

# Destruction of the Tertiary Ozone Maximum During a Solar Proton Event

A. Seppälä, P. T. Verronen, V. F. Sofieva, J. Tamminen, E. Kyrölä

Finnish Meteorological Institute, Earth Observation, Helsinki, Finland

C. J. Rodger

Physics Department, University of Otago, Dunedin, New Zealand

M. A. Clilverd

British Antarctic Survey (NERC), Cambridge, UK

Ozone observations from the GOMOS instrument together with a coupled ion and neutral chemistry model are used to study the effects of the January 2005 solar storms on the polar winter middle atmosphere. The model results indicate strong HO<sub>x</sub> and NO<sub>x</sub> enhancements in the mesosphere, and simultaneous ozone depletion maximizing between 70–80 km. During strong proton forcing GOMOS measurements show the destruction of the tertiary ozone maximum, observed at polar latitudes near 72 km before the events. This altitude is concurrent with the largest HO<sub>x</sub> enhancements in the model results. We observe for the first time the disappearance of the tertiary ozone maximum, and determine the underlying cause. With subsiding proton forcing GOMOS measurements show the reappearance of the tertiary ozone maximum, returning to normal values by Jan 24. Our results indicate that even moderate solar events (>10 MeV proton flux of >5000 pfu) can cause significant ozone depletion (>70%) in the middle atmosphere.

## 1. Introduction

Solar proton events (SPE) are a consequence of coronal mass ejections (CME), solar eruptions when large amounts of protons and heavier ions are emitted from the Sun. Guided by the Earth's magnetic field, the protons precipitate into the polar cap areas [Patterson *et al.*, 2001]. Since the protons can have very high energies, up to hundreds of MeVs, they deposit their energy in the mesosphere and stratosphere, thus providing a direct connection between the Sun and the middle atmosphere.

The precipitating particles produce odd hydrogen (HO<sub>x</sub>, H + OH + HO<sub>2</sub>), and odd nitrogen (NO<sub>x</sub>, N + NO + NO<sub>2</sub>) [Crutzen *et al.*, 1975; Solomon *et al.*, 1981; Rusch *et al.*, 1981]. HO<sub>x</sub> and NO<sub>x</sub> have an important role in the ozone balance of the middle atmosphere because they destroy odd oxygen (O<sub>x</sub>, O + O<sub>3</sub>) through catalytic reactions [see *e.g.* Brasseur and Solomon, 2005, pp. 401–416]. The produced HO<sub>x</sub> has a relatively short lifetime of only few days, but the chemical loss of NO<sub>x</sub>, which happens through photodissociation and is hence dependent of solar radiation, is ineffective during polar night conditions.

Significant depletion of middle atmospheric ozone after large SPEs has been predicted by atmospheric modeling

[Rusch *et al.*, 1981; Solomon *et al.*, 1983; Reid *et al.*, 1991; Jackman *et al.*, 1995; Verronen *et al.*, 2005] and has been observed by satellite measurements [Thomas *et al.*, 1983; McPeters and Jackman, 1985; Seppälä *et al.*, 2004; Randall *et al.*, 2005; López-Puertas *et al.*, 2005; Rohen *et al.*, 2005].

The tertiary ozone maximum, first reported by Marsh *et al.* [2001], occurs at approximately 72 km altitude near the polar night terminator. Model results have indicated that the maximum occurs as a result of O<sub>x</sub> loss by catalytic cycles of OH and HO<sub>2</sub> decreasing because HO<sub>x</sub> production from photolysis of water vapor decreases with reducing UV radiation [Marsh *et al.*, 2001; Hartogh *et al.*, 2004; Degenstein *et al.*, 2005]. Extensive observations of the tertiary ozone maximum and its seasonal development have thus far not been published.

In this paper we use ozone measurements from the GOMOS stellar occultation instrument [Bertaux *et al.*, 2000, 2004; Kyrölä *et al.*, 2004] on board the Envisat satellite together with the Sodankylä Ion Chemistry Model (SIC, Turunen *et al.* [1996]; Verronen *et al.* [2005]) to study the effects the January 2005 SPEs on the middle atmosphere. The model results show that the events that began on Jan 16 led to large HO<sub>x</sub>, and NO<sub>x</sub> enhancements in the mesosphere, the maximum enhancement taking place between 70 and 80 km. This further led to the destruction of the tertiary ozone maximum known to exist in the winter hemisphere high-latitudes and in previous winters also observed in the GOMOS measurements [Sofieva *et al.*, 2004]. The destruction as well as the recovery of the tertiary ozone maximum is observed in both the model calculations and the GOMOS measurements.

## 2. January 2005 Solar Storms

Early on Jan 16 began a series of SPEs following an X-class flare (X2.6: peak of 0.1–0.8 nm x-ray flux = 2.6 × 10<sup>-4</sup> Wm<sup>-2</sup>) observed on the previous day. On the following day (Jan 17) even a stronger flare (X3.8) and associated CME were observed, followed by yet a stronger flare (X7) and an associated CME on Jan 20. The flux of the protons with energy > 10 MeV, measured by the GOES-11 satellite, peaked only at 5040 pfu (Particle Flux Unit, particles cm<sup>-2</sup>s<sup>-1</sup>sr<sup>-1</sup>) after the Jan 17 event in contrast to the Oct 2003 events when the peak > 10 MeV flux was as high as 29500 pfu.

The Jan 20 X7 flare originated from the giant sunspot 720. This flare marked the start of an extraordinary solar proton storm: the flux of extremely high energy solar protons (> 100 MeV from GOES) was of the same order as in the well known October 1989 SPE [*e.g.* Reid *et al.*, 1991; Jackman *et al.*, 1995], whilst the lower energy fluxes

remained at moderate levels ( $> 10$  MeV proton flux peak 1860 pfu while the  $>100$  MeV protons peaked at 652 pfu), making the January event the hardest and most energetic proton event of Cycle 23 so far.

Fig. 1 presents the ionization rates in the atmosphere caused by the precipitating protons. These ionization rates have been calculated using GOES-11 proton measurements for the Jan 2005 SPE period and algorithm based on *Reid* [1961]. The figure shows that the greatest ionization takes place between Jan 17-18, and Jan 20, when the ionization rate peak is below 50 km.

### 3. Model results

Two model runs were made for the period of Jan 15-24 using the SIC model (version 6.7.2., for a model description see *Verronen et al.* [2005]). The first run was a basic model run for January conditions without any proton forcing. The second run included proton forcing calculated from the GOES-11 proton flux measurements. The model point is ( $70^\circ\text{N}$ ,  $0^\circ\text{E}$ ) in both runs. Analogous to *Verronen et al.* [2005] and *Chilverd et al.* [2005] the model electron densities were used to model low frequency radio wave propagation during the study period and compared against observed changes in trans-polar radio signal behavior, to verify that the SIC model electron densities have a right response to the proton precipitation. The model and measurements of the low frequency radio wave signal amplitude on the Maine (NAA) to Sodankylä, Finland, path (not shown here) show a good agreement indicating that the SIC model captures the solar proton impact on the ionosphere.

Fig. 2 shows the  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{O}_3$  model response to the proton precipitation. The event of Jan 18 causes greater than an order of magnitude increase in  $\text{HO}_x$  between 60-75 km but the enhancements recover shortly after the events.  $\text{NO}_x$  enhancements of  $> 200\%$  ( $> 20$  ppbv) are seen at altitudes 50-80 km continuing beyond the end of the modeling period. Greatest ozone depletion ( $>70\%$ ) is seen in the model during twilight and the nights of Jan 17-18, and Jan 18-19 between 70-80 km. Examination of the loss rates from the model indicates that the ozone depletion happens through  $\text{HO}_x$  chemistry. At 72 km altitude where the tertiary ozone maximum is located the main ozone loss takes place through reactions with  $\text{HO}_x$ , the  $\text{NO}_x$  reactions being of little consequence with two orders of magnitude smaller loss rates.

The Jan 20 hard proton spectrum event causes  $\text{HO}_x$  to spike at stratospheric altitudes but is quickly recovered after sunrise at the model location. This event has no apparent effect to ozone at the lower altitudes as the ozone loss at those altitudes is determined mainly by  $\text{NO}_x$  chemistry and the relative  $\text{NO}_x$  production from this event is not significant in the middle and lower stratosphere.

### 4. GOMOS measurements

The GOMOS ozone measurements presented here are from the period Jan 1-24. On Jan 24 an instrumental anomaly occurred and measurements were temporarily stopped. For this study we use only GOMOS dark limb (night-time) measurements from the Northern Hemisphere (GOMOS ground processing prototype, GOPR, version 6.0c) from occultations where the star temperature was  $> 10000\text{K}$ . The total number of measurements used is more than 2100. The error of the retrieved ozone profiles depends on the star temperature and magnitude. The accuracy in the mesosphere is best with hot and bright stars for ozone,

the error estimates being of the order of 1% (40-70 km), and 5% (70-90 km). For the zonal mean profiles used in the present study the accuracy can be roughly estimated to 1% below and 2% above 75 km.

Fig. 3 shows the zonal mean ozone mixing ratio [ppmv] in the Northern Hemisphere for altitudes 30-90 km before (Jan 9-15, top) and during the SPEs (Jan 16-24, bottom). The tertiary ozone maximum is observed before the SPEs at latitudes  $60^\circ\text{N}$ - $80^\circ\text{N}$  and altitudes around 72 km with values greater than 2 ppmv. During the later period values that high are not observed in the same area.

Fig. 4 shows the zonal mean ozone mixing ratio between latitudes  $65^\circ\text{N}$ - $75^\circ\text{N}$  for Jan 1-24 and for comparison with the model result shown in Fig. 2 the change from the average values before the event (Note the different x-axis in the panels of Fig. 4). The tertiary ozone maximum is observed in the altitude region around 70 km with maximum values greater than 2 ppmv. After the beginning of the first SPE on Jan 16 significantly lower mixing ratios are observed between 60 and 80 km. The lowest values observed around 70 km coincide with the event of Jan 17-18 seen in Fig. 1. After this event the gradual recovery of the tertiary maximum is observed between 60-78 km with values of 2 ppmv by Jan 24. When comparing the observed change in ozone (lower panel of Fig. 4) to the model predicted change shown in Fig. 2 one must keep in mind that the observations represent only night-time values and will therefore not show similar diurnal variation as the model predicted changes. Both the model results and GOMOS observations place the greatest ozone depletion to altitudes 70-80 km. The agreement between the duration and the magnitude of the modeled and observed ozone loss is quite good except for the night of Jan 19 when the model predicts  $> 80\%$  depletion between 70-80 km but the observations show values of 60-70%.

### 5. Discussion

We have used the GOMOS measurements from January 2005 to observe the disappearance of the tertiary ozone maximum during a Solar Proton Event for the first time. Coupled ion and neutral chemistry model results indicate that the tertiary ozone maximum was temporarily destroyed during the Jan 2005 solar events as a result of the  $\text{HO}_x$  enhancement from the increased ionization. Because of the short lifetime of the  $\text{HO}_x$  constituents, and ozone production from atomic oxygen in the mesosphere the tertiary maximum is only destroyed while the production of  $\text{HO}_x$  is greatest.

Model results and GOMOS stellar occultation measurements indicate that the Jan 2005 SPEs had a distinct effect on middle atmosphere  $\text{HO}_x$ ,  $\text{NO}_x$ , and ozone. The SIC model predicts ozone loss to take place in the mesosphere with the greatest loss ( $>70\%$ ) between 70-80 km taking place early on the Jan 2005 SPE period. The model indicates that this is caused primarily by the enhanced amount of  $\text{HO}_x$  at these altitudes. GOMOS ozone measurements confirm these model predictions. The tertiary ozone maximum that is well observed before the Jan 2005 SPEs is destroyed during the greatest forcing but emerges again when the proton forcing subsides (Figs. 3, 4).

In the polar cap region, where the energetic particles precipitate,  $\text{O}_x$  is mainly in the form of ozone during conditions when only little or no sunlight is available to produce atomic oxygen through photodissociation. At high solar zenith angles, near the polar night terminator, photolysis of water vapor decreases thus reducing the amount of  $\text{HO}_x$  in the atmosphere, which, in turn, decreases the effect of  $\text{HO}_x$  catalytic cycles on  $\text{O}_x$  loss. As a result the tertiary ozone maximum is formed. For the catalytic  $\text{HO}_x$  reactions atomic oxygen is needed. If an SPE takes place during a polar night season a large amount of  $\text{HO}_x$  can be produced in the polar cap

atmosphere. In the area where the tertiary ozone maximum is observed, the following two conditions important for the efficiency of the  $O_x$  loss through  $HO_x$  catalytic reactions would be fulfilled 1) Location in the polar cap region where the energetic particles precipitate, and 2) Atomic oxygen is available for the catalytic  $HO_x$  reaction cycles.  $O_x$  is also produced during SPEs, but the amount of atomic oxygen formed as a result of the increased ionization is small compared to the amount produced by photodissociation.

Our results indicate that even a moderate Solar Proton Event can, under certain conditions, be important to ozone loss in the middle atmosphere. Following the moderate SPE on Jan 17 when the peak  $> 10$  MeV proton flux was 5040 pfu significant ozone depletion of more than 70% was observed in the mesosphere with mixing ratios as low as 0.5 ppmv between 65-80 km.

**Acknowledgments.** The work of AS was supported by the Academy of Finland (Middle Atmosphere Interactions with Sun and Troposphere). AS thanks the Wihuri foundation for support during the preparation of this manuscript. We are thankful for G. Barrot and ACRI-ST for providing the GOMOS data, and we would also like to thank all GOMOS team members. AS thanks Dr. C.E. Randall and C.S. Singleton from LASP for helpful discussions. We thank the two anonymous reviewers for their helpful comments.

## References

- Bertaux, J. L., E. Kyrölä, and T. Wehr (2000), Stellar occultation technique for atmospheric ozone monitoring: GOMOS on Envisat, *Earth Observation Quarterly*, 67, 17–20.
- Bertaux, J. L., et al. (2004), First results on GOMOS/Envisat, *Adv. Space Res.*, 33, 1029–1035.
- Brasseur, G. P., and S. Solomon (2005), *Aeronomy of the Middle Atmosphere*, 3rd revised and enlarged ed., Springer, Dordrecht.
- Clilverd, M. A., C. J. Rodger, T. Ulich, A. Seppälä, E. Turunen, A. Botman, and N. R. Thomson (2005), Modelling a large solar proton event in the southern polar cap, *J. Geophys. Res.*, 110(A9), A09307, doi:10.1029/2004JA010922.
- Crutzen, P. J., I. S. A. Isaksen, and G. C. Reid (1975), Solar proton events: Stratospheric sources of nitric oxide, *Science*, 189, 457–458.
- Degenstein, D. A., N. D. Lloyd, A. E. Bourassa, R. L. Gattinger, and E. J. Llewellyn (2005), Observations of mesospheric ozone depletion during the October 28, 2003 solar proton event by OSIRIS, *Geophys. Res. Lett.*, 32.
- Hartogh, P., C. Jarchow, G. R. Sonnemann, and M. Grygalashvily (2004), On the spatiotemporal behaviour of ozone within the upper mesosphere/mesopause region under nearly polar night conditions, *J. Geophys. Res.*, 109, D18303, doi:10.1029/2004JD004576.
- Jackman, C. H., M. C. Cerniglia, J. E. Nielsen, D. J. Allen, J. M. Zawodny, R. D. McPeters, A. R. Douglass, J. E. Rosenfield, and R. B. Hood (1995), Two-dimensional and three-dimensional model simulations, measurements, and interpretation of the October 1989 solar proton events on the middle atmosphere, *J. Geophys. Res.*, 100, 11,641–11,660.
- Kyrölä, E., et al. (2004), GOMOS on Envisat: An overview, *Adv. Space Res.*, 33, 1020–1028.
- Lopéz-Puertas, M., B. Funke, S. Gil-López, T. v. Clarmann, G. P. Stiller, M. Höpfner, S. Kellmann, H. Fischer, and C. H. Jackman (2005), Observation of  $NO_x$  enhancement and ozone depletion in the northern and southern hemispheres after the October–November 2003 solar proton events, *J. Geophys. Res.*, 110, A09S43, doi:10.1029/2005JA011050.
- Marsh, D., A. Smith, G. Brasseur, M. Kaufmann, and K. Grossmann (2001), The existence of a tertiary ozone maximum in the high latitude middle mesosphere, *Geophys. Res. Lett.*, 28(24), 4531–4534.
- McPeters, R. D., and C. H. Jackman (1985), The response of Ozone to Solar Proton Events During Solar Cycle 21: The Observations, *J. Geophys. Res.*, 90, 7945–7954.
- Patterson, J. D., T. P. Armstrong, C. M. Laird, D. L. Detrick, and A. T. Weatherwax (2001), Correlation of solar energetic protons and polar cap absorption, *J. Geophys. Res.*, 101, 149–163.
- Randall, C. E., et al. (2005), Stratospheric effects of energetic particle precipitation in 2003–2004, *Geophys. Res. Lett.*, 32, L05802, doi:10.1029/2004GL022003.
- Reid, G. C. (1961), A study of the enhanced ionization produced by solar protons during a polar cap absorption event, *J. Geophys. Res.*, 66, 4071–4085.
- Reid, G. C., S. Solomon, and R. R. Garcia (1991), Response of the middle atmosphere to the solar proton events of August–December, 1989, *Geophys. Res. Lett.*, 18, 1019–1022.
- Rohen, G., et al. (2005), Ozone depletion during the solar proton events of October/November 2003 as seen by SCIAMACHY, *J. Geophys. Res.*, 110, A09S39.
- Rusch, D. W., J.-C. Gérard, S. Solomon, P. J. Crutzen, and G. C. Reid (1981), The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere – I. Odd nitrogen, *Planet. Space Sci.*, 29, 767–774.
- 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(19), L19107, doi:10.1029/2004GL021042.
- Sofieva, V. F., P. T. Verronen, S. Hassinen, E. Kyrölä, and GOMOS CAL/VAL team (2004), The tertiary ozone maximum in the middle mesosphere as seen by GOMOS on Envisat, in *Proceedings of the XX Quadrennial Ozone Symposium 1–8 June 2004, Kos, Greece*, vol. I, pp. 438–439.
- Solomon, S., D. W. Rusch, J.-C. Gérard, G. C. Reid, and P. J. Crutzen (1981), The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere: II. Odd hydrogen, *Planet. Space Sci.*, 8, 885–893.
- Solomon, S., G. C. Reid, D. W. Rusch, and R. J. Thomas (1983), Mesospheric ozone depletion during the solar proton event of July 13, 1982 Part II. Comparisons between theory and measurements, *Geophys. Res. Lett.*, 10, 257–260.
- Thomas, R. J., C. A. Barth, G. J. Rottman, D. W. Rusch, G. H. Mount, G. M. Lawrence, R. W. Sanders, G. E. Thomas, and L. E. Clemens (1983), Mesospheric ozone depletion during the solar proton event of July 13, 1982 Part I: Measurement, *Geophys. Res. Lett.*, 10, 253–255.
- Turunen, E., H. Matveinen, J. Tolvanen, and H. Ranta (1996), D-region ion chemistry model, in *STEP Handbook of Ionospheric Models*, edited by R. W. Schunk, pp. 1–25, SCOSTEP Secretariat, Boulder, Colorado, USA.
- Verronen, P. T., A. Seppälä, M. A. Clilverd, C. J. Rodger, E. Kyrölä, C.-F. Enell, T. Ulich, and E. Turunen (2005), Diurnal variation of ozone depletion during the October–November 2003 solar proton events, *J. Geophys. Res.*, 110, A09S32, doi:10.1029/2004JA010932.
- A. Seppälä, P. T. Verronen, V. F. Sofieva, J. Tamminen, and E. Kyrölä, Finnish Meteorological Institute, Earth Observation, P.O. Box 503, FI-00101 Helsinki, Finland. (annika.seppala@fmi.fi)
- C. J. Rodger, Dept. of Physics, University of Otago, P.O. Box 56, Dunedin, New Zealand.
- M. A. Clilverd, Physical Sciences Division, British Antarctic Survey, Madingley Road, Cambridge, CB3 0ET, U.K.

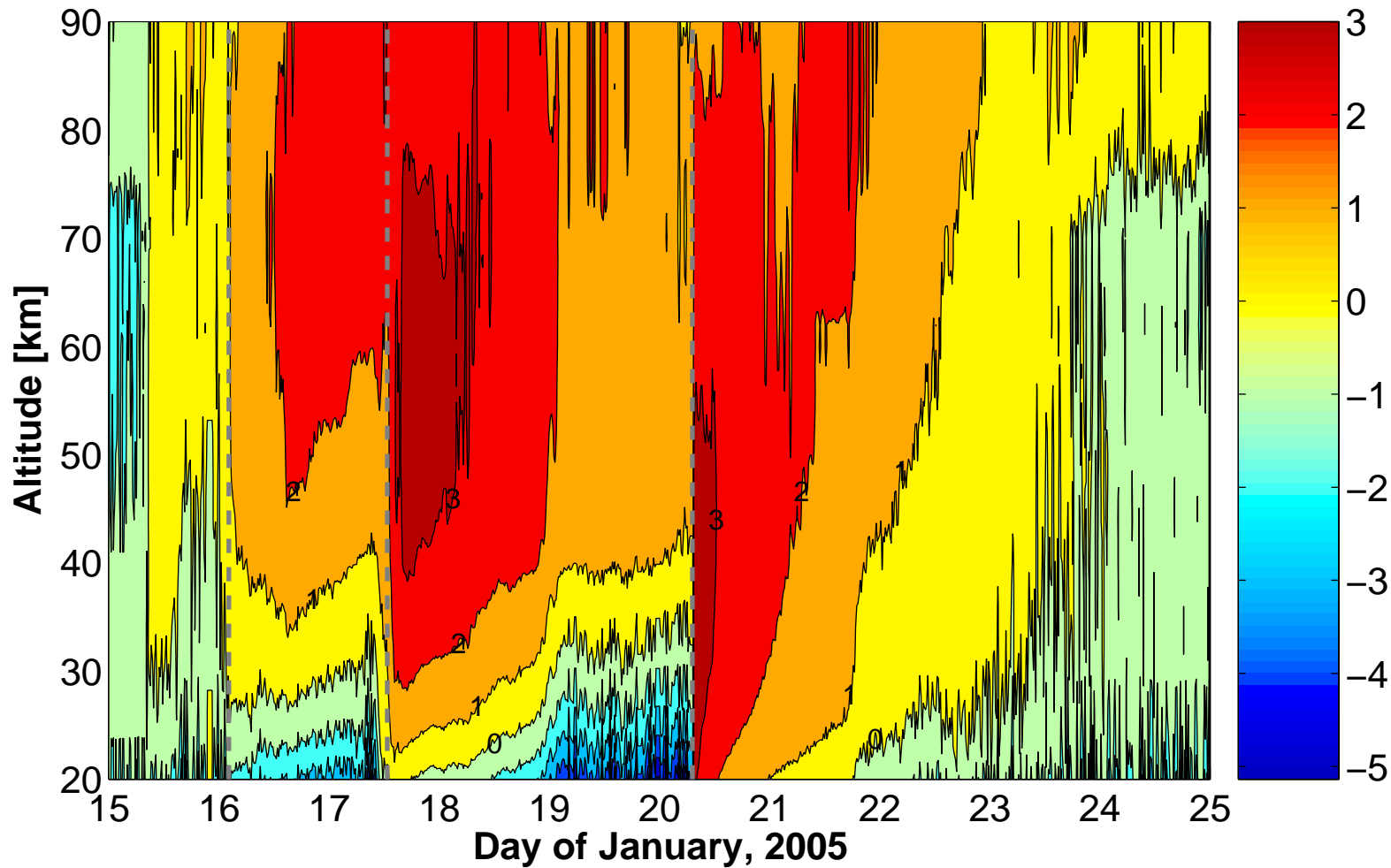
**Figure 1.** Atmospheric ionization rates between 20 and 90 km caused by the precipitating protons. The dashed lines mark the beginnings of the Proton Events.

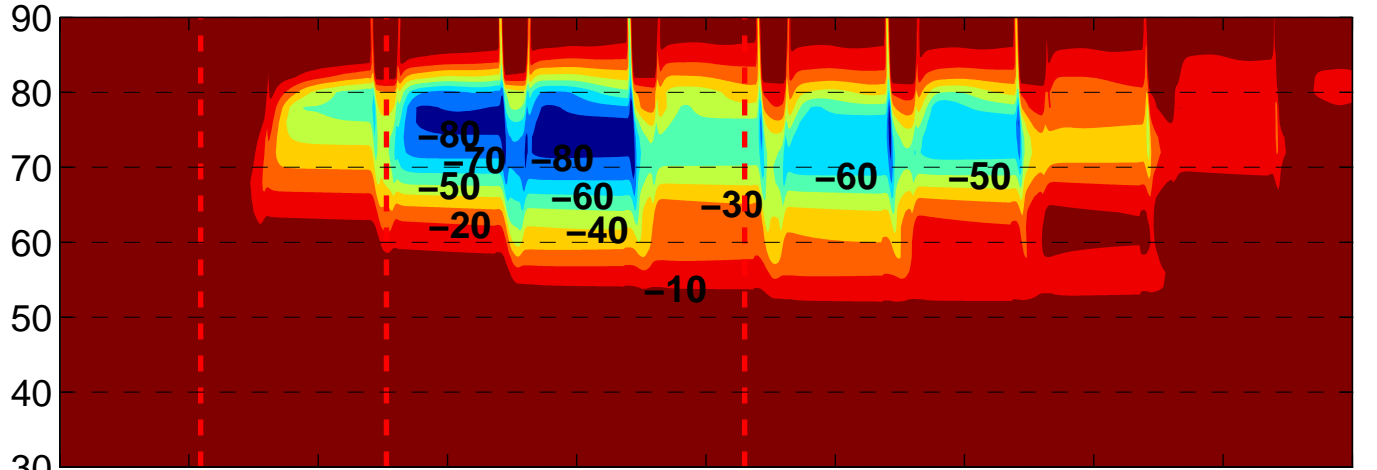
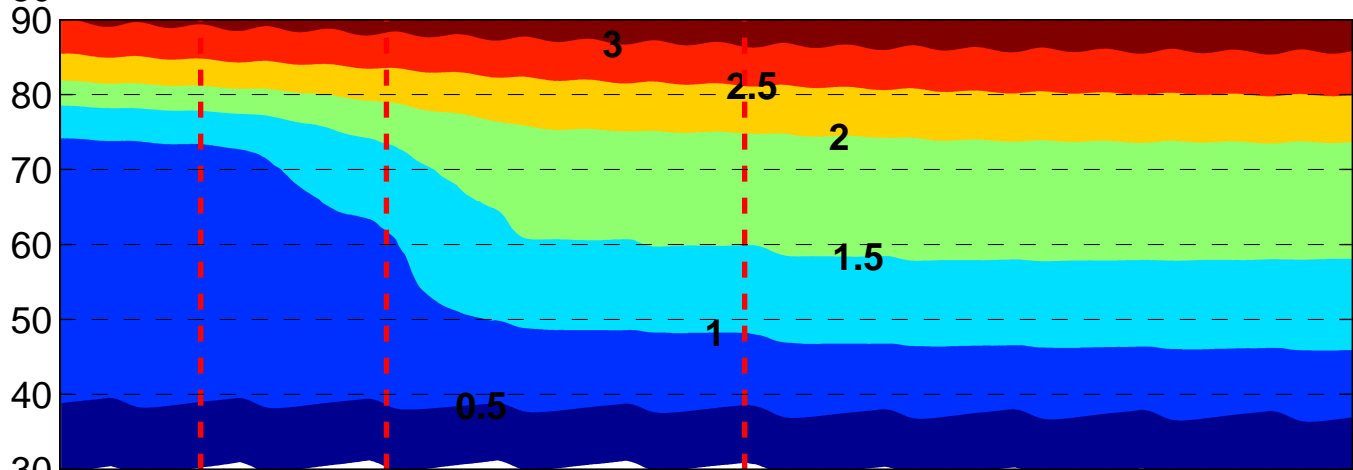
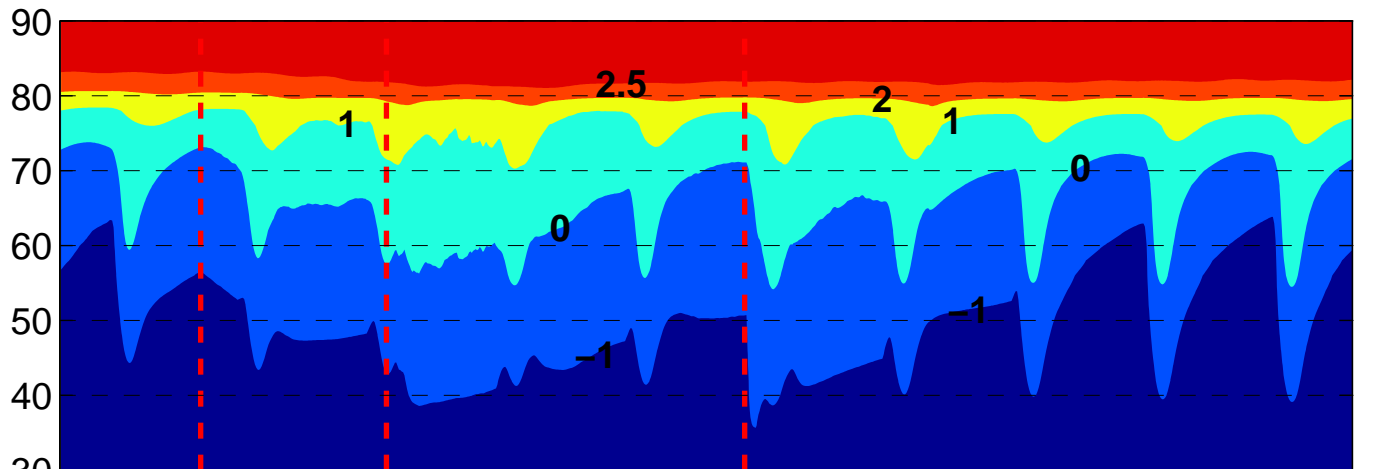
**Figure 2.** Top: model  $HO_x$  ( $H + OH + HO_2$ ) mixing ratio [ $\log_{10}$ (ppbv)], middle: model  $NO_x$  ( $N + NO + NO_2$ ) mixing ratio [ $\log_{10}$ (ppbv)], bottom:  $O_3$  change [%] due to precipitating protons. The contour lines are (0.1,  $10^{-0.5}$ , 1,  $10^{0.5}$ , 10,  $10^{1.5}$ , 100 ppbv), (10, 30, 50, 100, 150 ppbv), and (-80, -70, -60, -50, -40, -30, -20, -10%) respectively. The model point is ( $70^\circ N$ ,  $0^\circ E$ ). MSISE-90 model was used to calculate the mixing ratios.

**Figure 3.** Top: GOMOS zonal ozone mixing ratio [ppmv] in the Northern Hemisphere (latitudes  $40^{\circ}\text{N}$ - $90^{\circ}\text{N}$ ) during Jan 9-15, 2005. Bottom: as above but for Jan 16-24, 2005. The contour lines are (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7 ppmv)

**Figure 4.** Top: GOMOS daily (Jan 1-24, 2005) zonal mean night-time ozone mixing ratio [ppmv] at latitudes  $65^{\circ}\text{N}$ - $75^{\circ}\text{N}$ . Note the destruction of the tertiary ozone maximum at 72 km altitude following the SPE on Jan 17, 2005. Contour lines as in Fig. 3. Bottom: Ozone %-change (Jan 15-24) from the average of Jan 10-14. The contour lines are (-80, -70, -60, -50, -40, -30, -20, -10%). X-axis is the same as for the model results in Fig. 2. Note the different x-axis in the two panels.

# Ionization Rate by Protons [ $\log_{10}(\text{cm}^{-3}\text{s}^{-1})$ ]





Day of Jan 2005

