Abstract. Solar cycle 23 was extremely active with seven of the largest twelve solar proton events (SPEs) in the past forty years recorded. These events caused significant polar middle atmospheric changes that were observed by a number of satellites. The highly energetic protons produced ionizations, excitations, dissociations, and dissociative ionizations of the background constituents in the polar cap regions (> 60 degrees geomagnetic latitude), which led to the production of HOx (H, OH, HO2) and NOy (N, NO, NO2, NO3, N2O5, HNO3, HO2NO2, BrONO2, ClONO2). The HOx increases led to short-lived ozone decreases in the polar mesosphere and upper stratosphere due to the short lifetimes of the HOx constituents. Polar middle mesospheric ozone decreases greater than 50% were observed and computed to last for hours to days due to the enhanced HOx. The NOy increases led to long-lived polar stratospheric ozone changes because of the long lifetime of the NOy family in this region. Upper stratospheric ozone decreases of >10% were computed to last for several months past the solar events in the winter polar regions because of the enhanced NOy.

Keywords: ozone, NOy, solar proton event, middle atmosphere, stratosphere, mesosphere

1. Introduction

Solar eruptive events sometimes result in large fluxes of high-energy solar protons at the Earth. This period of time, wherein the solar proton flux is generally elevated for a few days, is known as a solar proton event (SPE) and primarily occurs near solar maximum. Solar cycle 23 experienced several very large SPEs, which occurred in July and November 2000, September and November 2001, October/November 2003, and January 2005. The twelve largest SPEs in the past 40 years are given in Table I and over half of them (seven) occurred in the past solar maximum period.

The Earth’s magnetic field guides the solar protons into the northern and southern polar cap regions (> 60° geomagnetic latitude), e.g., see Jackman and McPeters (2004). The protons interact with the neutral middle atmosphere (stratosphere and mesosphere) and produce ionizations, dissociations, dissociative ionizations, and excitations.

Both HOx (H, OH, HO2) and NOy (N, NO, NO2, NO3, N2O5, HNO3, HO2NO2, BrONO2, ClONO2) can be enhanced either directly by the protons and their
associated secondary electrons or through a photochemical sequence initiated by
the protons impacting the atmosphere (e.g., Warneck, 1972; Swider and Keneshea,
1973; Crutzen et al., 1975; Porter et al., 1976; Frederick, 1976; Jackman et al.,
Zadorozhny et al., 1992; Randall et al., 2001). Ozone can be influenced by the solar
protons through photochemical depletion processes caused by the enhanced HOx
and NOy (e.g., Weeks et al., 1972; Heath et al., 1977; McPeters et al., 1981; Solomon
and Crutzen, 1981; Thomas et al., 1983; Solomon et al., 1983; McPeters and Jack-
Reid et al., 1991; Seppala et al., 2004; Degenstein et al., 2005).

The first middle atmospheric impact of solar protons was measured with a rocket
by Weeks et al. (1972). These observations showed a very dramatic reduction in
mesospheric ozone caused by the November 1969 SPE, which was explained in
Swider and Keneshea (1973) as caused by HOx enhancements.

Crutzen et al. (1975) postulated that stratospheric ozone should be impacted by
NO generated through interaction of the protons with the atmosphere. Two years
later Heath et al. (1977) confirmed with satellite observations that stratospheric
ozone was dramatically reduced during the August 1972 SPE.

In this paper we discuss satellite observations of middle atmospheric impacts by
protons ejected by the Sun in solar cycle 23. There have been several publications in
the past few years on this subject including Jackman et al. (2001, 2005a,b), Randall
et al. (2001), Krivolutsky et al. (2003, 2005), Seppala et al. (2004), Degenstein

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### TABLE I
Largest twelve solar proton events in the past forty years.

<table>
<thead>
<tr>
<th>Date of SPEs</th>
<th>Rank in size</th>
<th>NO$_y$ production in the middle atmosphere (# of molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 19–27, 1989</td>
<td>1</td>
<td>$6.7 \times 10^{33}$</td>
</tr>
<tr>
<td>August 2–10, 1972</td>
<td>2</td>
<td>$3.6 \times 10^{33}$</td>
</tr>
<tr>
<td>July 14–16, 2000</td>
<td>3</td>
<td>$3.5 \times 10^{33}$</td>
</tr>
<tr>
<td>October 28–31, 2003</td>
<td>4</td>
<td>$3.4 \times 10^{33}$</td>
</tr>
<tr>
<td>November 5–7, 2001</td>
<td>5</td>
<td>$3.2 \times 10^{33}$</td>
</tr>
<tr>
<td>November 9–11, 2000</td>
<td>6</td>
<td>$2.3 \times 10^{33}$</td>
</tr>
<tr>
<td>September 24–30, 2001</td>
<td>7</td>
<td>$2.0 \times 10^{33}$</td>
</tr>
<tr>
<td>August 13–26, 1989</td>
<td>8</td>
<td>$1.8 \times 10^{33}$</td>
</tr>
<tr>
<td>November 23–25, 2001</td>
<td>9</td>
<td>$1.7 \times 10^{33}$</td>
</tr>
<tr>
<td>September 2–7, 1966</td>
<td>10</td>
<td>$1.2 \times 10^{33}$</td>
</tr>
<tr>
<td>January 15–23, 2005</td>
<td>11</td>
<td>$1.1 \times 10^{33}$</td>
</tr>
<tr>
<td>Sep. 29–Oct. 3, 1989</td>
<td>12</td>
<td>$1.0 \times 10^{33}$</td>
</tr>
</tbody>
</table>
et al. (2005), Semeniuk et al. (2005), Verronen et al. (2005), López-Puertas et al. (2005a,b, 2006), and Rohen et al. (2005). López-Puertas et al. (2006) as well as other papers (e.g., Natarajan et al., 2004; Randall et al., 2005; Orsolini et al., 2005; Rinsland et al., 2005) showed certain solar influences on the polar upper stratosphere from effects that may not have been caused by solar protons, but rather by energetic electrons and/or X-rays associated with the solar storms of October–November 2003, and will not be discussed here.

This paper contains seven primary sections, including the Introduction. The solar proton flux and production of HO$_x$ and NO$_y$ are discussed in Section 2. The observations of NO$_y$ constituents, ClO and HOCl constituents, and ozone change as a result of solar protons in solar cycle 23 are given in Sections 3, 4, and 5, respectively. Global model results during certain disturbed time periods are presented in Section 6. Finally, conclusions are given in Section 7.

2. Solar Proton Flux and Production of HO$_x$ and NO$_y$

The National Oceanic and Atmospheric Administration (NOAA) Space Environment Center (SEC) provides a proton flux dataset for the NOAA Geostationary Operational Environmental Satellites (GOES) on their website (see http://sec.noaa.gov/Data/goes.html). GOES proton fluxes are provided at this site in several energy intervals (>1 MeV, >5 MeV, >10 MeV, >30 MeV, >50 MeV, and >100 MeV), which are updated every five minutes.

As an example of a very large solar proton flux time period that occurred in solar cycle 23, we present the proton flux measured by GOES-11 for the October 26 through November 7, 2003 time period in Figure 1. The proton fluxes are given for 1 and 100 MeV, which reach to altitudes of about 87 and 33 km, respectively.

![Figure 1. GOES-11 proton flux measurements in 2003 for energies >1 MeV (solid line) and >100 MeV (dashed line). These data are provided by the NOAA SEC at their website (http://sec.noaa.gov/Data/goes.html). Taken from Figure 1 of Jackman et al. (2005a).](image-url)
The very fast moving protons with energies $>100$ MeV arrive at Earth early in the solar event, whereas the slower moving protons with energies $>1$ MeV mostly arrive later. The most intense time period of proton fluxes occurred during October 28–30.

Using the energy deposition methodology discussed in Vitt and Jackman (1996), the daily average ion pair production can be computed. HO$_x$ is created through ion chemistry (e.g., Solomon et al., 1981) wherein: (1) two (HO$_x$) constituents are produced per ion pair up to about 70 km; and (2) less than two (HO$_x$) constituents are produced per ion pair above 70 km.

The solar protons and associated secondary electrons (produced in ionization events) create atomic nitrogen through dissociations, predissociations, or dissociative ionization collisions with N$_2$. Porter et al. (1976) showed that approximately 1.25 N atoms are produced per ion pair. About 45% or 0.55 per ion pair of the N atoms are in the ground state and about 55% or 0.7 per ion pair are in excited states. Although excited state N atoms are more likely to produce other NO$_y$ constituents, both types of N atoms can have an impact on the middle atmosphere.

3. Satellite Measurements of NO$_y$ Constituent Changes from SPEs

3.1. NO$_x$ (NO + NO$_2$) Observations

Substantial changes in NO$_y$ constituents as a result of SPEs have been measured by several satellite instruments during solar cycle 23. Very large fluxes of solar protons in July 2000 produced huge increases ($>50$ ppbv in the mesosphere) in polar Northern Hemisphere NO$_x$ measured by the Upper Atmosphere Research Satellite (UARS) Halogen Occultation Experiment (HALOE) (Jackman et al., 2001). Randall et al. (2001) demonstrated that the polar Southern Hemisphere NO$_x$ was also influenced by this very large SPE. Using UARS HALOE and Polar Ozone and Aerosol Measurement (POAM) III data, Randall et al. (2001) showed evidence of large NO$_x$ enhancements in September 2000 in the middle stratosphere that were almost certainly caused by the July 2000 SPE.

The large solar storms in late October and early November 2003 also caused very large proton fluxes (see Figure 1) that created NO$_x$ and was measured by UARS HALOE (Jackman et al., 2005a) and Envisat Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) (López-Puertas et al., 2005a). Jackman et al. (2005a) showed polar Southern Hemisphere NO$_x$ enhancements during the very large SPEs that were nearly as large as those that were measured during the July 2000 SPE. López-Puertas et al. (2005a) showed huge NO$_x$ increases in both the polar Northern and Southern Hemispheres, which lasted for at least two weeks after the major SPEs in the Northern polar regions. These measurements by Envisat MIPAS showed polar SPE-driven changes in both the winter (dark) and summer (daylight) hemispheres (López-Puertas et al., 2005a). A plot of this interhemispheric difference is shown in this issue of Space Science Reviews in
Figure 1 of Langen (2006), which is similar to that given in Figure 4 of López-Puertas et al. (2005a). Seppala et al. (2004) showed NO₂ enhancements over several hundred per cent in the middle to upper stratosphere using Envisat Global Ozone Monitoring by Occultation of Stars (GOMOS) data.

3.2. HNO₃, N₂O₅, AND ClONO₂ OBSERVATIONS

Other NOₓ constituents were also elevated as a result of the huge SPEs that occurred in Oct–Nov 2003. López-Puertas et al. (2005b) showed polar HNO₃, N₂O₅, and ClONO₂ changes using Envisat MIPAS. Nitric acid (HNO₃) enhancements of 1–2 ppbv (100%) in the middle to upper stratosphere occurred in conjunction with the SPEs in both Hemispheres. Given the sudden nature of this HNO₃ enhancement, it was suggested to be most likely caused by gas phase chemistry (López-Puertas et al., 2005b), in particular, NO₂ + OH + M → HNO₃ + M. There were measured increases in NO₂ (e.g., Jackman et al., 2005a; López-Puertas et al., 2005b) and predicted increases in OH (Jackman et al., 2005a) as a result of the Oct–Nov 2003 solar events, thus the reaction would likely be accelerated. Orsolini et al. (2005) examined the anomalous HNO₃ layer observed by MIPAS over a longer period of time (November 4, 2003 to February 20, 2004). They found that there were two periods of enhanced upper stratospheric HNO₃ in November 2003, one observed November 4–5 (early) and the other observed November 20–30 (late). Only the early enhanced HNO₃ period was thought to be caused directly by solar protons. The late November enhanced HNO₃ period was likely caused by production of NOₓ by energetic particle precipitation in the mesosphere followed by descent to the stratosphere (Orsolini et al., 2005).

Dinitrogen pentoxide (N₂O₅) was increased around 40 km by about 0.5 to 1.2 ppbv (20–60%) in the polar Northern middle to upper stratosphere several days after the very large SPEs (López-Puertas et al., 2005b). These enhancements were delayed because the most likely production mechanism NO₂ + NO₃ + M → N₂O₅ + M is relatively slow.

Chlorine nitrate (ClONO₂) was enhanced because of the previously discussed NO₂ increases speeding up the ClO + NO₂ + M → ClONO₂ + M reaction. López-Puertas et al. (2005b) showed polar Northern ClONO₂ enhancements of a maximum of about 0.4 ppbv (40%) near 32 km.

4. Satellite Measurements of ClO and HOCl Constituents Change from SPEs

Envisat MIPAS measurements showed significant increases of ClO and HOCl in Oct–Nov 2003 (von Clarmann et al., 2005). These observations gave indirect proof of enhanced HOₓ abundances as a result of the large SPEs in late October 2003. Northern polar ClO increased by 0.2 to 0.4 ppbv and HOCl increased by 0.3 ppbv
at altitudes above 32 km (von Clarmann et al., 2005). These measurements, along with the observed ClONO\textsubscript{2} enhancements discussed in Section 3.2, suggest that HCl was destroyed either through reaction with OH or via ion cluster chemistry (von Clarmann et al., 2005).

5. Satellite Measurements of Ozone Changes from SPEs

Several satellite instruments measured ozone decreases during solar cycle 23 as a result of SPEs including the UARS HALOE; NOAA 14 and 16 Solar Backscatter Ultraviolet 2 (SBUV/2) instruments; POAM III; Envisat GOMOS, MIPAS and Scanning Imaging Absorption spectrometer for Atmospheric Chartography (SCIAMACHY); and Odin OSIRIS. Substantial mesospheric and upper stratospheric ozone decreases during and after the July 2000 SPE were measured by UARS HALOE and NOAA 14 SBUV/2 (Jackman et al., 2001). Randall et al. (2001) used POAM III observations to show middle stratospheric ozone decreases in September 2000 as a result of the July 2000 SPE.

The most-studied period (to date) of ozone decreases as a result of SPEs occurred in October 26–November 7, 2003. Seppala et al. (2004) and Verronen et al. (2005) showed long lasting ozone depletions of 20 to 60% in the Northern Hemisphere polar lower mesosphere and upper stratosphere as a result of the events using Envisat GOMOS. Jackman et al. (2005a) found short-term ozone depletions of 40% in the Southern Hemisphere polar lower mesosphere with ozone depletions of 5–8% lasting days beyond the events in the upper stratosphere using NOAA 16 SBUV/2. The ozone decreases from a quiescent baseline day (October 25) over the October 28–November 1, 2003 disturbed period are given in Figure 2a.

López-Puertas et al. (2005a) showed significant polar lower mesosphere and upper stratosphere ozone decreases (10–70%) during the events using Envisat MIPAS. They also showed large differences between the two Hemispheres, with substantially more polar ozone depletion in the Northern (>20%) than in the Southern Hemisphere (5–10%). This interhemispheric difference is shown in this issue of Space Science Review in Figure 1 of Langen (2006), which is similar to that given in Figure 4 of López-Puertas et al. (2005a). Envisat SCIAMACHY measurements generally agreed with these Envisat MIPAS observations of ozone depletion (Rohen et al., 2005).

6. Model Predictions of SPE Influences

Models have also been used to help interpret the influence of SPEs on the atmosphere during solar cycle 23. Jackman et al. (2001) model predictions showed reasonable agreement with measured NO\textsubscript{x} enhancements and ozone depletions caused by the July 2000 SPE. Verronen et al. (2005) studied the diurnal variation of ozone de-
Figure 2. Percentage ozone change from October 25, 2003 values for the polar Southern Hemisphere from (a) NOAA 16 SBUV/2 measurements (top level of 0.5 hPa) and (b) the GSFC 2D model over the October 28–November 1, 2003 period. These plots show the influence of the Oct–Nov 2003 SPEs. Contour levels plotted are $-5\%$, $-10\%$, $-30\%$, $-50\%$, and $-70\%$.


The Jackman et al. (2005a) simulations using the Goddard Space Flight Center (GSFC) two-dimensional (2D) model for ozone decreases during and after the Oct–Nov 2003 very large SPEs are presented in Figure 2b. Huge ozone depletions (>70%) are calculated near 0.1 hPa on October 29 during the period of maximum proton flux intensity (see Figure 1). The short-lived depletion is caused by the enhanced HOx constituents, which last only during and for a few hours after the events. The longer-lived ozone depletion between about 0.3 and 3 hPa is caused by the NOy family. The modeled ozone change is in reasonable agreement during the SPEs. After the SPEs, the computed ozone change is slightly higher (lower) than that measured for the 0.3 to 2 hPa (2 to 7 hPa) altitude region. Ozone is also undergoing other changes at this time of year not connected with the SPEs, thus the apparent model/measurement disagreement does require further analysis.

It is important to note that the UARS HALOE measured and GSFC 2D model computed NOx changes are in fairly good agreement in the lower mesosphere and upper mesosphere over the October 30 to November 7 period (Jackman et al., 2005a). The long-lived NOx enhancements drive the ozone changes over the months after the very large SPEs.
Figure 3. Model computed percentage total ozone changes from 2000–2005 resulting from SPEs in 2000–2003. Contour intervals are $-3\%$, $-2\%$, $-1\%$, $-0.5\%$, $-0.2\%$, and $-0.1\%$. The gray highlighted areas indicate total ozone decreases greater than 1%. Taken from Figure 4 of Jackman et al. (2005b).

Jackman et al. (2005a) and Rohen et al. (2005) both show model results confirming the very large interhemispheric differences observed in the Oct–Nov 2003 SPEs impacts on the middle atmosphere. These studies showed a much larger impact from these SPEs in the Northern than in the Southern Hemisphere. The NOy family has a much longer lifetime in the late Fall/Winter than in the late Spring/Summer for two reasons:

1. the NOy is lost through the mechanism NO + hν (<191 nm) → N + O followed by N + NO → N2 + O, thus when the sunlight is intense (e.g., Summer and late Spring) the loss is greater;
2. the NOy is transported to lower levels in the atmosphere where it is more effectively shielded from loss by sunlight.

Jackman et al. (2005b) simulated all the SPEs in the 2000–2003 period with the GSFC 2D model. The computed impact on total ozone in this simulation is shown in Figure 3 for the 2000–2005 time period. Total ozone is reduced by a maximum of about 3% in the polar Southern latitudes in late 2001 and 2002 that is primarily driven by the July 2000 SPE, a Winter SPE in this hemisphere. Both polar regions had extended periods of depleted ozone greater than 1% as a result of SPEs. Although the SPE-driven total ozone change is significant at polar latitudes, the computed annually-averaged global ozone change is fairly small (<0.5%).

7. Conclusions

Solar cycle 23 was extremely active with seven of the largest twelve SPEs in the past forty years recorded, especially in the years 2000, 2001, 2003, and 2005.
These events caused significant polar middle atmospheric changes that were observed by a number of satellites. The atmospheric impacts from the July 2000 and Oct–Nov 2003 SPEs were discussed in several papers published between 2001 and 2005. These SPEs produced both HOx and NOy constituents. Most of the substantial polar ozone decreases caused by the SPEs were short-lived and driven by the HOx enhancements, however, the longer-lived ozone depletions caused by NOy increases were observed to last for months past the events in the late Fall and Winter seasons. These longer term impacts from SPEs should be considered when quantifying other natural as well as anthropogenic influences on the middle atmosphere, especially near solar maximum in the polar regions.

Acknowledgements

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References


