AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2017GL075966

Key Points:
- Solar proton events cause ozone destruction at locations in the polar vortex. There is no change in ozone at sites outside the polar vortex
- Ozone depletion following SPEs is ~5–10%. The ozone partial pressure decreases rapidly and remains depleted for >30 days
- Very rapid descent of NO_x species in the polar vortex is the likely cause of stratospheric ozone destruction following SPEs

Supporting Information:
- Supporting Information S1

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Citation:
Denton, M. H., Kivi, R., Ulich, T., Clilverd, M. A., Rodger, C. J., & von der Gathen, P. (2018). Northern hemisphere stratospheric ozone depletion caused by solar proton events: The role of the polar vortex. *Geophysical Research Letters*, *45*, 2115–2124. https://doi.org/10.1002/2017GL075966

Received 6 OCT 2017
Accepted 11 FEB 2018
Accepted article online 16 FEB 2018
Published online 28 FEB 2018

Northern Hemisphere Stratospheric Ozone Depletion Caused by Solar Proton Events: The Role of the Polar Vortex

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Abstract Ozonesonde data from four sites are analyzed in relation to 191 solar proton events from 1989 to 2016. Analysis shows ozone depletion (~10–35 km altitude) commencing following the SPEs. Seasonally corrected ozone data demonstrate that depletions occur only in winter/early spring above sites where the northern hemisphere polar vortex (PV) can be present. A rapid reduction in stratospheric ozone is observed with the maximum decrease occurring ~10–20 days after solar proton events. Ozone levels remain depleted in excess of 30 days. No depletion is observed above sites completely outside the PV. No depletion is observed in relation to 191 random epochs at any site at any time of year. Results point to the role of indirect ozone destruction, most likely via the rapid descent of long-lived NO_x species in the PV during the polar winter.

1. Introduction

Numerous factors influence the spatial and temporal variabilities of stratospheric ozone. The annual cycle in the Arctic stratosphere is primarily due to ozone transport from lower latitudes toward the poles (e.g., Butchart, 2014, and references therein). Transport is strongest in winter and early spring, and ozone variability is maximized during this period (Christiansen et al., 2017; Kivi et al., 2007). Ozone decreases substantially in late spring and summer at high latitudes. This is due to ozone production and transport being too slow to offset the destruction of ozone via catalytic reactions involving odd-nitrogen (NO_x) species. In contrast, the occurrence of sudden stratospheric warmings can also dramatically increase the level of ozone in the stratosphere, particularly during late winter/early spring (see Kivi et al. (2007) for a detailed discussion of the annual ozone cycle, interannual variability, and day-to-day changes in ozone in the northern hemisphere Arctic region).

NO_x species are long-lived in the absence of sunlight and persist for many days at mesospheric altitudes. During winter the polar vortex (PV) greatly increases the rate of descent of NO_x species from higher altitudes down into the stratosphere where catalytic destruction of ozone occurs (e.g., Jackman et al., 1995, 2009; Solomon et al., 1982). Descent can be greatest at the edge of the PV where the temperature is also relatively high (Tegtmeier et al., 2008). We concentrate on the northern hemisphere in this study since descent rates can be greater here than in the southern hemisphere. The amount of time that a location is within (or at the edge of) the PV and the amount of NO_x present at higher altitudes are factors to consider when evaluating the destruction of ozone via catalytic reactions.

Solar proton events (SPEs) are identified by the measurement of fluxes of energetic protons detected in the Earth's magnetosphere. SPEs occur due to energetic processes on the Sun and energization processes (e.g., shocks) in interplanetary space (e.g., Kurt et al., 2004; Oh et al., 2010; Reames, 1999; Tylka et al., 2006). Sufficiently energetic protons penetrate the Earth's magnetosphere around the poles and precipitate into the atmosphere. The proton energy determines the depth into the atmosphere reached before collision with neutral atmospheric constituents (Jackman & McPeters, 1985; McPeters & Jackman, 1985). The most energetic protons penetrate through the atmosphere and reach ground level. The proton energy also determines its rigidity (momentum-per-unit-charge). Protons require a minimum rigidity to penetrate to a particular geomagnetic latitude (Neal et al., 2013; Rodger et al., 2006).

Different forms of energetic particle precipitation (EPP), including SPEs, have been linked to creation of odd nitrogen (NO_x) and odd hydrogen (HO_x) species in the mesosphere and stratosphere (e.g., Clilverd et al., 2005; Crutzen et al., 1975; Shumilov et al., 2003; Solomon et al., 1981; Turunen et al., 2016). Changes in ozone following the largest SPEs demonstrate that ozone in the mesosphere and stratosphere decreases over a period of hours to weeks (e.g., Heath et al., 1977; Lopéz-Puertas et al., 2005; Seppälä et al., 2004, 2006, 2008; Thomas et al., 1983; Weeks et al., 1972). Theoretical investigations have provided estimates of long-term and short-term implications for atmospheric ozone balance (e.g., Jackman et al., 1996, 2009; Jackman & McPeters, 1985; Rodger et al., 2008; Sinnhuber et al., 2006). In general, two major processes are believed to occur. Process A: the short-term "direct" destruction of ozone due to production of HO_x species by incident solar protons (e.g., Solomon et al., 1981). The lifetime of HO_x is approximately hours in the stratosphere and mesosphere, and hence, the effects of HO_x-induced ozone destruction last at most for a few days (e.g., Jackman & McPeters, 1985). For this current study, involving balloon-based measurements up to ~35 km altitude, energies of ~100–1,000 MeV would be required (cf. Figure 4 of Turunen et al. (2009)). Process B: the delayed "indirect" destruction of stratospheric ozone, following initial generation of NO_x species over a range of altitudes. Given the right conditions these long-lived species descend to lower altitudes where they cause ozone depletion (Jackman et al., 1980). Randall et al., (2001) demonstrated that NO_x persists for >2 months after generation by SPEs. However, the descent of NO_x can be slow (e.g., around 8 km/month at ~50 km altitude; Manney et al., 1994; Rinsland et al., 2005). Hence, a more gradual response in the ozonesonde observations is expected for the indirect route, rather than a decrease immediately following solar-proton arrival at Earth, via the direct route. For the indirect route, the continual circulation and mixing of the atmosphere complicate our ability to reveal definitive cause/effect relationships. Other pathways for ozone destruction have been noted in the literature (Damiani et al., 2008, 2009, 2012; Jackman et al., 2009). It seems certain that a combination of physical processes, each potentially causing ozone destruction, occurs in the atmosphere following SPEs.

Understanding and quantifying the effects of EPP upon the atmosphere is a major unsolved problem in magnetospheric and atmospheric physics (Denton et al., 2016). Recently, Damiani et al. (2016) used Aura satellite data to reveal an ~10–15% decrease in stratospheric ozone in the southern polar regions during geomagnetically active periods, as measured by the Auroral Electrojet (Ae) and Average Planetary (Ap) indices (Davis & Sugiura, 1966). Descent of mesospheric NO_x down to stratospheric heights, via the PV, was proposed as causing the ozone depletion. A more recent statistical study of the effects of SPEs above northern Finland showed that significant ozone depletion occurred, but only when the PV was present during winter/early spring; ozone was unchanged during summer/early autumn (Denton et al., 2017). Here we study SPE effects using in situ observations of stratospheric ozone over a much greater geographic region. We use extensive data sets of balloon-based observations of ozone from four sites. Initially, the ozone climatology at each site is determined. The effects of SPEs are then explored by means of superposed epoch analysis of multiple SPEs. Finally, the effects of the PV on stratospheric ozone destruction at each of the sites are considered and the implications discussed.

2. Data

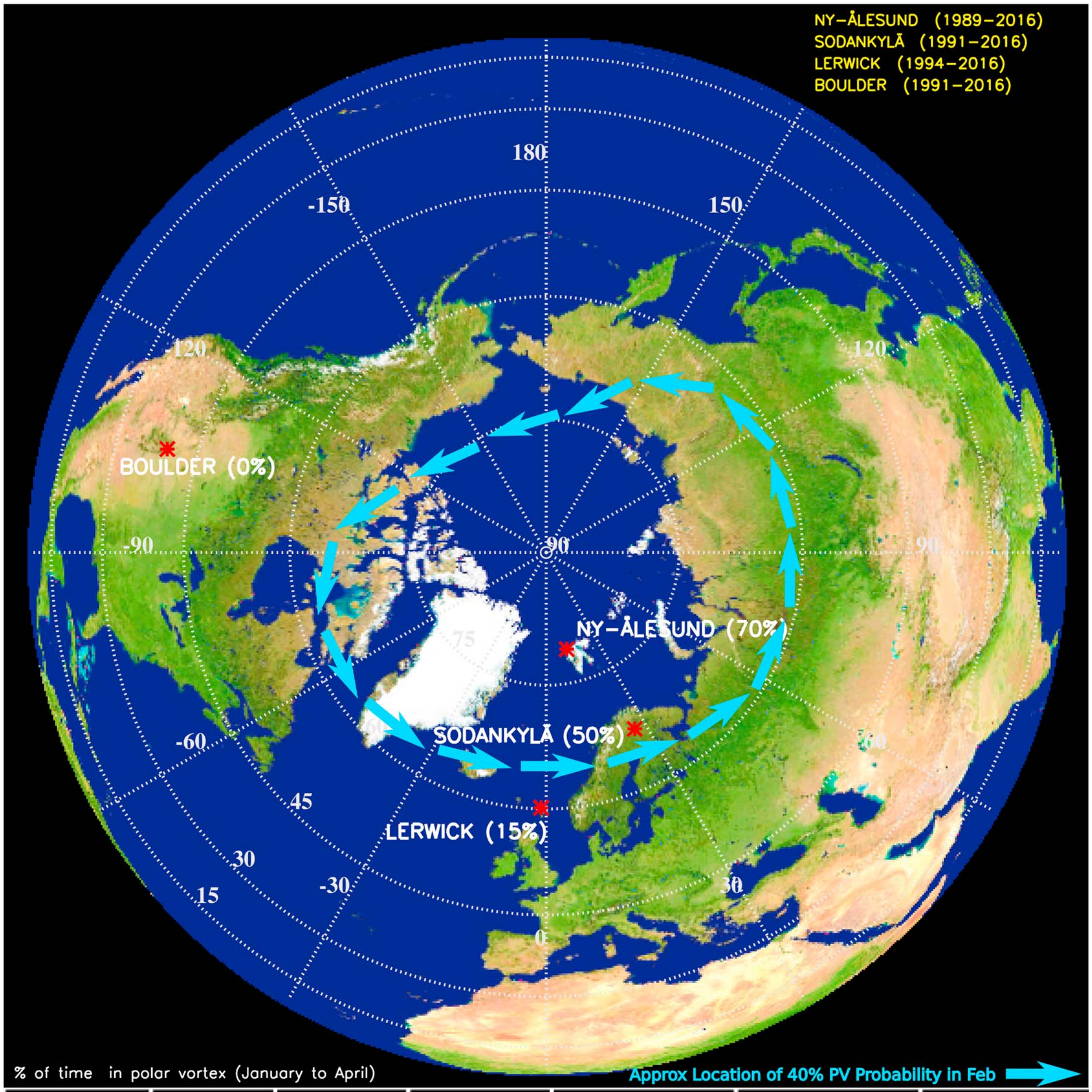
Ozone profiles used in this study originate from four "ozonesonde" launch sites in the northern hemisphere: Ny-Ålesund (NY-Å), Sodankylä (SOD), Lerwick (LER), and Boulder (BOU). Figure 1 shows the location of the ozonesonde launch sites and the average period each site resides within the PV during the months of January, February, March, and April (JFMA) (Karpetchko et al., 2005; Kivi et al., 2007). Data coverage for each site is also shown. Magnetic latitudes are calculated from the International Geomagnetic Reference Frame (Thébault et al., 2015) in corrected geomagnetic coordinates.

Ozonesondes are primarily electrochemical concentration cell (ECC) detectors (Deshler et al., 2008, 2017; Kivi et al., 2007; Smit and ASOPOS Panel, 2014). Stations were selected to provide a spread of observations within the PV (NY-Å and SOD), near the edge of the PV (LER), and never within the PV (BOU). The blue arrows in Figure 1 denote that the approximate location where the PV is present ~40% of the time during February (after Karpetchko et al., 2005).

3. Methodology and Results

3.1. Climatology

To determine changes in stratospheric ozone due to external causes, it is necessary to understand the climatology near each station. Variations occur due to (i) "internal" effects such as the quasi-biennial oscillation



Sites	Latitude (GLAT)	Longitude (GLONG)	Magnetic Latitude (CGM)	Average Time in PV (Jan-Apr)	#Ozonesondes in Analysis	Reference
Ny-Ålesund	78.90	12.00	76.15	~70%	2350 (1991-2016)	*Rex et al.* [2000]
Sodankylä	67.37	26.63	26.63	~50%	1886 (1989-2016)	*Kivi et al.* [2007]
Lerwick	60.15	-1.15	58.03	~15%	1289 (1994-2016)	*Smedley et al.* [2012]
Boulder	40.01	-105.27	48.90	~0%	1287 (1991-2016)	*Johnson et al.* [2002]

Figure 1. Ozonesonde launch sites. The location where the polar vortex (PV) is present ~40% of the time (on average) in February is shown by light-blue arrows (after Karpetchko et al., 2005). The percentage of time that the PV is above each site between January and April is also indicated (Kivi et al., 2007).

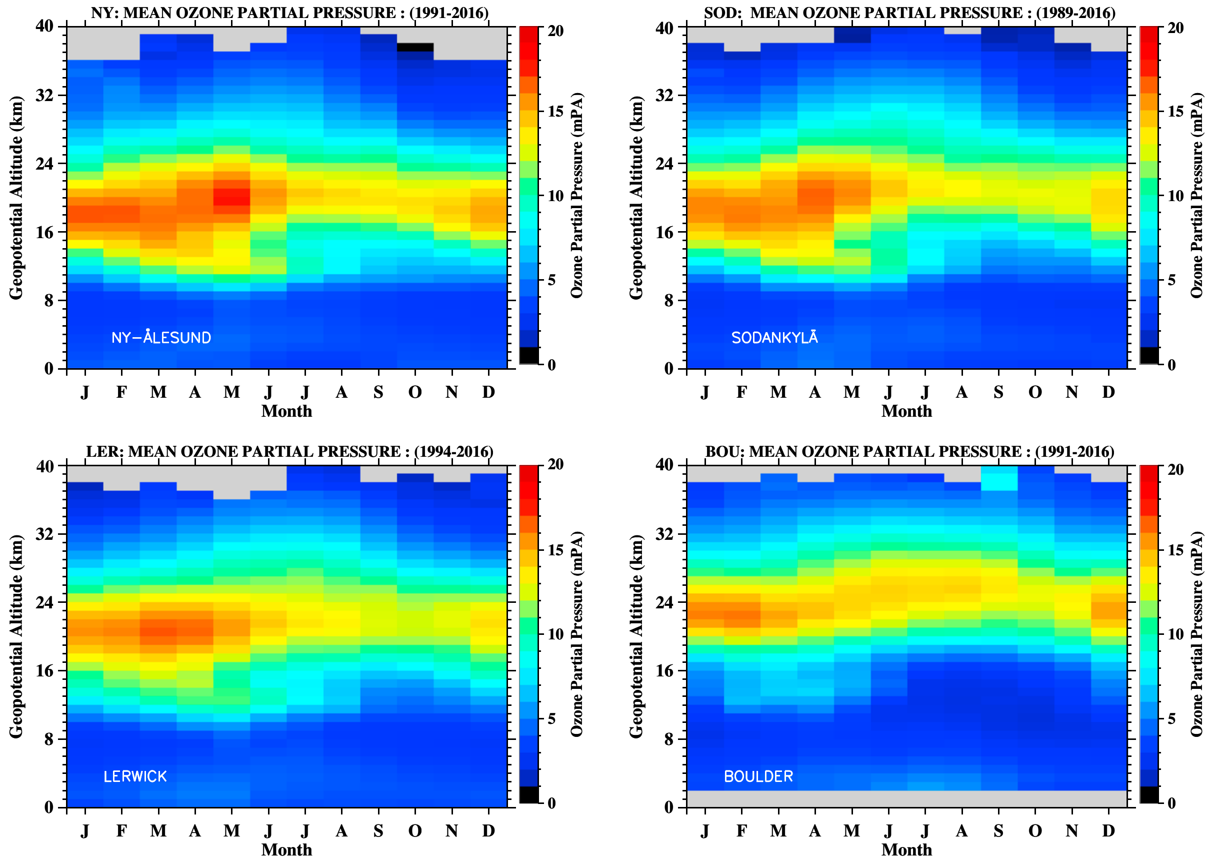


Figure 2. The mean ozone partial pressure as a function of geopotential altitude for the four sites.

cycle, volcanic eruptions that perturb aerosol concentrations, (ii) "external" effects such as the 11 year solar cycle, and (iii) longer-term internal trends, e.g., due to anthropogenic causes (Kivi et al., 2007; Manney et al., 2011). Climatology is determined by calculating the mean ozone partial pressure (in mPa) as a function of geopotential altitude (in km) and month of the year, for all available data to 2016. Results are shown in Figure 2. (Note: for comparison the mean ozone at the southern hemisphere site of Syowa can be found in the supporting information of this paper.) The climatology is similar at each site. The highest ozone levels occur in late winter/spring, and the lowest ozone levels occur in late summer/autumn. Ozone partial pressure also varies with geographic latitude. The highest values are observed at NY-Å, and the lowest values are observed at BOU. The altitude of peak ozone is higher closer to the equator and lower toward the pole. In addition, the highest ozone partial pressure occurs earlier in the year at lower latitudes (e.g., February above BOU) and later at higher latitudes (e.g., May above NY-Å). Analysis of changes in ozone partial pressure that consider time periods beyond a few days will need to account for this climatology.

3.2. Solar-Proton Events and Stratospheric Ozone Depletion

We examine external driving of the atmosphere following 191 SPEs (1989–2016) selected from the U.S. National Oceanic and Atmospheric Administration Space Weather Prediction Center list (ftp://ftp.swpc.noaa.gov/pub/indices/SPE.txt). Epoch times for the superposed epoch analysis, taken from this list, are times when three consecutive data points measured by the GOES spacecraft at geosynchronous orbit exceed 10 particle flux units at energies $>$10 MeV.

The analysis uses methodology similar to Denton et al. (2017) in their study of ozone over SOD (1989–2015). Results from that study were somewhat ambiguous since only one location was considered. Here data from four different sites are analyzed. In brief, all available data for the months January to April (inclusive) are binned as a function of epoch time (1 day epoch time bins) and geopotential altitude (1 km altitude bins). Restricting data to these months ensures that the PV may be present at sites in the northern hemisphere.

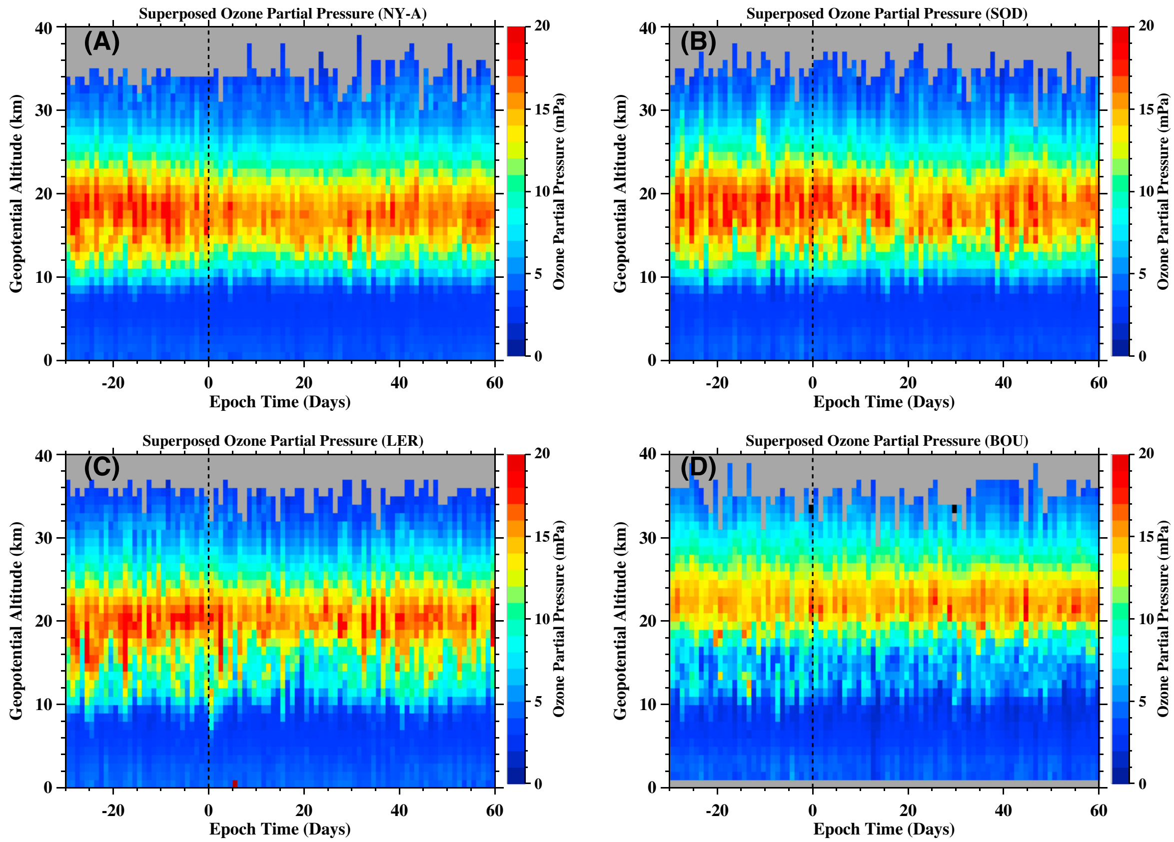


Figure 3. Superpositions of ozone partial pressure over four sites during 191 SPEs. Zero epoch marks the start of the SPE and a subsequent decrease in ozone is apparent at Ny-Ålesund, Sodankylä, and Lerwick.

Each site has a different likelihood of being within the PV during these months (see Figure 1). Binning is carried out for 90 days of epoch time, from 30 days prior to zero epoch to 60 days after zero epoch and results are shown in Figure 3.

Visual inspection of the plots reveals evidence for a decrease in stratospheric ozone for ~20 days following zero epoch at NY-Å and SOD. The onset of ozone depletion appears to be delayed from zero epoch by a few days, but loss is rapid thereafter. NY-Å and SOD are frequently within the PV during winter/early spring. LER is within the PV infrequently; a decrease in ozone following zero epoch is less clear at this site. For BOU (outside the PV) there is little evidence of any change in the ozone partial pressure.

Although the plots in Figure 3 are suggestive, the analysis takes no account of climatological variations in stratospheric ozone. To better quantify the changes following SPEs we first correct for seasonal effects. This is done by computing the (logged) ratio of the measured ozone to the appropriate monthly mean ozone value at each site (i.e., from Figure 2) for each measured data point. Any change from zero from this value will thus be (largely) independent of seasonal changes. Previously, Denton et al. (2017) used similar methodology for the SOD data up to 2015 and compared against 2500 randomly selected epochs, generated using the methodology of Park and Miller (1988). They concluded that the PV was necessary for ozone depletion above northern Finland following SPEs. A decrease in ozone was observed during winter months of January–April (JFMA), when compared with July–October (JASO), and when compared with random epochs in these months. Here we extend this work to the four sites in Figure 1. To ensure the same statistical noise for all the analyses, we use 191 random epochs for comparison. Results in Figure 4 show 15 day running means of the ratio of the measured ozone to the monthly mean ozone (logged) at the altitude of peak ozone (~18 km for NY-Å and SOD, ~21 km for LER, and ~22 km for BOU). To provide an estimate of the statistical significance of the plots we also plot the 95% confidence interval about the mean (Wilks, 2006). A similar technique has been used in comparable superposed epoch studies (e.g., Morley et al., 2010; Morley &

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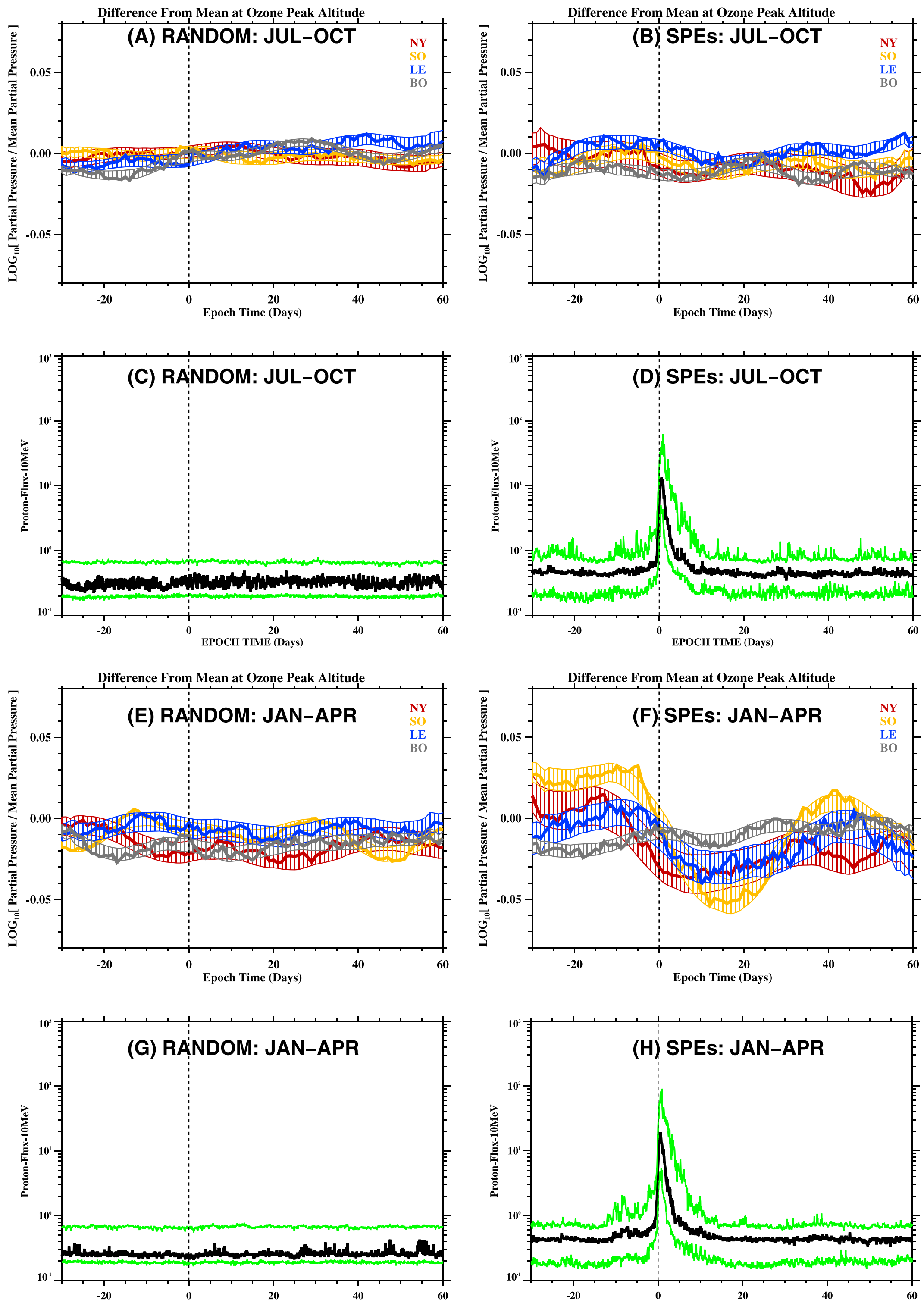

Figure 4. Showing 15 day running means (thick lines) of the ratio of ozone partial pressure to monthly mean ozone partial pressure, at the peak altitude of the ozone layer during (left) 191 random epochs and (right) 191 solar proton events. The 95% confidence interval about the mean is also plotted. Plots are shown for July–October and January, February, March, and April. Also shown are corresponding solar proton fluxes for $E > 10$ MeV. In these panels the black line is the median of the superposition while the green lines are upper and lower quartiles.

Freeman, 2007). Results are shown for 191 random epochs and 191 SPEs, for summer (JASO) and winter (JFMA) months. Also plotted is the median solar proton flux at energies $E > 10$ MeV (black) measured by GOES satellites at geosynchronous orbit, taken from the OMNI2 database (King & Papitashvili, 2005). Upper and lower quartiles are also plotted (green).

It is clear from Figure 4 that there is little change in ozone when the PV is absent from all sites in JASO, for both SPEs and random epochs (Figures 4a and 4b). Fluctuations around the mean ozone value are observed with no discernible trend. During JFMA, when the PV may be present at some of the sites, the ozone shows slightly larger fluctuations for the random epochs (Figure 4e). However, the fluctuations again show no clear trend. In contrast, for the SPE epochs (Figure 4f), there are large changes in the ozone partial pressure at NY-Å, SOD, and LER. A substantial decrease commences around zero epoch, and ozone remains depressed for ~30 days. Note: The decrease in ozone appears to commence a few days before the zero epoch at NY-Å and SOD. On investigation, this is likely due to either (a) the averaged proton flux at >10 MeV also increasing slightly before zero epoch (Figure 4h) and/or (b) the use of a 15 day running mean of ozone partial pressure. A similar effect was observed in Denton et al. (2017) where the raw data did not start to decline until zero epoch even though the 15 day running mean showed a decrease prior to zero epoch. All three sites where the ozone depletions occur are within the PV for some proportion of the time, although for LER, this is only ~15% of the total. At BOU, continually outside the PV, where solar protons essentially do not have direct access, there is no clear change in ozone partial pressure after zero epoch. We have confidence, at the 95% level, that the "true" mean of the data lies between the confidence intervals as plotted. The variations of ozone following SPEs are, for NY-Å, SOD, and LER, substantially greater than the spread in the confidence interval indicating a real effect due to SPEs. Since electrochemical concentration cell ozonesondes also measure temperature, we carried out a corresponding analysis of the temperature at each site to check for other effects that may affect stratospheric ozone. No clear trend in the superposed temperature was measured at any site in this period (see supporting information for the superposed temperature during JFMA at the NY-Å site).

4. Discussion

The motivation for this study stems from the need to separate "external" influences on stratospheric ozone (e.g., EPP effects) from "internal" influences (e.g., anthropogenic changes to the Earth's atmosphere). Climate models typically concentrate on the latter, although we acknowledge recent efforts to include EPP effects into coupled climate models (e.g., Matthes et al., 2017).

The analyses and results above quantify the effects of SPEs upon stratospheric ozone with respect to the PV. By removing seasonal effects, we show that SPEs are causing ozone depletion only in the presence of the PV. Although accurate quantification of the depletion is difficult, a change of ~1–2 mPa following SPEs equates to a maximum change of ~5–10%. The rapidity of the change (with decrease and subsequent increase taking ~few days) suggests that SPE effects are largely decoupled from other factors influencing ozone dynamics. Stratospheric ozone appears to fully recover following each SPE, although given the complex dynamics and transport in the northern hemisphere, the cumulative effects of many SPEs are unclear. Modeling studies could likely shed light on this better than observations.

Previous studies have revealed that local changes in stratospheric ozone occur following some of the largest SPEs (e.g., Heath et al., 1977; Lopéz-Puertas et al., 2005; Päivärinta et al., 2013; Seppälä et al., 2006, 2008; Thomas et al., 1983; Weeks et al., 1972). The effects of smaller (but more numerous) SPEs may not be appreciated in case studies which, by their nature, tend to concern the largest events where the greatest effects are apparent, and when the direct and indirect effects are both likely contribute to the impact. More subtle decreases in ozone, during events where the proton flux is lower have, up until now received much less attention in the literature.

Superposed epoch analysis of SPEs has enabled a statistical investigation of average changes in ozone partial pressures to be carried out. Results indicate that SPEs are linked to an ~5–10% decrease in ozone at ~20 km altitude. Ozone depletion occurs only when a site spends at least some time in the PV during the polar winter. No decreases in ozone occur following SPEs when the PV is not present. The greatest decrease occurs ~10–20 days following SPEs with ozone depleted for ~30 days on average. While the observational evidence of a decrease in ozone is clear, an explanation of the physical cause of the change is challenging. Of the two main processes mooted as causing ozone destruction (processes A and B, described in section 1), the first is expected to cause a rapid decrease in ozone within a few hours/days, and the second is expected to cause a delayed decrease in ozone some days/weeks later, but rarely reaching ~20 km altitude. Our results indicate that the initial depletion is commencing close to zero epoch and that the depletion in stratospheric ozone extends for up to ~30 days on average. This suggests a role for indirect ozone destruction via the descent of NO_x species (cf. Turunen et al., 2016). Obviously, the hardness of the proton energy spectrum for each SPE used in the statistical averages analyzed here will play a role in the efficacy of each mechanism, since the depth of penetration of solar protons is correlated with their incident energy. The rapidity of descent of NO_x may be crucial, as may time-spent-in-darkness. Although the flux of very high-energy protons may not be sufficient to influence ozone directly, if the PV is present, then NO_x can be rapidly transported to lower altitudes. Such downward transport is very variable and can be fastest at the edges of the PV (Tegtmeier et al., 2008), which may explain the large relative decrease seen at LER, even though LER is only in the PV ~15% of the time during JFMA. However, LER is generally close to the edge of the PV where descent may be maximized. In a further complication, air parcels sampled above each site are not static but rather are in continual motion. Air that is sampled days after the SPE was certainly at a different location when the solar protons actually impacted the atmosphere. There is thus a need to investigate complicating effects such as transport, mixing, time-spent-in-darkness, etc., in future observational and theoretical studies.

In general, discussions of the long-term and short-term changes in stratospheric ozone may concentrate on internal terrestrial variables (Staehelin et al., 2001), or solar changes (Haigh, 2003), and do not always consider the effects of EPP such as that which occurs during SPEs. Some work has considered SPEs in theoretical studies of ozone depletion (e.g., Jackman et al., 1996; Jackman & McPeters, 1985; Rodger et al., 2008), although the inclusion of SPE effects in global models remains quite limited (cf. Matthes et al., 2017). We hope the results outlined above will provide additional impetus to explore and quantify external influences that perturb the stratospheric ozone budget.

5. Conclusions

Ozone observations above four locations in the northern hemisphere have been analyzed. We conclude the following:

1. Stratospheric ozone measurements from sites that are within the PV show a decrease in ozone partial pressure following SPEs. The decrease in ozone partial pressure at the altitude of peak ozone is ~5–10%, commences close to zero epoch, and persists for ~30 days.
2. No decrease in stratospheric ozone is detected following SPEs in late summer or autumn. No decrease is detected following a set of random epochs. No decrease is detected for sites that are situated completely outside the PV.
3. The PV is an essential and necessary factor for causing stratospheric ozone depletion following SPEs. Results suggest that delayed (indirect) destruction of ozone plays a role in the stratospheric ozone budget following SPEs.

Acknowledgments
This work was supported at New Mexico Consortium by NASA's prime contract NAS5-01072. Ozonesonde work at the FMI was supported by the Academy of Finland (grant 140408), an EU Project GAIA-CLIM, the ESA's Climate Change Initiative program, and the Ozone_cci subproject in particular. The SPE list is available at ftp://ftp.swpc.noaa.gov/pub/indices/SPE.txt. All ozone data used in this study can be obtained from the World Ozone and Ultraviolet Radiation Data Center (http://www.woudc.org) operated by Environment Canada. We thank David Moore (UK Met Office) and Bryan Johnson (NOAA). M.H.D. offers thanks to all at FMI and SGO, to K. Jumisko and family, and to all members of SSC at SOD, for their hospitality during his visit to Finland in the spring of 2017, We also thank J. Denton for assistance in the preparation of Figure 1 and J. Borovsky, B. Larsen, and G. Reeves for useful discussions and support during the preparation of this manuscript.

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