The Effect of Solar Proton Events on Ozone and Other Constituents

Charles H. Jackman and Richard D. McPeters

Brief, Popular Summary of the Paper:

This is a review paper about solar proton events, which have caused changes in mesospheric and stratospheric ozone and other constituents. The influence of these natural processes on ozone need to be more fully understood so that the human-made impact on ozone can be more reliably predicted.

Large-scale explosions on the Sun near solar maximum lead to emissions of charged particles (mainly protons and electrons) from the Sun. Occasionally the Earth is positioned in its orbit such that these solar particles interact with the Earth’s magnetosphere and rain down on the polar regions. “Solar proton events” have been used to describe these phenomena since the protons associated with these solar events cause the most atmospheric disturbance.

Solar proton events create hydrogen- and nitrogen-containing compounds, which can lead to ozone destruction in the mesosphere and upper stratosphere. There have been eleven solar proton events since 1969 that caused measurable changes in the Earth’s atmosphere. Three of these events produced observed increases in nitrogen oxides. All eleven events caused measurable ozone decreases. The increases in the hydrogen-containing constituents produced significant mesospheric ozone decreases during all the events, whereas the increases in the longer-lived nitrogen oxides by the two largest of these events caused significant stratospheric ozone decreases that lasted for several weeks past the events.

Temperature changes (both heating and cooling) have been predicted to occur because of these events. Direct heating in the mesosphere is a result the transfer of energy from the solar particles to the atmospheric constituents. Indirect cooling in the stratosphere is caused by decreases in the solar heating from ozone, which is depleted during and after these events.

These solar events occur more often near solar maximum, are fairly sporadic, and can cause significant atmospheric impacts in the polar regions. The global impacts of these events, however, are relatively small compared to other natural and human-made impacts.
The Effect of Solar Proton Events on Ozone and Other Constituents

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Solar proton events (SPEs) can cause changes in constituents in the Earth's middle atmosphere. The highly energetic protons cause ionizations, excitations, dissociations, and dissociative ionizations of the background constituents. Complicated ion chemistry leads to HO\(_x\) production and dissociation of N\(_2\) leads to NO\(_y\) production. Both the HO\(_x\) and NO\(_y\) increases can result in changes to ozone in the stratosphere and mesosphere. The HO\(_x\) increases lead to short-lived ozone decreases in the mesosphere and upper stratosphere due to the short lifetimes of the HO\(_x\) constituents. The NO\(_y\) increases lead to long-lived stratospheric ozone changes because of the long lifetime of NO\(_y\) constituents in this region. The NO\(_y\)-induced ozone changes are generally decreases, however, the NO\(_y\) constituents can interfere with chlorine and bromine radicals in the lowest part of the stratosphere and cause ozone increases. Temperature changes have been predicted to occur as a result of the larger SPEs. Eleven SPEs have caused measurable atmospheric variations since 1969. Neutral wind variations were measured shortly after the July 1982 and April 1984 SPEs. The recent July 2000 SPE caused NO\(_x\) increases that lasted for two months past the event. The two periods of largest SPEs (August 1972 and October 1989) caused ozone decreases that lasted for several weeks past the events.

1. INTRODUCTION

Periodically, the Sun erupts in a solar flare and an associated coronal mass ejection (CME) that results in an intense flux of solar particles in interplanetary space. The solar particles from a CME can impact the Earth's magnetosphere if the location of the Earth is aligned relative to the solar flare and the solar magnetic field (see Figure 1). This is known as a solar proton event (SPE). The sunward side of the magnetosphere flattens and the tail elongates. Most particles are then drawn in on the far side of the magnetosphere and are carried into the polar cap regions (generally >60° geomagnetic latitude).
Figure 1. Schematic indicating the Earth and associated magnetosphere interacting with solar particles from a CME. The CME resulted from an explosion on the Sun (lower left corner) and caused the flattening of the sunward side of the magnetosphere and the elongation of tail. This was taken from an image on the CDROM entitled “The Dynamic Sun 4.0” from the NASA/ESA Solar and Heliospheric Observatory (SOHO) Mission.

The eruptions of solar protons, which are more frequent near solar maximum, can produce ionizations, dissociations, dissociative ionizations, and excitations in the middle atmosphere. The very important middle atmospheric families of HOx (H, OH, HO2) and NOx (N, NO, NO2, NO3, N2O5, HNO3, HO2NO2, ClONO2, BrONO2) are produced either directly or through a photochemical sequence. As a result, the chemistry of the polar middle atmosphere can be dramatically altered by large solar proton events.

There has been proof that the Sun can produce significant fluxes of highly energetic particles for about 60 years [Forbush, 1946]. A large SPE that occurred over 30 years ago in November 1969 gave the first evidence that ozone could be depleted by these solar eruptions [Weeks et al., 1972]. The influence of SPEs on the atmosphere has matured over the years and evidence of impacts by at least 11 large events (see Table 1) is well documented and will be discussed below.
<table>
<thead>
<tr>
<th>Date of SPEs</th>
<th>Effects of SPEs</th>
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<tbody>
<tr>
<td>November 1969</td>
<td>Ozone</td>
</tr>
<tr>
<td>January 1971</td>
<td>Ozone</td>
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<td>September 1971</td>
<td>Ozone</td>
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<td>Ozone</td>
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<tr>
<td>October 1989</td>
<td>Ozone, NO, NO₂</td>
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<tr>
<td>July 2000</td>
<td>Ozone, NO, NO₂</td>
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</table>

Table 1. List of solar proton events (SPEs) and measured atmospheric constituent influence. The effects on ozone were all decreases and the effects on NO and NO₂ were all increases.

This paper is divided into seven primary sections, including the introduction. We discuss the very important solar proton measurements in section 2. Knowledge of the solar proton flux is crucial in computing the atmospheric impacts. The production of the very significant HOₓ and NOᵧ families is discussed in sections 3 and 4, respectively. The impact of the SPEs on ozone is discussed in section 5 and the temperature and dynamical changes from SPEs are discussed in section 6. Finally, the conclusions are given in section 7.

2. SOLAR PROTON MEASUREMENTS

Solar protons have been measured by several satellites over the past few decades. The Interplanetary Monitoring Platform (IMP) series of satellites has provided measurements from 1963 to the present. The IMP satellites are in orbits that position them in interplanetary space most of the time. The last of these satellites, IMP-8, launched on October 26, 1973, is in a near circular, 35 Earth radii, 12-day orbit. The NOAA Geostationary Operational Environmental Satellites (GOES) have provided measurements since 1975. The GOES series of satellites are in geosynchronous orbits at 35,000 km above the Earth. These IMP and GOES satellite orbits, far from the Earth's atmosphere, provide reliable measurements of incoming solar protons.

The solar proton flux can change dramatically within a matter of minutes and primarily influences the polar regions. The temporal characteristics and spatial influence of the solar protons will be discussed in the next two subsections.
2.1. Temporal Characteristics

The solar proton flux is generally quite small for protons with sufficient energy to penetrate into the middle atmosphere. The October 1989 SPEs, which produced the highest flux of solar protons in the past thirty years, shows very large changes in proton fluxes over a short period of time. The protons with energies from 4.2 to 8.7 MeV, which deposit most of their energy between about 75 and 85 km, increased their flux by about a thousand in minutes. Ultimately, the increase in proton flux was five orders of magnitude above background in a couple of hours.

![Figure 2. Taken from Fig. 1 of Zadorozhny et al. [1992]. The solar proton flux (E=4.2-8.7 MeV) from GOES-7 for the second half of October 1989.](image)

2.2. Spatial Influence

Higher energy protons deposit their energy lower in the atmosphere. The precipitating protons primarily lose their energy in the creation of ion pairs in the atmosphere. An ion pair is created when a precipitating proton removes an electron (called a secondary electron) from the neutral molecule or atom, leaving behind a positive ion. The protons impart energy on the secondary electrons and these freed charged particles also cause further ionizations in the atmosphere. A computation of the rate of ionizations by incoming monoenergetic protons and their associated electrons is given in Figure 3. These protons have a flux of 1 cm$^{-2}$ s$^{-1}$ ster$^{-1}$ and are isotropic in distribution. Approximately 35 eV is expended in the production of an ion pair [Porter et al., 1976]. The total ionization rate for an SPE is computed using the actual particle
spectrum multiplied by the individual monoenergetic deposition values.

Figure 3. Taken from Fig. 1 of Reid [1986]. Rate of production of ion pairs in the atmosphere by monoenergetic fluxes of protons incident isotropically over the upward-looking hemisphere with a flux of 1 proton cm\(^{-2}\) s\(^{-1}\) ster\(^{-1}\). Curves are for energies from 0.3 MeV to 1000 MeV.

Because of the guiding influence of the Earth’s magnetic field, the effects are generally confined to the polar regions and have their largest influence on the regions of the polar caps, defined as the northern and southern areas with latitudes greater than about 60° geomagnetic. The impact of the very large July 2000 SPE on mesospheric ozone is illustrated in Figure 4. This figure shows the NOAA 14 SBUV/2 ozone measurements for the 0.5 hPa (~55 km) level [Jackman et al., 2001]. The plot on the left indicates ozone amounts on July 13, before the SPE. The plot on the right indicates ozone amounts on July 14-15, during the maximum intensity of the SPE. The polar cap (>60° geomagnetic) is outlined by the thick white oval. The figure was originally published in color, however, even in black-and-white it is still apparent that there are very significant changes in ozone during the SPE that are generally confined to the polar cap. The ozone reduction slightly outside the polar cap near 90°E longitude is probably caused by the Earth’s magnetic field being perturbed somewhat during this very significant solar disturbance. The ozone in the area outside the polar cap region did not change significantly from July 13 to July 14/15.
The atmospheric influence of a SPE is dependent on the energy spectrum of the solar protons and the absolute flux levels at the particular energies. The August 1972 SPEs were the second largest in the past 30 years and caused very significant atmospheric effects (discussed later). The computed ionization rates for these very large SPEs are given in Figure 5.

The largest values of ionization rate were computed to occur within several hours after the onset of these SPEs, and were caused by the highest energy protons. These SPEs were very "hard spectrum" events with a huge flux of very energetic protons. These fast moving protons (with energies greater than 30 MeV) arrived first and dominated the first several hours of these SPEs (Figure 5). These particular SPEs had computed ionization rates of over 1000 cm$^{-3}$ s$^{-1}$ for over a day with peak ion rates over 40000 cm$^{-3}$ s$^{-1}$ in the stratosphere (~10-50 km). Not all SPEs cause such large ion pair production in the stratosphere and, in general, most large SPEs induce atmospheric changes primarily in the mesosphere (~50-90 km).
3. PRODUCTION OF HO\textsubscript{X} CONSTITUENTS BY SPEs – MODEL COMPUTATIONS

Precipitating protons also produce HO\textsubscript{x} constituents. The basic theory for the HO\textsubscript{x} production by these particles has been known for the past thirty years. Solomon et al. [1981] provide a clear analysis of the current understanding of this process. Some earlier papers that discussed this process are Swider and Keneshea [1973] and Frederick [1976]. The production of HO\textsubscript{x} relies on complicated ion chemistry that takes place after the initial formation of ion pairs.

The production of the original positive ions N\textsubscript{2}\textsuperscript{+}, O\textsubscript{2}\textsuperscript{+}, N\textsuperscript{+}, and O\textsuperscript{+} depends on the efficiency for production from both the primary protons and their associated electrons. The O\textsubscript{2}\textsuperscript{+} constituent has a smaller ionization potential than N\textsubscript{2}\textsuperscript{+}, N\textsuperscript{+}, or O\textsuperscript{+}, thus most ions rapidly charge exchange to form it. NO\textsuperscript{+}, also a potential source of odd hydrogen [Solomon et al., 1981], is formed when N\textsuperscript{+} and O\textsuperscript{+} atoms react with O\textsubscript{2} and N\textsubscript{2}, respectively. The oxonium ion (O\textsubscript{4}\textsuperscript{+}) is generally formed from O\textsubscript{2}\textsuperscript{+} via the path

\[ \text{O}_2^+ \text{ + O}_2 \text{ + M} \rightarrow \text{O}_4^+ \text{ + M} \]

Water cluster ions are then formed via

\[ \text{O}_4^+ \text{ + H}_2\text{O} \rightarrow \text{O}_2^+\text{H}_2\text{O} \text{ + O}_2. \]
Further clustering follows this reaction with an ultimate recombination between the positive ion and an electron or negative ion. The shortest path leading to HO\(_x\) production is given by:

\[
\begin{align*}
\text{O}_2^+\cdot\text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+\cdot\text{OH} + \text{O}_2 \\
\text{H}_3\text{O}^+\cdot\text{OH} + e^- & \rightarrow \text{H} + \text{OH} + \text{H}_2\text{O}
\end{align*}
\]

Net: \(\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}\).

Solomon et al. [1981] discuss other paths for \(\text{O}_2^+\cdot\text{H}_2\text{O}\), which lead to HO\(_x\) production through recombination with free electrons. The negative ions (especially NO\(_3^-\)) become more abundant than the free electrons below about 70 km. A possible path in this region is:

\[
\begin{align*}
\text{O}_2^+\cdot\text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+\cdot\text{OH} + \text{O}_2 \\
\text{H}_3\text{O}^+\cdot\text{OH} + \text{H}_2\text{O} & \rightarrow \text{H}^+\cdot(\text{H}_2\text{O})_2 + \text{OH} \\
\text{H}^+\cdot(\text{H}_2\text{O})_2 + \text{NO}_3^- & \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O} \\
\text{HNO}_3 + \text{hv} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{Net: } \text{H}_2\text{O} + \text{NO}_3^- & \rightarrow \text{OH} + \text{OH} + \text{NO}_2.
\end{align*}
\]

Either this path or a similar one takes place in the region where negative ions prevail. The number of HO\(_x\) constituents produced per ionization as a function of altitude and ionization rate is shown in Figure 6 for daytime, polar summer conditions of temperature, air density, and solar zenith angle. Each ion pair produces about two HO\(_x\) constituents up to an altitude of approximately 70 km. Above 70 km, the production is less than two HO\(_x\) constituents per ion pair [Solomon et al., 1981]. As the ionization rate increases the computed electron density increases and the probability of the recombination of the intermediate positive ions with the electrons or negative ions increases. Thus at all altitudes the number of HO\(_x\) constituents produced per ion pair is seen to decrease with ionization rate. The production of the HO\(_x\) constituents produced per ion pair is not very dependent on solar zenith angle and will be as effective at night as during the daytime.
The HOx constituents react fairly quickly to destroy each other through reactions like

\[
OH + HO_2 \rightarrow H_2O + O_2.
\]

Therefore, the lifetime of HOx is only on the order of hours in the upper stratosphere and mesosphere. Any corresponding change in the atmosphere caused by the HOx species would only last for a couple of hours past any SPE (see section 5.1).

Large changes in HOx constituents have been computed to result from SPEs. For example, during the July 2000 SPE, HOx was computed to increase by over 100% [Jackman et al., 2001] at sunrise. To the best of our knowledge there are no published measurements of HOx changes during SPEs. Such measurements would be extremely useful to validate the theory of the HOx production during SPEs.

4. PRODUCTION OF NOy CONSTITUENTS BY SPEs

Three periods of very large SPEs have caused measurable influences on NOy constituents in the atmosphere
(Table 1). The SPEs in July 1982, October 1989, and July 2000 all showed substantial NO or NO\textsubscript{2} increases. McPeters [1986] used Nimbus 7 SBUV measurements to derive NO increases during the July 1982 SPE. Zadorozhny et al. [1992] used rockets for NO and Jackman et al. [1995] employed SAGE II measurements for NO\textsubscript{2} to derive the influences of the October 1989 SPEs on NO\textsubscript{y}. Jackman et al. [2001] and Randall et al. [2001] used the Upper Atmosphere Research Satellite (UARS) HALOE instrument data to establish the July 2000 SPE increases in NO\textsubscript{y} (NO+NO\textsubscript{2}). The influence of SPEs on NO\textsubscript{y} in the atmosphere through both measurements and model simulations will be discussed in this section.

4.1. Measurements and Model Computations of SPE-caused NO\textsubscript{y}

The precipitating protons and associated secondary electrons also produce atomic nitrogen (N) via dissociations, predissociations, or dissociative ionizations in collisions with N\textsubscript{2}. Estimates of the number of NO\textsubscript{y} constituents created per ion pair range from 0.33 [Warneck, 1972] up to 2.5 [Fabian et al., 1979]. Recent publications show only small differences and range from 1.25 [Jackman et al., 1990] up to 1.3 [Reid et al., 1991] NO\textsubscript{y} constituents produced per ion pair.

The production of NO\textsubscript{y} by SPEs has been predicted since the mid-1970s [Crutzen et al., 1975]. The NO increase after the July 1982 SPE was inferred from the Nimbus 7 SBUV instrument to be about 6 x 10\textsuperscript{14} NO molecules cm\textsuperscript{-2} above 1 hPa at polar latitudes [McPeters, 1986]. Jackman et al. [1990] computed an NO increase of 7 x 10\textsuperscript{14} above 1 hPa from the July SPE using an assumption that all the NO\textsubscript{y} produced during this SPE resulted in the production of NO. Zadorozhny et al. [1992] measured NO enhancements of 2.6 x 10\textsuperscript{15} cm\textsuperscript{-2} between 50 and 90 km at southern polar latitudes with a rocket-borne instrument as a result of the October 1989 SPEs. Jackman et al. [1995] computed a production of NO in that altitude range of 3.0 x 10\textsuperscript{15} cm\textsuperscript{-2}, again assuming all the NO\textsubscript{y} produced during these October 1989 SPEs resulted in the production of NO. Both of these computations are in reasonable agreement but higher than the measurements because some of the NO would be destroyed in the daytime through the reactions

\[ \text{NO} + \text{hv} \rightarrow \text{N} + \text{O} \]

followed by \[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}. \]

This mechanism is the primary method whereby odd nitrogen (NO\textsubscript{y}) is returned to even nitrogen (N\textsubscript{2}).

4.2. Model Computations—Yearly Production of NO\textsubscript{y}
There are other sources of NO$_y$ in the atmosphere and the importance of SPEs in producing NO$_y$ becomes clear only when comparing to these other sources. A summary of the computations of the production of NO$_y$ molecules per year is given in Figure 7 for the northern polar stratosphere (latitudes >$50^\circ$N) over the 1955 to 1993 time period [Jackman et al., 2000]. The sources include SPEs, galactic cosmic rays (GCRs), “in situ” oxidation of N$_2$O, and horizontal transport from lower latitudes.

The full histograms indicate the SPE-caused NO$_y$ production for both the stratosphere and mesosphere, while the light gray areas of the histograms indicate the SPE-caused stratospheric NO$_y$ production only. The annual production rates of NO$_y$ from GCRs, “in situ” oxidation of N$_2$O, and horizontal transport from lower latitudes are represented in Figure 7 by the dash-dot-dot-dot, dash-dot, and dashed lines, respectively. There is only about a 10% variation in the “in situ” oxidation of N$_2$O and horizontal transport from lower latitudes [Vitt and Jackman, 1996]. This minor variation is hardly noticeable on the log scale used for the ordinate in the figure and the constant values of $1 \times 10^{33}$ and $9 \times 10^{33}$ NO$_y$ molecules/year are assumed for the “in situ” oxidation of N$_2$O and horizontal transport of NO$_y$ from lower latitudes, respectively. The GCR contribution to NO$_y$ was computed to vary from 6.9 to 9.6 $\times 10^{32}$ molecules/year.

The oxidation of N$_2$O at lower latitudes and subsequent horizontal transport of NO$_y$ into the polar regions is about an order of magnitude larger than the NO$_y$ sources of GCRs and “in situ” oxidation of N$_2$O. The NO$_y$ production from SPEs for the periods 1955-1973 and 1974-1993 was taken from Jackman et al. [1980] and Vitt and Jackman [1996], respectively. This SPE-generated annual production of NO$_y$ is computed to vary by orders of magnitude over the 1955-1993 time period. There is a general solar cycle dependence with more (less) SPE-produced NO$_y$ near solar maximum (minimum). The annual SPE source of NO$_y$ in the Northern Hemisphere was larger than $1.2 \times 10^{33}$ NO$_y$ molecules/year during only 2 years (1972 and 1989). These were years in which very large fluxes of extremely energetic protons accompanied the SPEs in August 1972 and October 1989.
4.3. Measurements and Model Computations of July 2000 SPE-produced NOx

The recent SPE of July 2000 also produced substantial changes in NOx. Measurements of HALOE NO and NO2 during [Jackman et al., 2001] and a couple of months after the event [Randall et al., 2001] indicated very large increases as a result of this event. Figure 8a shows the increases in HALOE Version 19 NOx (NO+NO2) above background. The HALOE measurements were taken at different longitudes and slightly different latitudes (65.4°N to 68.5°N) over the July 12-15 period, however, the NOx changes resulting from the July 2000 SPE dominated any of the geographically-caused differences. The apparent enhancements in HALOE NOx above 0.03 hPa during the first half of July 14 are probably related to other natural variabilities and not due to the SPE. Enhancements of NOx greater than 50 ppbv and 200 ppbv are observed at 0.3 hPa and 0.01 hPa, respectively, near the end of July 15. Background NOx levels are typically 1-5 ppbv at 0.3 hPa and 20-60 ppbv at 0.01 hPa, thus the NOx increases caused by this SPE were very large.
Model computed NO\textsubscript{x} changes for 65°N are given in Figure 8b. The predicted increase in the NO\textsubscript{x} constituents from the SPE are similar to the measurements in the stratosphere and lower mesosphere up to \sim 0.3 hPa. However, in the middle and upper mesosphere (\sim 0.3 hPa), the model predicts larger increases in the NO\textsubscript{x} than observed. It is possible that some of these model/measurement differences may be related to the fraction of atomic N produced by the protons and associated electrons that end up in excited states (e.g., N(\textsuperscript{2}D)) or the ground state (N(\textsuperscript{4}S)). The family modeling approach
of Jackman et al. [2001] assumed that virtually all the NO$_x$ produced above 0.3 hPa by the July 2000 SPE was in the form of NO, implying a nearly 100% production of N($^3$D) by the precipitating particles. Rusch et al. [1981] showed that there are huge differences in the final results of model computations of NO$_y$ enhancements from SPEs that depend strongly on the branching ratios of the N atoms produced. Further study of these model/measurement differences is needed to sort out the discrepancies.

Randall et al. [2001] showed evidence that the large NO$_x$ enhancements from the July 2000 SPE lasted for at least two months past the event. They showed HALOE measurements in early September 2000 in the Southern Hemisphere polar vortex, indicating substantial enhancements of NO$_x$ in the middle stratosphere. These large increases were almost certainly caused by the July 2000 SPE. The NO$_x$ peak in the southern polar middle stratosphere occurred near 32 km and was probably a result of descent of the SPE-created NO$_x$ from the mesosphere and upper stratosphere during the winter [Randall et al., 2001].

5. OZONE EFFECTS BY SPEs

Eleven large SPEs have caused measurable influences on the atmosphere (Table 1). These SPEs all showed ozone decreases and three of the SPEs had NO or NO$_2$ increases that were measured as well as discussed in the previous section. Several papers over a span of nearly 30 years have provided the evidence of these SPE influences on ozone in the atmosphere.

Solar cycle 20 provided the first evidence of atmospheric effects by SPEs. Weeks et al. [1972] described large mesospheric ozone decreases associated with the November 1969 SPE in this solar cycle. The ozone decreases caused by the August 1972 SPEs, the second largest SPE in the past 30 years, were originally shown in the Nimbus 4 satellite BUV instrument data in Heath et al. [1977] and were reanalyzed by McPeters et al. [1981], who was able to subtract the direct effects of the high energy protons on the BUV instrument. Reagan et al. [1981] showed the spatial extent of the ozone depletion and Jackman and McPeters [1987] were able to provide ozone depletion information for nearly two months after the August 1972 SPEs, again using BUV data. McPeters et al. [1981] was also able to provide reliable information about substantial short-lived ozone depletion at 1 mbar (~50 km) and above as a result of the January and September 1971 SPEs using BUV data.

Both the Solar Mesosphere Explorer (SME) satellite [Thomas et al., 1983] and the SBUV instrument aboard Nimbus 7 [McPeters and Jackman, 1985] showed large mesospheric depletions during the large July 1982 SPE. McPeters and Jackman [1985] studied other SPEs in solar...
cycle 21 and provided evidence of ozone depletion in June and August 1979, October 1981, and December 1982.

The largest SPEs of the past 30 years occurred in solar cycle 22 in October 1989. Measurements by NOAA-11 SBUV/2 [Jackman et al., 1993] and SAGE II [Jackman et al., 1995] indicated very substantial long-term ozone depletion caused by this event.

A more recent SPE in July 2000 during solar cycle 23 caused ozone depletion that was measured by the NOAA-14 SBUV/2 and UARS HALOE instruments [Jackman et al., 2001]. This SPE was the third largest SPE in the past 30 years and provided good information about the spatial and temporal extent of the ozone changes caused by this atmospheric disturbance. Other large SPEs in this solar cycle that probably caused ozone decreases occurred in November 2000 and November 2001.

Some of these SPE-related ozone influences are short-term, caused by the HOx increases, whereas others are longer-term, caused by the NOy increases. These different ozone effects will be discussed below.

5.1. Short-term Effects from HOx Constituents

The depletion of ozone by the SPE-enhanced HOx constituents has been simulated in several papers [e.g., Swider and Keneshea, 1973; Frederick, 1976; Swider et al., 1978; Solomon et al., 1981; Jackman and McPeters, 1985]. All the SPEs given in Table 1 have a HOx-induced ozone depletion associated with them. As noted in section 3, the HOx constituents do not last more than a couple of hours after an SPE. However, the HOx constituents can have very significant influences on ozone, especially in the mesosphere. There are several catalytic processes through which the HOx constituents destroy ozone.

An important catalytic process in the stratosphere (∼10-50 km) which leads to ozone destruction is:

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 \\
\text{Net: O}_3 + \text{O} \rightarrow 2\text{O}_2.
\]

At mesospheric altitudes (∼50-90 km) the catalytic process

\[
\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 \\
\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 \\
\text{Net: O} + \text{O}_3 \rightarrow 2\text{O}_2
\]

is a dominant mechanism for ozone destruction.

The influence of a SPE on ozone through the HOx constituents is very dependent on the solar zenith angle. The ambient HOx level is maintained by the following two mechanisms
H₂O + hν → H + OH (dominant above 70 km)

and O(D) + H₂O → OH + OH (dominant below 70 km).

Both of these reactions are only active in the sunlight. The first mechanism is directly dependent on the sun and the second mechanism is dependent on the production of O(D), a very short-lived constituent, which is produced by the photolysis of O₃. Since the HOₓ production by the SPEs is not dependent on sunlight (see section 3), the SPE-produced HOₓ will have a larger impact on ozone at larger solar zenith angles, where the ambient HOₓ production is less. Solomon et al. [1983] and Jackman and McPeters [1985] provide further details about this solar zenith angle dependence of the SPE-produced HOₓ impact on ozone.

This dependence of the ozone depletion caused by SPE-produced HOₓ on solar zenith angle can be seen quite well in Figure 9 [Solomon et al., 1983]. The figure shows both model computations and measurements during different portions of the Solar Mesosphere Explorer (SME) orbit. The model computations are close to the observations during the AM portions of the SME orbit, the AM portion of the orbit being at the very large solar zenith angles. There is less agreement between the model and observations during the PM portions of the SME orbit. Notice that the measurements show larger amounts of ozone depletion at the larger solar zenith angles, consistent with theoretical predictions.
The ozone depletion during the July 2000 SPE was also mostly caused by the HOx production (shown in Figure 8). The percentage decreases in the HALOE sunrise ozone measurements are given in Figure 8c where the July 14-15 values are compared to the background average of the July 12-13 observations. The HALOE observed ozone reductions start on July 14 and reach over 70% during most of July 15 in the middle mesosphere between 0.3 and 0.01 hPa. The model computations in Figure 8d are fairly similar to the HALOE measurements during most of the event.
Although there appears to be reasonable agreement between the model and HALOE measurements, Jackman et al. [2001] did point out some discrepancies between the model and SBUV/2 measurements at 1-2 hPa (~45-50 km). The SBUV/2 measurements indicated a larger ozone depletion than predicted. Reaction rate adjustments for HOx constituents discussed in Conway et al. [2000] did not help the model/measurement agreement. These discrepancies need to be investigated further.

5.2. Long-term Effects from NOy Constituents

The influence of the SPE-enhanced NOy constituents on ozone has been understood nearly as long as the impact of the SPE-enhanced HOx constituents. Crutzen et al. [1975] predicted that the nitric oxide (NO) produced during three large SPEs between 1960 and 1972 would probably have been enough to cause an ozone change. The Heath et al. [1977] results showed that there were large stratospheric ozone reductions apparent in the Nimbus-4 BUV instrument data up to 19 days past the August 1972 events and were probably caused by the NOy enhancements. Several other papers, including Fabian et al. [1979], Maeda and Heath [1980/1981], Reagan et al. [1981], Solomon and Crutzen [1981], Rusch et al. [1981], and Jackman et al. [1990, 1995, 2000], studied various aspects of NOy influence on stratospheric ozone. The primary catalytic cycle for NOy destruction of ozone is

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \\
\text{Net: } \text{O}_3 + \text{O} & \rightarrow 2\text{O}_2.
\end{align*}
\]

A comparison of the Nimbus 4 BUV measurements and model predictions of ozone destruction caused by the extremely large August 1972 SPEs is given in Figure 10. Virtually all the ozone destruction observed beyond day 222 was caused by the NOy enhancements from this SPE. Both the measurements and model computations indicate ozone depletions of over 20% in the upper stratosphere during the SPE with depletions of over 15% persisting for about two months after the SPE. The major difference between the measurements and model results is in the upper stratospheric and lower mesospheric region (near 50 km), where the model indicates a faster recovery from the initial SPE-caused ozone depletion than is indicated in the measurements.
Figure 10. Taken from Figs. 6a and 7a of Jackman et al. [1990]. (a) Nimbus 4 BUV measured ozone percentage change as a function of day of year in 1972 for 70°-80°N band. (b) Model predicted ozone percentage change as a function of day of year in 1972 for 75°N. The contour levels of -30, -20, -15, -10, -5, 0, +1, +2, and +3%.

The long lifetime of the NOy constituents allows the influence on ozone to last for a number of months past the event. Figure 11 shows the model predicted temporal behavior of profile ozone and NOy for 1989-1992 at 75°N. Predicted upper stratospheric increases in NOy over 100% during and shortly after the extremely large October 1989 SPEs produced significant upper stratospheric ozone decreases (>10%). The downward transport in the late fall and winter caused the very large enhancements of NOy in the upper stratosphere to be moved to lower stratospheric levels with a corresponding ozone decrease. NOy en-
 enhancements of over 10% accompanied by ozone decreases of greater than 2% persisted for over a year past these events. Ozone decreases down to 100 mbar (~16 km) were predicted by the spring of 1990 as a result of these events in 1989.

![Figure 11. Taken from Fig. 6 of Jackman et al. [2000]. Model-computed percentage changes in NO\textsubscript{r} and O\textsubscript{3} at 75°N for 1989-1992 resulting from SPEs. Contour intervals for NO\textsubscript{r} are 0, 1, 2, 10, 20, 100, and 200%. Contour intervals for O\textsubscript{3} are +2, 0, -2, -1, -2, -10, and -20%.]

5.3. Self-healing and Halogen Interference Leading to Ozone Increases

Ozone is usually depleted by SPE enhancements of HO\textsubscript{x} and NO\textsubscript{y}, but it can also be increased in certain regions. Jackman and McPeters [1985] showed that ozone “self-healing” should also be associated with SPEs. When ozone is decreased at a higher altitude, increased ultraviolet (UV) radiation penetrates to lower altitudes. The increased UV radiation at very low altitudes (or extremely large solar zenith angles) can lead to an ozone production due to an increase in O\textsubscript{2} dissociation

\[
\text{O}_2 + \text{hv} (<242 \text{ nm}) \rightarrow \text{O} + \text{O}
\]

followed by

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3,
\]

and

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3.
\]

Predicted ozone increases below about 40 mbar (~22 km) in 1989 in Figure 11 (lower graph) are the result of self-healing. Such effects are small and the ozone self-
healing only partially compensates for the higher altitude depletion of ozone caused by the SPE-enhanced NOy.

The ozone enhancements in the lowest part of the stratosphere (below ~22 km) in late 1990, 1991, and 1992 shown in Figure 11 (lower graph) were caused by the interference of downward transported NOy with chlorine and bromine constituents [Jackman et al., 2000]. More ClO and BrO radicals were tied up into reservoir species ClONO2 and BrONO2 by the enhanced NO2 in the lower stratosphere through

\[
\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M} \\
\text{and BrO} + \text{NO}_2 + \text{M} \rightarrow \text{BrONO}_2 + \text{M}.
\]

Since the chlorine and bromine radicals are very important in the control of ozone in the lower stratosphere, the interference production of the reservoir species ClONO2 and BrONO2 resulted in a net decrease in the catalytic loss of ozone. This process then led to a predicted ozone increase, which is especially important in periods of high chlorine and bromine loading such as the present time [Jackman et al., 2000].

5.4. Total Column Ozone Changes

The predicted influence of the SPEs in October 1989 on total column ozone is illustrated in Figure 12. This largest SPE of the past 30 years was predicted to have caused a maximum total ozone depletion of about 2%. The largest predicted ozone depletions due to these SPEs were in late 1989 and 1990. Total ozone depletions were less in 1991 and were almost non-existent or positive in 1992. These impacts on total column ozone are fairly small and would be difficult to discern in measurements because of large daily fluctuations at polar latitudes due to meteorological and seasonal variations [e.g., see WMO, 1999]. Marin and Lastovicka [1998] were not able to find any signal for SPEs in a Dobson total ozone record for central Europe (50°N).
The influence of SPEs on global total ozone variations was compared to the other natural (solar cycle ultraviolet variations and large volcanic eruptions) fluctuations as well as the anthropogenically-caused ozone variations in Jackman et al. [1996]. The annually averaged almost global total ozone, computed between 65°S and 65°N, was predicted in Jackman et al. [1996] to: 1) decrease about 4% from 1979 to 1995 due to anthropogenically-induced increases of chlorine and bromine; 2) decrease a maximum of about 2.8% in 1992 as a result of the very large Mt. Pinatubo volcanic eruption; 3) vary by about 1.2% as a result of solar ultraviolet flux variations over a solar cycle; 4) decrease by about 0.2% as a result of the extremely large SPEs in October 1989; and 5) vary by about 0.02% as a result of GCRs over a solar cycle. The influence of SPEs on global total ozone variations is thus rather small compared to other natural and humankind-caused fluctuations or trends.

6. SPE-CAUSED TEMPERATURE AND DYNAMICAL VARIATIONS

Large SPEs can also influence temperature and dynamics in the middle atmosphere. The temperature change associated with SPEs has been discussed in previous studies [e.g., Banks, 1979; Reagan et al., 1981; Jackman and McPeters, 1985; Roble et al., 1987; Reid et al., 1991; and Jackman et al., 1995]. Other studies [Rottger, 1992; Johnson and Luhmann, 1993] have documented changes in long-period gravity waves and neutral winds in the polar mesosphere as a result of SPEs.

SPEs can cause both heating and cooling of the middle atmosphere. Direct atmospheric heating is caused by the
precipitating particles through Joule heating. Banks [1979] computed Joule dissipation temperature rate changes of 1° to 10°K per day in the mesosphere as a result of the very large August 1972 SPEs. Roble et al. [1987] computed similar mesospheric temperature rate changes during the July 1982 SPE. The July 1982 SPE was comparable to the August 1972 SPEs in the mesosphere. These mesospheric temperature rate forcings from Joule heating are comparable to or larger than the solar ultraviolet heating in this region and could cause small short-term temperature increases. Negligible temperature rate changes via Joule heating were computed in the stratosphere as a result of these SPEs.

Since ozone is one of the primary radiative absorbing (heating) gases of the middle atmosphere, a decrease in ozone as a result of SPEs could be expected to result in lower temperatures. Reagan et al. [1981] calculated a temperature decrease of 2.2°K at 50 km during the extremely large August 1972 SPEs. Jackman and McPeters [1985] computed a temperature decrease of a maximum of 1.1°K due to the July 1982 SPE. The July 1982 SPE was smaller than the August 1972 SPEs in the stratosphere. Reid et al. [1991] and Jackman et al. [1995] calculated maximum temperature decreases of about 3°K at 75°S in the upper stratosphere (40-50 km) as a result of the very large October 1989 SPEs. These temperature changes are longer-lived than those associated with the Joule heating and would last as long as the SPE-caused ozone decreases, which could be for several months in the stratosphere.

Rottger [1992] discussed large wave amplitudes in the meridional wind (long-period gravity waves) in the polar lower mesosphere during SPEs in October and December of 1989. These changes may be caused by the Joule heating as well as the heating rate changes generated from ozone depletions, both effects from SPEs. Such SPE-caused atmospheric variations follow a certain temporal and spatial variation and could produce vertical wavelengths of about 10 km and northward velocities up to ±40 m s⁻¹ due to the wave [Rottger, 1992].

Consistent with these observations by Rottger [1992], Johnson and Luhmann [1993] showed observations of variations in upper mesospheric neutral winds accompanying the July 1982 and April 1984 SPEs. As a result of the July 1982 SPE, the mean wind shifted to the west-southwest by 5-30 m s⁻¹ over the 81-90 km range, which was approximately twice the normal standard deviation. Similar mean wind shifts were observed as a result of the April 1984 SPE, although this occurred primarily at lower altitudes (65-75 km). Johnson and Luhmann [1993] speculate that the Joule heating and ozone depletion probably played a role in the SPE-related wind changes.
7. CONCLUSIONS

The polar middle atmosphere is readily influenced by large SPEs. SPEs can cause huge changes in the constituents in the polar middle atmosphere and can be used to study the natural variations in ozone. HOx increases of greater than 100% at high solar zenith angles were computed in the mesosphere as a result of large SPEs. The NOx-induced stratospheric increases from SPEs are more persistent and are computed to be greater than 10% for over a year past the extremely large October 1989 SPEs.

Eleven SPEs have caused measured ozone depletions in the last 32 years. All these SPEs showed ozone depletions during the events, which were primarily HOx-induced. The HOx-induced ozone depletions from the larger SPEs were computed and measured at high solar zenith angles to be quite large (>50%) in the middle to upper mesosphere. Three of these SPEs had lingering ozone depletions past the events, which were primarily NOx-induced. Ozone depletions of 15% from the extremely large August 1972 SPEs persisted for two months after these events in the upper stratosphere.

Polar total column ozone was computed to be decreased by a maximum of about 2% depletion as a result of the extremely large October 1989 SPEs. Annually averaged global total ozone decreases were calculated to be 0.2% in 1990 as a result of these events, relatively small compared to other natural and humankind related changes.

SPEs may also change the temperature and dynamics of the middle atmosphere either directly through Joule heating or indirectly through an associated ozone depletion. Joule heating from very large SPEs was comparable to or larger in the mesosphere to the solar ultraviolet heating. Polar mesospheric temperatures were predicted to be lowered through ozone depletion in the upper stratosphere by 2-3°K as a result of extremely large SPEs. Gravity waves and winds in the mesosphere were observed to vary as a result of these changed heating rates from the SPEs.

These solar events input quantifiable amounts of HOx and NOy into the atmosphere and can be used to test the current understanding of the atmospheric chemistry and dynamics. Although there is a general agreement between model predictions and measurements concerning SPE-induced ozone influences, some differences remain. The largest differences between the measured and modeled ozone depletions caused by SPEs occur in the upper stratosphere, both for the HOx- and the NOy-induced changes. This region should be further scrutinized during large SPEs to resolve these model/measurement inconsistencies.

Acknowledgments. We thank NASA Headquarters Atmospheric Chemistry Modeling and Analysis Program for support.
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**EFFECT OF SPEs ON OZONE AND OTHER CONSTITUENTS**

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