed, and the new data, including the missing data from 2004 will be available soon for future analysis. MIPAS is an infrared limb sounder; the retrieval of the verticals profiles (version 4.61) is difficult in the middle and upper stratosphere; thus, the vertical sampling interval is 5–7 km in the 40–65 km altitude range. Due to a technical problem, the instrument was switched off after March 25, 2004.

[6] All the nighttime measurements presented here were obtained in the first part of the night (22 UT ± 2). The GOMOS profiles are smooth and can be used individually. On the other hand, the MIPAS profiles exhibit significant errors bars, and must be averaged.

3. Increases in NO_2 in the Winter of 2003–2004

[7] Figure 1 presents two NO_2 profiles obtained in the stratosphere over Scandinavia on March 4, 2004 by GOMOS and MIPAS. These profiles have been validated

[1] Laboratoire de Physique et Chimie de l'Environnement/CNRS, Orléans, France.
[2] Service d'Aéronomie/CNRS, Verrières le Buisson, France.
[3] Norwegian Institute for Air Research, Kjeller, Norway.

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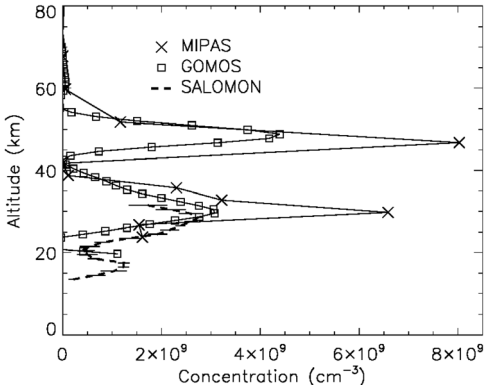

Figure 1. Typical NO_2 profile obtained in the stratosphere above Scandinavia on March 4, 2004, around 22:00 UT by GOMOS, MIPAS and balloon-borne SALOMON instrument. The unrealistic GOMOS data below 20 km are removed.

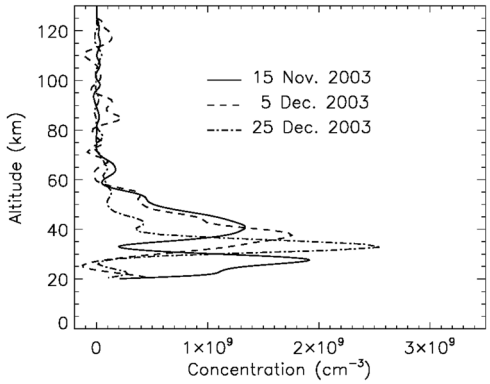

Figure 2. NO_2 measurements by GOMOS at the end of 2003, inside the Arctic Circle (latitude 72° ± 1°). No increase is detected in the mesosphere.

by balloon-borne measurements performed by the nighttime UV-visible spectrometer SALOMON [*Renard et al.*, 2000] in the 15–40 km altitude range. Although the validation of GOMOS and MIPAS measurements by balloon-borne instruments will be reported in future papers, some preliminary conclusions can be pointed out. The GOMOS measurements are unrealistic below 20 km and are not plotted in Figure 1. At the other altitudes, absolute values of concentrations are in excellent agreement between GOMOS and SALOMON, taking into account a vertical offset of 1.5 km that could be due to smoothing procedures in the GOMOS and SALOMON data reduction (this will be discussed in detail in an upcoming paper dedicated to the validation of GOMOS by balloon-borne instruments). The altitudes of the NO_2 increases are also in good agreement between GOMOS and MIPAS. On the other hand, the absolute values of the increases in concentrations are overestimated by a factor 2 on the MIPAS profile. Then, in the following, we can be confident about the estimation of the altitudes of increases (with uncertainties typically less than 2 km), while the MIPAS concentrations values must be considered cautiously.

[8] The altitude of the maximum of the NO_2 concentration at an altitude of 30 km is typical of the NO_2 content at the end of polar winter. On the other hand, the second maximum concentration at 50 km is abnormal. It is hard to believe that this concentration excess is the same as the one observed at similar altitude at the end of 2003. The excess concentration remaining at a few 10^9 molecules per cm^{-3} and staying at an altitude of about 50 km seems to be in contradiction with a downward transport during October-November 2003 pointed out by *Seppälä et al.* [2004]. In addition, one can speculate that the 2004 increase could be the result of downward transport of NO_2 produced in the (upper) mesosphere during the October/November 2003 event at altitudes too high to be retrieved from most of the satellite measurements. Fortunately, GOMOS instrument can perform mesospheric measurements when bright stars are used. Figure 2 presents some GOMOS measurements at the end of 2003 inside the Arctic Circle at altitudes up to 130 km. No mesospheric NO_2 increase has been detected, ruling out the hypothesis of mesospheric downward transport. Therefore, a new event causing the 2004 increase must be searched for.

[9] The altitude of the NO_2 enhancement in the upper stratosphere and lower mesosphere is presented in Figure 3 for the October 2003–April 2004 period, using both MIPAS and GOMOS data for latitudes higher than 65°N. The daily-averaged MIPAS data are used in order to reduce the scatter, but the poor vertical resolution of the instrument produces artificial steps in the plot. Nevertheless, some unambiguous conclusions can be drawn. The decrease of maximum concentration altitude is confirmed for the end of 2003. Then, a second sudden increase appears around January 20, 2004, 15 km higher than the first one (~60 km instead of ~45 km). The maximum concentration value is at least three times greater for the second event than for the first one. Converted to mixing ratios, more than 0.2 ppmv of NO_2 has been detected in January 2004, instead of about 40 ppbv in late 2003. For both events, a downward transport occurs from mesosphere to middle stratosphere, with a descent rate of 250 ± 50 meters per day, as shown also by *Orsolini et al.* [2005].

[10] The analysis of the latitude dependence of the two concentration increases using both MIPAS and GOMOS data shows that the increases are located at latitudes above

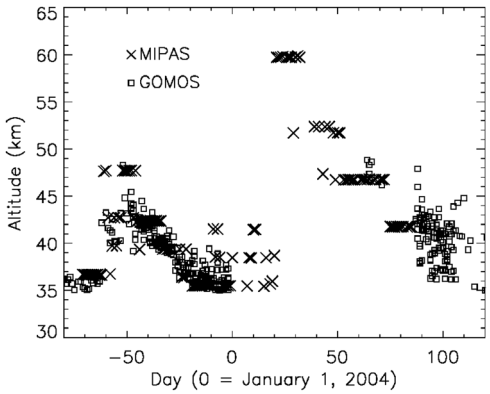

Figure 3. Evolution of the altitude of the upper NO_2 maximum concentration, from October 2003 to April 2004, using GOMOS and MIPAS data for latitude higher than 65°N. The poor vertical resolution of MIPAS induces artificial steps.

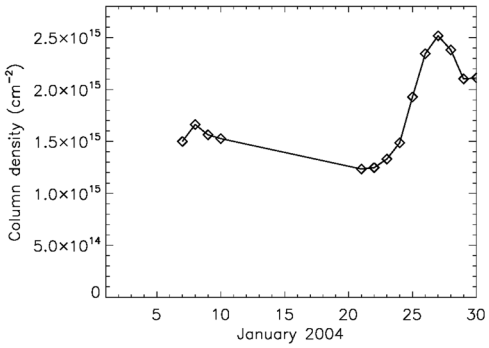

Figure 4. Vertical column density of NO_2 from ground-based UV-visible spectrometer SAOZ at Sodankyla, Finland.

65°N, thus in the vicinity of the northern auroral region. In particular, no NO_2 increase was detected by MIPAS in the southern polar region during the same period.

[11] Furthermore, no strong solar protons event occurred in January 2004. Then one can conclude that the origin of the second event must differ from the first one.

4. Date of the January 2004 Event

[12] The exact date of the beginning of the NO_2 enhancement is not easily detectable in the MIPAS data. On the other hand, UV-visible ground based-measurements of scattered sunlight inside the Arctic Circle can be used in order to monitor the NO_2 increase. Figure 4 presents the NO_2 vertical column densities obtained by the UV-visible spectrometer SAOZ [*Pommereau and Goutail*, 1988] from Sodankyla, just inside the Arctic Circle, during January 2004. The "background" values of the order of 1.5×10^{15} cm^{-2} at the beginning of January can be attributed to the usual amount of NO_2 in the troposphere and in the stratosphere at this time of the year. The SAOZ data show that the increase is detectable after January 22, 2004.

5. Origin of the Event

[13] Two solar coronal mass ejections were detected on January 20 and 21, 2004. At the Earth orbit, they induce a geomagnetic storm with a geomagnetic impulse occurring at 01:40 UT on January 22. This was referenced as a major event, but the induced perturbation was much less intense than the November 2003 event. A close examination of the data of the geostationary satellites GOES shows that there is no enhancement of the flux for protons of energies higher than 4 MeV, as it was the case for the 2003 event [see *Jackman et al.*, 2005, Figure 1]. This has been confirmed by the electrons and protons measurements of SAMPEX satellite and the NOAA satellites POES during the perturbation (data are available on http://www.ngdc.noaa.gov/stp/NOAA/noaa_poes.html). Figure 5 shows the mean integrated fluxes for electrons and protons obtained by POES at the maximum of the perturbation above 78° geographic latitude in both hemispheres on January 22. There is no significant difference between the measurements made by the three POES satellites (POES 15, POES 16 and POES 17), which moreover shows no asymmetry between the two hemispheres. The main point is that the core of the particle flux is below

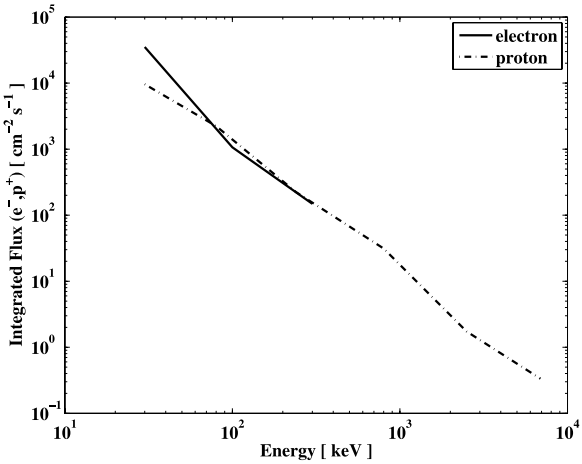

Figure 5. Integrated flux for electrons (full line) and protons (dashed line) averaged over POES-15, POES-16 and POES-17 satellites for measurements at geographic latitude higher than 78° in both hemispheres, on January 22, 2004.

1 MeV for both kinds of particles. Above 1 MeV, the atmospheric impact of proton flux becoming negligible since the flux is lower than 10 particles per cm^2 per second. On the other hand, the flux is 100 times higher below 100 KeV (Figure 5). Due to the energy of the particles, we can affirm that electrons and protons originate from the magnetosphere and not directly from the Sun. Moreover, since the radiation belts are located at lower latitudes, the particles are originated from the external magnetosphere.

[14] Figure 6 presents the altitude of penetration versus the energy of precipitating particles (electrons or protons), assuming a monoenergetic beam. The electron results were obtained using the ionospheric numerical model TRANSCAR [*Blelly et al.*, 2005], and the protons results come from the National Institute of Standards and Technology

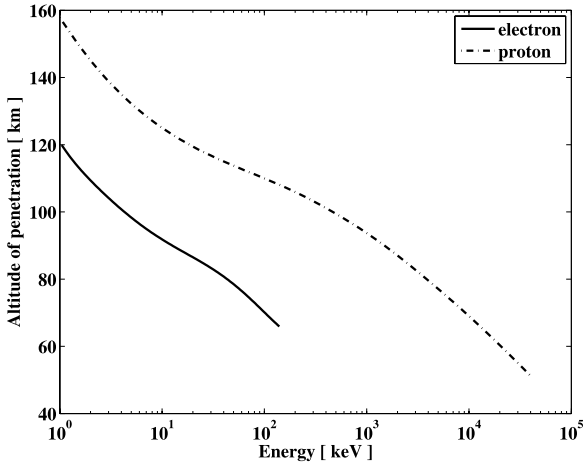

Figure 6. Altitude of penetration of precipitating particle as a function of the energy, assuming a monoenergetic beam. The curve for electrons (full lines) has been obtained using TRANSCAR ionospheric model and the curve for protons (dashed lines) is derived from NIST PSTAR database.

and more specifically the PSTAR databases [*International Commission on Radiation Units and Measurements*, 1984, 1987] From this figure, it is clear that protons with energy below 4 MeV do not reach altitude below 90 km, while electrons with energy higher than 150 keV go below 70 km. Thus, the NO_2 increase observed at high latitude around 60 km in January 2004 cannot be associated to of a production induced by proton precipitation and consequently, the electrons are most likely to be the source of the production of NO_2 in the lower mesosphere. However, in this case, the energy involved is not sufficient to invoke a similar mechanism as in the stratosphere (the breaking of N_2 molecules by high energy protons). With such "low-energy" particles, the main process is the ionization of molecules, which is the basis of a chemical scheme involving ionospheric ions. These ionospheric ions belong to the *D* region, which is the most complex region of the ionosphere. Indeed, this region is characterized by the presence of positive clustered ions, negative ions and electrons [*Turunen et al.*, 1996] and is very sensitive to the sunlight. The ratio between negative ions and free electrons strongly depends on the illumination. In the darkness, almost all the electrons disappear and only negative ions are present [*Rodriguez and Inan*, 1994], whereas the opposite occurs during the day. It occurs that during the period of the event, the region of the atmosphere located above 75° in the northern hemisphere is in the darkness up to about 90 km. Thus an asymmetry is likely to be observed between the two hemispheres if the ionosphere is involved in the process. As a matter of fact, the observations on NO_2 show that both hemispheres are different, with no NO_2 enhancement in the southern hemisphere. This plays in favour of mechanisms involving electron impact and ionospheric chemistry, instead of proton impact.

[15] So, in the first instance, the production of NO_2 could be due to the lack of electrons, and then could be reinforced by chemical reactions involving the negative ions. Thus, such a mechanism would represent a new scheme of production of this molecule; this requires further investigation, in particular with numerical simulations. The important point about the observations is that there is an asymmetry between northern and southern hemispheres, with the summer hemisphere showing no production of NO_2. This indicates that this production is related to the darkness.

[16] The same phenomenon could have occurred also at the end of May 2003, when a strong NO_2 increase was detected within the Antarctic Circle [*Funke et al.*, 2005]. Although the authors proposed a NO_2 production in the lower thermosphere by background auroral electrons, there are similarities between this event and the January 2004 event with the occurrence of a "low" energy electrons event at the end of May 2003, and for the altitudes of the two NO_2 increases.

6. Conclusion

[17] We have proposed here that the January 2004 mesospheric NO_2 enhancement could be due to an in-situ production involving "low" energy electrons and a particular chemistry in the *D* region of the ionosphere. The exact location and altitude of the event, as well as its spatial and temporal evolutions, would be better analyzed when all the 2004 GOMOS data will be available and validated. Such NO_2 production could have a strong consequence for polar ozone chemistry, and could be taken into account for future modeling calculations. Then, it will be necessary to better document the occurrence and the intensity of such events. This will be done in the near future using up-coming long-term series of NO_2 measurements in the mesosphere available from Envisat instruments, and also by investigating the chemical scheme itself.

[18] **Acknowledgments.** The authors would like to thank M. Pirre, G. Berthet, and B. Funke for valuable scientific discussions, and the space French agency CNES balloon launching team. The SALOMON flight was funded by ESA and CNES during the Envisat validation project.

References

Blelly, P.-L., C. Lathuillère, B. Emery, J. Lilensten, J. Fontanari, and D. Alcaydé (2005), An extended TRANSCAR model including ionospheric convection: Simulation of EISCAT observations using inputs from AMIE, *Ann. Geophys.*, *23*, 419–431.

Funke, B., M. López-Puertas, S. Gil-López, T. von Clarmann, G. P. Stiller, H. Fischer, and S. Kellmann (2005), Downward transport of upper atmospheric NOx into the polar stratosphere and lower mesosphere during the Antarctic 2003 and Arctic 2002/2003 winters, *J. Geophys. Res.*, *110*, D24308, doi:10.1029/2005JD006463.

International Commission on Radiation Units and Measurements (1984), Stopping powers for electrons and positrons, *Rep. 37*, Bethesda, Md.

International Commission on Radiation Units and Measurements (1987), Stopping powers and ranges for protons and alpha particles, *Rep. 49*, Bethesda, Md.

Jackman, C. H., and R. D. McPeters (2004), The effect of solar proton events on ozone and other constituents, in *Solar Variability and its Effects on Climate*, *Geophys. Monogr. Ser.*, vol. 141, 305–319, AGU, Washington, D. C.

Natarajan, M., E. E. Remsberg, L. E. Deaver, and J. M. Russell III (2004), Anomalously high levels of NO_x in the polar upper stratosphere during April, 2004: Photochemical consistency of HALOE observations, *Geophys. Res. Lett.*, *31*, L15113, doi:10.1029/2004GL020566.

Orsolini, Y. J., G. L. Manney, M. L. Santee, and C. E. Randall (2005), An upper stratospheric layer of enhanced HNO_3 following exceptional solar storms, *Geophys. Res. Lett.*, *32*, L12S01, doi:10.1029/2004GL021588.

Pommereau, J. P., and F. Goutail (1988), O_3 and NO_2 ground-based measurements by visible spectrometry during arctic winter and spring 1988, *Geophys. Res. Lett.*, *15*(8), 891–894.

Randall, C. E., et al. (2005), Stratospheric effects of energetic particle precipitation in 2003–2004, *Geophys. Res. Lett.*, *32*, L05802, doi:10.1029/2004GL022003.

Renard, J.-B., et al. (2000), SALOMON: A new, light balloonborne UV-visible spectrometer for nighttime observations of stratospheric trace-gas species, *Appl. Opt.*, *39*(3), 386–392.

Rinsland, C. P., C. Boone, R. Nassar, K. Walker, P. Bernath, J. C. McConnell, and L. Chiou (2005), Atmospheric Chemistry Experiment (ACE) Arctic stratospheric measurements of NO_x during February and March 2004: Impact of intense solar flares, *Geophys. Res. Lett.*, *32*, L16S05, doi:10.1029/2005GL022425.

Rodriguez, J. V., and U. S. Inan (1994), Electron density changes in the nighttime D region due to heating by very-low frequency transmitters, *Geophys. Res. Lett.*, *21*(2), 93–96.

Seppälä, A., P. T. Verronen, E. Kyrölä, S. Hassinen, L. Backman, A. Hauchecorne, J. L. Bertaux, and D. Fussen (2004), Solar proton events of October–November 2003: Ozone depletion in the Northern Hemisphere polar winter as seen by GOMOS/Envisat, *Geophys. Res. Lett.*, *31*, L19107, doi:10.1029/2004GL021042.

Turunen, E., H. Matveinen, J. Tolvanen, and H. Ranta (1996), D-region ion chemistry model, in *Solar Terrestrail Energy Program (STEP): Handbook of Ionospheric Models*, edited by R. W. Schunk, pp. 1–25, Sol. Terr. Energy Program, Boulder, Colo.

P.-L. Blelly, Q. Bourgeois, M. Chartier, and J.-B. Renard, Laboratoire de Physique et Chimie de l'Environnement/CNRS, 3A avenue de la recherche scientifique, F-45071 Orléans cedex 2, France. (jbrenard@cnrs-orleans.fr)

F. Goutail, Service d'Aéronomie/CNRS, BP3, F-91371, Verrières le Buisson cedex, France.

Y. J. Orsolini, Norwegian Institute for Air Research, Instituttveien 18, P.O. Box 100, N-2027 Kjeller, Norway.