

## **Nitrate deposition to surface snow at Summit, Greenland following the 9 November 2000 solar proton event**

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## Abstract

This study considers whether spurious peaks in nitrate ions in snow sampled at Summit, Greenland from August 2000 to August 2002 are related to solar proton events. After  
5 identifying tropospheric sources of nitrate on the basis of correlations with sulfate, ammonium, sodium, and calcium, we use the three-dimensional global Whole Atmosphere Community Climate Model (WACCM) to examine unaccounted for nitrate spikes. Model calculations confirm that solar proton events significantly impact  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{O}_3$  levels in the mesosphere and stratosphere during the weeks and months  
10 following the major 9 November 2000 solar proton event. However, SPE-enhanced  $\text{NO}_y$  calculated within the atmospheric column is too small to account for the observed nitrate ion peaks in surface snow. Instead, our WACCM results suggest that nitrate spikes not readily accounted for by measurement correlations are likely of anthropogenic origin. These results, consistent with other recent studies, imply that nitrate spikes in ice cores  
15 are not suitable proxies for individual SPEs and motivate the need to identify alternative proxies.

## 1. Introduction

20 Identifying the impact of solar particle storms on the atmosphere remains fundamental  
in understanding the Sun's influence on Earth's climate [*Gray et al.*, 2010; *National  
Research Council*, 2012]. High-energy particles from these solar events increase odd  
nitrogen and odd hydrogen, catalytically destroying ozone and thereby potentially  
impacting climate through the chemistry, radiative budget, and dynamics of the upper  
25 atmosphere [e.g., *Randall et al.*, 2005; *Jackman et al.*, 2008]. In addition, these space  
weather events have the potential to disrupt power grids, communications technology,  
and spacecraft [*National Research Council*, 2008].

Direct observations of solar energetic particle events have only been available since  
the mid-20th century. A broader understanding of the potential frequency and intensity of  
30 these events requires a more extensive record of historical occurrences, motivating the  
search for indirect proxy evidence [*Schrijver et al.*, 2012]. There is extensive analytical  
and predictive research using nitrate variability in polar ice cores as a proxy for solar  
energetic particle events [e.g., *Zeller and Parker*, 1981; *Dreschhoff and Zeller*,  
1990; *McCracken et al.*, 2001a; *Shea et al.*, 2006; *Kepko et al.*, 2009]. However, this  
35 relationship has been questioned, particularly with regard to the short timescales  
associated with individual events [e.g., *Legrand and Delmas*, 1986; *Wolff et al.*, 2008;  
*Wolff et al.*, 2012]. Contemporary progress toward predicting space weather urgently  
awaits the resolution of whether or not nitrate ion spikes in ice cores can be used to infer  
past events [e.g., *Barnard et al.*, 2011; *Riley*, 2012].

40 *Zeller and Parker* [1981] associated nitrate levels with solar activity through the  
correlation of nitrate ions ( $\text{NO}_3^-$ ) in Antarctic ice cores with cosmogenic carbon isotopes

( $^{14}\text{C}$ ) in tree rings. Statistical correlation studies confirm the covariance between nitrate ions and cosmogenic radionuclides  $^{14}\text{C}$  and  $^{10}\text{Be}$  on centennial to millennial timescales [e.g., *McCracken et al.*, 2001b; *Traversi et al.*, 2012; *Ogurtsov and Oinonen*, 2014].

45 However, attempts to find a correlation between nitrate ions and solar variability on smaller timescales, such as the 11-year solar cycle or individual events, have been unsuccessful [e.g., *Legrand and Delmas*, 1986; *Legrand and Kirchner*, 1990; *Legrand et al.*, 1996; *Traversi et al.*, 2012]. Instead, the variability of nitrate ions in polar ice is attributable to lightning from lower latitudes and downward transport from the lower  
50 stratosphere [*Legrand and Delmas*, 1986; *Legrand et al.*, 1989; *Legrand et al.*, 1996], with potential contributions in the Arctic from anthropogenic pollution [*Mayewski et al.*, 1990] and biomass burning [e.g., *Whitlow et al.*, 1994; *Dibb and Jafrezzo*, 1997; *Savarino and Legrand*, 1998].

Efforts to attribute sharp nitrate ion peaks in ice cores to individual solar proton events  
55 are exemplified by the *Zeller and Dreschhoff* [1995] analysis of 8000 years of nitrate data from the GISP2-H Greenland ice core and the estimated cumulative probabilities of solar event occurrences by *McCracken et al.* [2001a]. *Palmer et al.* [2001] provide observational evidence of a small statistical background increase in nitrate ions as a result of individual SPE events. However, theoretical considerations and model simulations  
60 suggest that enhancements of nitrogen species from individual solar events are unlikely to produce sharp peaks in nitrate ions at the surface, given the slow rate of vertical transport in the stratosphere, horizontal mixing and dilution to lower latitudes, and diabatic recirculation [e.g., *Legrand et al.*, 1989; *Legrand and Kirchner*, 1990]. In addition, *Weller et al.* [2011] find no indication of individual solar events in 25 years of

65 atmospheric aerosol measurements in Antarctica. *Wolff et al.* [2008; 2012] are able  
instead to attribute nitrate ion peaks to tropospheric sources using correlations among a  
suite of ions in surface snow.

This paper presents a case study adding to a growing literature that challenges the  
validity of using nitrate spikes in ice as proxies for individual solar energetic particle  
70 events. A three-dimensional global simulation of the 9 November 2000 solar proton event  
using the Whole Atmosphere Community Climate Model (WACCM) combined with  
daily samples of nitrate ions in surface snow at Summit, Greenland demonstrates the  
difficulty in generating impulsive enhancements in nitrate deposition in snow and ice  
from a single event. The results of this study, however, reiterate the significant influence  
75 of solar energetic particles on the chemical composition of the Arctic polar stratosphere  
and mesosphere, especially levels of odd nitrogen and ozone, encouraging the search for  
robust proxies other than nitrate to determine the frequency and intensity of historical  
solar events.

## 80 **2. Methods**

### **2.1. Schematic of Solar Protons Events and Nitrate Precursors**

Solar energetic particles precipitating into our atmosphere include electrons, protons,  
and more massive ions. Our study focuses on solar proton events (SPEs), as solar protons  
uniquely possess sufficient energies to penetrate and modify the chemistry of the  
85 mesosphere and stratosphere, potentially leading to chemical signatures within the  
troposphere and at the surface. Figure 1 presents a schematic of the perturbations caused  
by solar energetic protons within the polar atmosphere. High-energy protons from solar

flares and coronal mass ejections precipitate over the polar caps, commonly extending to geomagnetic latitudes greater than 60 degrees [Smart and Shea, 1994]. These high-energy protons, along with collisional secondary electrons, ionize and dissociate molecular nitrogen and oxygen, resulting in the formation of odd hydrogen ( $\text{HO}_x = \text{H} + \text{OH} + \text{HO}_2$ ) and reactive odd nitrogen ( $\text{NO}_x = \text{N} + \text{NO} + \text{NO}_2$ ) [e.g., Crutzen et al., 1975; Jackman et al., 1980; Solomon et al., 1981].

Enhancements of  $\text{HO}_x$  cause short-lived catalytic ozone destruction in the mesosphere and upper stratosphere during an SPE and for a few days following the event [e.g., Solomon et al., 1981; Jackman et al., 2008; Damiani et al., 2010].  $\text{NO}_x$  has a short lifetime in the upper mesosphere and thermosphere, but the lifetime increases to months during polar night in the stratosphere. During winter, when downward transport within the isolated polar vortex is strong and photochemistry is limited,  $\text{NO}_x$  produced by SPEs in the mesosphere and upper stratosphere can be transported to the middle and lower stratosphere [Lopez-Puertes et al., 2005; Randall et al., 2005; Jackman et al., 2009; Randall et al., 2009]. Loss of  $\text{O}_3$  from the oxidation of SPE-enhanced  $\text{NO}_x$  mainly results in nitric acid ( $\text{HNO}_3$ ) and dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ). These species eventually mix with the large pool of total odd nitrogen ( $\text{NO}_y = \text{N} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HO}_2\text{NO}_2 + (\text{HONO}) + \text{ClONO}_2 + \text{BrONO}_2$ ) in the lower stratosphere, a background reservoir produced primarily by the oxidation of nitrous oxides ( $\text{N}_2\text{O}$ ) emitted at the surface [Vitt and Jackman, 1996]. With the return of sunlight to the polar region,  $\text{NO}_x$  can more effectively destroy stratospheric ozone through catalytic reactions.

Total odd nitrogen species such as  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ ,  $\text{ClONO}_2$ , and  $\text{N}_2\text{O}_5$  serve as precursors to soluble nitrate ions ( $\text{NO}_3^-$ ) deposited in snow. Nitrate ions from  $\text{HNO}_3$ , and

to a less extent  $\text{HO}_2\text{NO}_2$ , can reach the surface through stratosphere-troposphere exchange followed by wet deposition. In the winter polar vortex,  $\text{HNO}_3$  also condenses to form polar stratospheric cloud (PSC) particles, which can gravitationally sediment to the troposphere if the particles grow large enough. In addition, heterogeneous reactions of

115  $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$  and  $\text{ClONO}_2 + \text{HCl}$  occur on the surfaces of PSCs to form  $\text{HNO}_3$ , condensing and sedimenting out of the stratosphere. On the basis of inferences from nitrate layers in ice core data, *McCracken et al.* [2001a] and *Shea et al.* [2006] suggest that the deposition of nitrate to the surface resulting from SPEs occurs 2-6 weeks following each event. This contradicts calculations by *Legrand et al.* [1989] that suggest

120 a two-year transport time of enhanced odd nitrogen from the upper stratosphere to lower stratosphere, a consequence of horizontal diffusion to lower latitudes and vertical diabatic recirculation.

A viable mechanism for SPE nitrate precursors to progress from the upper atmosphere to the surface snow within a 2-6 week timeframe would require: 1) rapid downward

125 transport from the upper stratosphere; 2) levels of  $\text{NO}_y$  produced by SPEs high enough to compete with the background reservoir of  $\text{NO}_y$  in the lower stratosphere; and 3) a mechanism for quickly depositing nitrate from the lower stratosphere to the surface. High temporal resolution would be necessary to identify these events at the surface, requiring ice core sampling techniques such as continuous flow analysis (CFA) [e.g., *Sigg et al.*,

130 1994; *Roethlisberger et al.*, 2000; *Kepko et al.*, 2009] or high frequency sampling of surface snow or ambient air [e.g., *Wolff et al.*, 2008; *Weller et al.*, 2011].

Using daily measurements of surface snow at Summit, Greenland, the investigation described in this paper considers much higher resolution nitrate variability than prior ice

cores studies, resolving nitrate deposition on timescales that should be able to capture an  
135 individual SPE. Although there are larger SPE events during meteorological periods of  
stronger downward transport, we target the SPE of 9 November 2000 because daily  
surface snow measurements following this event are complete enough to infer alternative  
tropospheric sources of nitrate ion spikes through correlation analysis with sulfate,  
ammonium, sodium, and calcium as discussed in Section 3.1. The 9 November 2000  
140 event is the sixth largest SPE in the last 50 years with respect to the calculated production  
of  $\text{NO}_y$ , four times weaker than the largest event on 19-27 October 1989 [*Jackman et al.*,  
2008].

## 2.2. The Whole Atmosphere Community Climate Model

145 The Whole Atmosphere Community Climate Model (WACCM) is a component of the  
Community Earth System Model (CESM) at the National Center for Atmospheric  
Research (NCAR). Model documentation is available at the CESM website  
([www2.cesm.ucar.edu](http://www2.cesm.ucar.edu)). Simulations in this study use version cesm1.0.5 (WACCM4),  
with active atmospheric and land models, prescribed ice, and fixed ocean (specified sea  
150 surface temperatures). The WACCM atmospheric component of the model combines the  
Community Atmosphere Model (CAM5), the Thermosphere-Ionosphere-Mesosphere-  
Electrodynamics General Circulation Model (TIME-GCM), and the Model for OZone  
and Related chemical Tracers (MOZART) to simulate dynamics and chemistry from the  
surface to the lower thermosphere [*Garcia et al.*, 2007; *Kinnison et al.*, 2007; *Emmons et*  
155 *al.*, 2010; *Marsh et al.*, 2013; *Neale et al.*, 2013].



The chemical solver and reaction rates are based on MOZART chemistry [Kinnison *et al.*, 2007; Emmons *et al.*, 2010]. Observed solar spectral irradiance and geomagnetic activity force the heating and photolysis rates [Marsh *et al.*, 2007]. The chemical mechanism includes 59 species and involves reactions of O<sub>x</sub>, NO<sub>x</sub>, HO<sub>x</sub>, ClO<sub>x</sub>, and BrO<sub>x</sub> chemical families as well as methane and carbon monoxide oxidation. The mechanism contains heterogeneous reactions on stratospheric aerosols, including liquid sulfate aerosols along with nitric acid trihydrate (NAT), supercooled ternary solution (STS), and water ice associated with PSCs [Kinnison *et al.*, 2007]. Concentrations of longer-lived greenhouse gases and halogen species are specified from observations [Garcia *et al.*, 2007]. Surface emissions are represented by flux boundary conditions associated with the most recently available compilation supported by WACCM and described by Lamarque *et al.* [2012]: anthropogenic emissions from POET (Precursors of Ozone and their Effects on the Troposphere) [Granier *et al.*, 2005] and REAS (Regional Emissions inventory in ASia); monthly biomass burning emissions from GFED-v2 (Global Fire Emissions Database) [van der Werf *et al.*, 2006]; and biogenic, soil, ocean, and volcanic emissions from POET and GEIA (the Global Emissions Inventory Activity). These inventories correspond to emissions used in the Coupled Model Intercomparison Project phase 5 (CMIP5) [Taylor *et al.*, 2012].

The WACCM simulations used here have a resolution of 1.9° latitude, 2.5° longitude, and 88 vertical layers extending from the surface to approximately 140 km. The model chemistry applies 30-minute time steps. We use the specified dynamics version of WACCM (SD-WACCM) in which meteorology is forced by NASA's Modern Era Retrospective analysis for Research Applications (MERRA) fields [Rienecker *et al.*,

2011]. WACCM achieves this forcing by relaxing horizontal winds and temperatures to  
180 MERRA fields from 0 to 40 km. The model is free running above 50 km, with a linear  
reduction of forcing between 40 and 50 km.

WACCM modelers have participated in a series of intercomparisons and validation  
studies, most recently CMIP5 [Taylor *et al.*, 2012]. Funke *et al.* [2011] include WACCM  
in an intercomparison focused on the SPEs of October 2003, validating results with  
185 observations from the Michelson Interferometer for Passive Atmospheric Sounding  
(MIPAS) on Envisat. The authors show a general agreement between model calculations  
and measurements, including O<sub>3</sub> loss within 5% and model NO<sub>y</sub> enhancement within  
30% at 1 hPa.

Previous WACCM simulations studying SPEs include Jackman *et al.* [2008; 2009;  
190 2011] and Funke *et al.* [2011]. The WACCM simulations presented in this paper are  
motivated in part by Figure 6 from Jackman *et al.* [2009], showing a tongue of enhanced  
NO<sub>y</sub> and decreased O<sub>3</sub> extending into the northern polar lower stratosphere following the  
9 November 2000 SPE. The present simulations differ by: 1) forcing the model with  
MERRA re-analysis meteorological fields specific to the 2000-2001 time period; 2) using  
195 a more recent version of WACCM with improvements including parameterizations for  
wave interactions resulting from turbulent mountain stress; and 3) using a higher  
horizontal resolution to better resolve transport (1.9° latitude by 2.5° longitude in contrast  
to the Jackman *et al.* [2009] 4° latitude by 5° longitude).

### 200 **2.3. Modeling the November 9, 2000 Solar Proton Event**

Following a coronal mass ejection on 8 November 2000 (23:26 UTC), the GOES8 satellite measured a solar proton event (SPE) beginning on 8 November (23:50 UTC) and reaching a maximum on 9 November (15:55 UTC). A smaller event occurred in late November, peaking on 26 November (20:30 UTC). The proton flux for energies greater than 10 MeV reach a maximum of 14,800 pfu (pfu = proton flux units = particles·sr<sup>-1</sup>·cm<sup>-2</sup>·s<sup>-1</sup>) for the 9 November event and 940 pfu for the 26 November event (<http://www.swpc.noaa.gov>).

The WACCM model assumes a uniform distribution of proton flux at geomagnetic latitudes greater than 60 degrees, using calculations of daily-averaged ion pair production rates as a function of pressure based on GOES8 proton flux measurements [*Jackman et al.*, 1980; 2005; 2008]. WACCM includes HO<sub>x</sub> production rates as a function of altitude and ion pairs using a table from *Jackman et al.* [2005] based on the dissociation of O<sub>2</sub> followed by water cluster ion formation and neutralization described by *Solomon et al.* [1981]. NO<sub>x</sub> formation results from the ionization and dissociation of N<sub>2</sub> and O<sub>2</sub>, producing ~1.25 N per ion pair [*Porter et al.*, 1976] partitioned into 45% ground state N(<sup>4</sup>S) and 55% excited state N(<sup>2</sup>D). The excited state N(<sup>2</sup>D) determines net NO<sub>x</sub> production [*Rusch et al.*, 1981]. Tabulated calculations and detailed descriptions of NO<sub>x</sub> and HO<sub>x</sub> production rates by SPEs are available at the SPARC/SOLARIS website ([http://sparcsolaris.geomar.de/input\\_data.php](http://sparcsolaris.geomar.de/input_data.php)).

WACCM calculations of gas phase chemical species include loss rates for dry deposition, wet deposition, and heterogeneous reactions on stratospheric aerosols. Dry deposition follows a resistance approach, dependent on land cover type and surface roughness. WACCM calculates the dry deposition flux for a given species as the product

of deposition velocities (varying by time and horizontal grid location) and concentrations  
225 at a reference height (~10 m) above the surface.

There are two wet deposition schemes available for WACCM: the traditional  
MOZART scheme [*Rasch et al.*, 1997; *Horowitz et al.*, 2003] and a more extensive  
scheme detailed by *Neu and Prather* [2012]. The MOZART scheme addresses convective  
updrafts, in-cloud nucleation scavenging (rainout), below-cloud impaction scavenging  
230 (washout), and evaporation in clear ambient air. Precipitation rates, cloud water content,  
and cloud fractions are taken from meteorological data fields, and effective Henry's law  
coefficients are prescribed. The *Neu and Prather* [2011] wet deposition scheme includes  
a more resolved sub-grid scale treatment of cloud overlap and a burial method for the  
uptake of soluble gases on ice, resulting in slower uptake of  $\text{HNO}_3$  by ice and snow. This  
235 study uses the MOZART scheme in an effort to provide an upper limit for wet deposition  
of  $\text{HNO}_3$ , consistent with the search for the maximum potential deposition of nitrate  
following SPEs.

WACCM treats wet deposition as a first order gas-phase loss process at the end of  
each time step. The model does not explicitly account for the accumulation of condensed  
240 species within cloud droplets or aqueous chemistry, nor does it archive soluble ions  
deposited to the surface. The results presented in this paper estimate the variability in  
nitrate deposition by integrating gas-phase loss through wet deposition over the total  
atmospheric column and then dividing by precipitation amounts, filtering model output  
when precipitation values are extremely low to prevent anomalous spikes. These  
245 calculations are expected to overestimate the magnitude of nitrate ions deposited to the

snow but allow a comparison of modeled variability in nitrate deposition with observed variability in surface snow measurements.

WACCM also calculates the uptake of  $\text{HNO}_3$  by stratospheric aerosols and the gravitational settling of stratospheric cloud particles. Combining the sedimentation of condensed phase  $\text{HNO}_3$  with the heterogeneous conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  on polar stratospheric clouds allows WACCM to calculate the contribution of nitrate to the troposphere through irreversible denitrification of the stratosphere.

#### 2.4. Observations of Nitrate in Surface Snow at Summit, Greenland

Summit Station, originally the site of the Greenland Ice Sheet Project 2 (GISP2), is located in the middle of the Greenland ice sheet, approximately 3200 meters above sea level at  $72^\circ 34'$  N latitude and  $38^\circ 29'$  W longitude. Atmospheric measurements have been made at the site since 1989, with a variety of intensive measurements throughout the 1980s and 1990s, culminating in a full suite of continuous measurements beginning in 2003 as part of the Arctic Observing Network (<http://www.geosummit.org>).

Year-round daily measurements of soluble ion content in surface snow are available during 1997-1998 and from August 2000 to August 2002 [Dibb *et al.*, 2007]. Vertical profiles from monthly one-meter snow pits accompany these measurements. Sampled ions include sodium ( $\text{Na}^+$ ), ammonium ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ). Sampling procedures, transport, and ion chromatography techniques and uncertainties are described in detail by Dibb *et al.* [2007]. Briefly, snow was sampled daily from an area upwind of Summit camp to avoid contamination from local sources. Samples from the uppermost

stratigraphic layer were collected in groups of three adjacent replicates, with companion  
270 blanks generated every nine samples. Samples remained at -20 C until analysis, melted in  
small batches and immediately analyzed by ion chromatography.

The use of chemical profiles to infer historical atmospheric conditions such as the  
influence of solar proton events depends on preservation within the snowpack. The  
analysis of surface snow and snow pit data reveals that levels of most ions are  
275 preserved (at approximately 80%) in layers within the snow pits [Dibb *et al.*, 2007]. The  
exception is nitrate, where post-depositional processes may significantly modify nitrate  
ion concentrations [Dibb *et al.*, 2007]. Evidence of post-depositional modifications have  
been observed at both poles [e.g., Dibb and Whitlow, 1996; Dibb and Jaffrezo, 1997;  
*Rothlisberger et al.*, 2002], with significant differences expected among sites as a result  
280 of the physical and chemical environments. These modifications involve snow-air  
exchange attributed to photolysis, sublimation and condensation associated with the  
growth of snow grains, and the uptake and release of volatile species such as nitric acid  
[e.g. Legrand *et al.*, 1996; Sturm and Benson, 1997; Honrath *et al.*, 1999; Dibb *et al.*,  
2002; Grannas *et al.*, 2007]. Traversi *et al.* [2012] suggest that ideal conditions for  
285 preserving nitrate in firn with respect to post-depositional effects involve accumulation  
rates above 50 mm water equivalent per year. While sites in Greenland such as Summit  
are well above this threshold, many Antarctic plateau sites fall below the limit, including  
Vostok, and Dome C [Traversi *et al.*, 2012 and references therein]. In addition, long  
periods between snowfalls may allow significant post-depositional processing near the  
290 surface.

Post-depositional modifications also depend on the chemical composition of air near the surface, the composition of the snow (particularly with regard to acidity), and the altitude and temperature of the site [e.g., *Rothlisberger et al.*, 2000; *Burkhart et al.*, 2004]. Recent measurements of oxygen isotopes of nitrate at Summit suggest that post-  
295 depositional photolysis of nitrate in surface snow is limited ( $\sim 2\%$  in summer) [*Fibiger et al.*, 2013]. Furthermore, in the absence of solar radiation, we would not expect post-depositional loss process involving photochemistry and thermal desorption to extensively reduce concentrations during the polar winter. However, modifications of nitrate ion levels may result from the migration, diffusion, and chemistry associated with the  
300 physical evolution of the snowpack, particularly with regard to the metamorphism and compaction of grains [*Bartels-Rausch et al.*, 2012].

The seasonal cycles of long-lived chemical tracers, greenhouse gases, and non-methane hydrocarbons demonstrate that this site is representative of well-mixed, remote Arctic air, with most organic compounds in their final stage of oxidation [*Dibb et al.*,  
305 2007]. *Kahl et al.* [1997] show westerly flow dominating at Summit, with wintertime trajectories at 500 hPa identifying long-range transport from Asia or Europe and trajectories at 700 hPa suggesting less rapid flow from North America.

Summit receives  $\sim 65$  cm of snow ( $\sim 24$  cm water equivalence) per year, with snow accumulation reaching a maximum in spring and a minimum in winter  
310 [*Dibb and Fehsenfeld, 2004*]. Periods of fresh snow are relatively infrequent during the 2000-2001 winter: six events in November 2000 (0.72 cm water equivalence); two events in December 2000 (0.29 cm water equivalence); and two events in January 2001 (0.56 cm water equivalence). In addition to fresh snow events, field notes indicate frequent periods

of thick fog and rime, ice-crystals and diamond dust as well as high winds and blowing  
315 snow strong enough to obscure visibility.

### 3. Results and Discussion

#### 3.1. Correlations Between Nitrate Ions and Other Ions in Surface Snow at Summit

Concurrent measurements of nitrate ( $\text{NO}_3^-$ ) with other ions such as sulfate ( $\text{SO}_4^{2-}$ ),  
320 calcium ( $\text{Ca}^{2+}$ ), sodium ( $\text{Na}^+$ ), and ammonium ( $\text{NH}_4^+$ ) provide a means for attributing  
nitrate spikes in snow to tropospheric sources, either by direct association with industrial  
pollution and biomass burning plumes from Europe and North America or from increased  
nitrate deposition involving particulates such as sea salt and dust. *Mayewski et al.* [1990]  
credit a rising trend in both  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in Greenland to industrial continental  
325 pollution. Anthropogenic pollution not only is characterized by high levels of  $\text{HNO}_3$  but  
also is the dominant source of sulfate in comparison to sea salt, dust, volcanoes, and  
biogenic emissions. Chemical signatures of continental biomass burning include elevated  
levels of  $\text{NH}_4^+$  and formate in Greenland ice, with concurrent enhancements of  $\text{NO}_3^-$   
present in some events and absent in others [e.g., *Legrand et al.*, 1992; *Whitlow et al.*,  
330 1994; *Legrand and de Angelis*, 1996; and *Savarino and Legrand*, 1998]. *Dibb et al.*  
[1996] and *Dibb and Jafrezzo* [1997] confirm biomass burning in Northern Canada as a  
source of enhanced  $\text{NH}_4^+$ , carboxylic acids, and nitrate at Summit using back-trajectories  
in conjunction with with atmospheric and snow measurements.

Observations of atmospheric aerosols at Summit near ground level (1.5 m) show  
335 minimal concentrations of particulate nitrate, often below the detection limit of  
instruments, suggesting that the majority of atmospheric nitrate in snow originates from



gas phase  $\text{HNO}_3$  [Dibb *et al.*, 1994; Dibb *et al.*, 1998]. Contemporaneous measurements of gaseous  $\text{HNO}_3$ , atmospheric aerosol nitrate, and nitrate ions in snow during the summer of 1993 show mean  $\text{HNO}_3$  concentrations of  $0.9 \pm 0.6 \text{ nmol/m}^3$  an order of magnitude larger than mean aerosol nitrate concentrations  $0.06 \pm 0.6 \text{ nmol/m}^3$  [Dibb *et al.*, 1994].  $\text{N}_2\text{O}_5$  could potentially be an additional source of nitrate ions in snow, particularly in winter, when  $\text{N}_2\text{O}_5$  accumulates in the absence of photochemistry and subsequently reacts heterogeneously with the snow [Huff *et al.*, 2011].

Wolff *et al.* [2008] attribute correlations between  $\text{NO}_3^-$  and  $\text{Na}^+$  at Halley, Antarctica to increased rates of conversion of gaseous to aerosol nitrate on coarse sea salt aerosols or salty snow surfaces. The authors propose the potential for similar correlations involving  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$  at inland polar sites like Summit. Dibb *et al.* [2007] identify a spring maximum in crustal dust ( $\text{Ca}^{2+}$ ) at Summit, most likely long-range transport originating from Asia [Dibb *et al.*, 2003] as well as a summer peak in  $\text{NH}_4^+$  [Dibb *et al.*, 2007], characteristic of biomass burning from North America and Europe. Wolff *et al.* [2008] recommend that future analyses of nitrate ions in snow and ice use ion correlations to screen for known tropospheric sources before searching the residual nitrate data for potential SPEs. This study adopts such a technique, identifying tropospheric sources through ion correlations at Summit from 2000-2002 followed by WACCM model simulations to investigate nitrate spikes not readily attributable to tropospheric sources.

Figure 2 presents time series plots of  $\text{NO}_3^-$  paired with  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{SO}_4^{2-}$  at Summit along with solar proton fluxes from GOES8. Visual examination shows that nitrate spikes on 21 August 2000, 5 September 2000, 16 June 2001, and 4 July 2002 correlate with  $\text{NH}_4^+$ , a tracer of biomass burning. High levels of the anthropogenic

360 pollutant tracer  $\text{SO}_4^{2-}$  accompany nitrate spikes on 25-30 November 2000, 26 June 2001,  
and 19 February 2002. Levels of  $\text{Na}^+$  associated with sea salt are enhanced along with  
 $\text{NO}_3^-$  on 12 January 2002 and 19 February 2002. This leaves four nitrate ion spikes that  
are not readily attributable to tropospheric sources: 22-24 November 2000, 13 December  
2000, 25 January 2001, and 22 October 2001. The GOES8 proton fluxes indicate SPEs  
365 on 9 Nov 2000, 24 Sep 2001, 4 Nov 2001, and 22 Nov 2001. This study uses the  
WACCM model to analyze the three candidate nitrate spikes that occur during polar  
winter (22-24 November 2000, 13 December 2000, 25 January 2001), specifically  
searching for a potential mechanism to explain how a nitrate signal from the 9 November  
2000 SPE might impulsively arrive at the surface through chemistry, transport, and  
370 deposition processes within the winter polar vortex.

### 3.2. Modeling the Impact of the November 9 SPE on $\text{HO}_x$ , $\text{NO}_x$ , and $\text{O}_3$

Comparing WACCM simulations with and without SPEs isolates the impact of solar  
protons on upper atmospheric processes and identifies potential scenarios leading to  
375 enhanced nitrate deposition. The model is initially run from January through October to  
allow chemical species to reach equilibrium throughout the atmosphere, with solar  
protons (e.g., the 14 July 2000 "Bastille Day" solar proton event) included during this  
"spin-up" period. At the start of November, the solar proton flux is allowed to continue in  
a "with SPEs" simulation but is set to zero in a "no SPEs" simulation, thereby more  
380 effectively highlighting perturbations specific to the 9 November SPE.

Figure 3 shows the time evolution of the vertical structure of modeled  $\text{HO}_x$ ,  $\text{NO}_x$ , and  
 $\text{O}_3$  (in mole ratios) during November. Top plots show WACCM simulations with SPEs.

Middle plots show WACCM simulations without SPEs. Bottom plots show the SPE enhancements of HO<sub>x</sub> and NO<sub>x</sub> and the SPE reduction of O<sub>3</sub>. These contour plots  
385 represent average profiles calculated within the meandering polar vortex, the region most likely associated with strong polar winter descent. Potential temperature ( $\theta$ ) serves as the vertical coordinate on the left axis, while the right axis indicates the approximate geopotential height ( $Z$ ). The boundary of the polar vortex is objectively determined by identifying grid points within the stratosphere where scaled potential vorticity (sPV)  
390 calculated on isentropic surfaces exceeds  $1.4 \times 10^{-4} \text{ s}^{-1}$  [Dunkerton and Delisi, 1986; Brakebusch *et al.*, 2013]. Scaled potential vorticity retains the conservation properties of Ertel's potential vorticity on isentropic surfaces. However, by normalizing with respect to U.S. Standard Atmosphere [COESA, 1976], sPV removes vertical disparities in potential vorticity caused by the exponential increase of potential temperature with decreasing  
395 pressure. The vortex is assumed to remain in a constant location above 2500 K (~55 km), as the sPV method no longer adequately delineates the vortex edge as a result of the temperature profile above the stratopause.

Figure 3 highlights the significant impact of the 9 November SPE event on the chemistry of the Arctic mesosphere and stratosphere. Short-lived enhancements up to 100  
400 ppbv HO<sub>x</sub> occur above 80 km in the mesosphere, with enhancements of 0.1 to 1 ppbv extending throughout the stratosphere during the days following the 9 November SPE (Figure 3a). SPE production of NO<sub>x</sub> peaks around 50 ppbv in the mesosphere, exceeding 30 ppbv throughout the upper stratosphere during the days following the event (Figure 3b). The NO<sub>x</sub> enhancements slowly descend within the stratosphere throughout  
405 the month, maintaining levels an order of magnitude above background. Losses of O<sub>3</sub> up

to 800 ppbv occur above 70 km immediately following the 9 November SPE (Figure 3c). A 30 to 40% depletion of O<sub>3</sub> (> 100 ppbv) occurs throughout the stratosphere, most likely associated with the short-lived enhancement of HO<sub>x</sub>. O<sub>3</sub> reduction continues in the stratosphere throughout the rest of November, consistent with the descent of SPE-enhanced NO<sub>x</sub>. The smaller SPE at the end of November is also evident in the plots for all three species.

Figure 4 presents the vortex-averaged SPE enhancement of NO<sub>x</sub> and reduction of O<sub>3</sub> from November through March. NO<sub>x</sub> enhancements of 10 to 40 ppbv (10 to 20 times background levels) descend from the upper stratosphere to the middle stratosphere throughout November and December at a rate of ~10 km/month. By January, increases of 3 to 5 ppbv (2 to 3 times background levels) persist from 30 to 35 km, with remnant enhancements continuing into spring.

Figure 4 supports the supposition that the enhancement of NO<sub>x</sub> during the months following the 9 November SPE drives longer-lived destruction of O<sub>3</sub> in the stratosphere. The reduction of O<sub>3</sub> in the stratosphere follows the descent of SPE-enhanced NO<sub>x</sub>, reaching losses of 500 ppbv during December and early January. Reductions of ozone remain at 400 to 500 ppbv (5 to 10%) from 25 to 30 km until spring. Although most of the ozone reduction occurs above the stratospheric ozone layer, where number densities peak from 15 to 20 km, ozone losses could nonetheless reduce oxidation rates in the middle to lower stratosphere and impact the chemistry, dynamics, and radiative properties of this region.

Not surprisingly, the behavior of HO<sub>x</sub>, NO<sub>x</sub>, and O<sub>3</sub> following the 9 November 2000 SPE in these simulations is similar to the *Jackman et al.*, [2009] WACCM results.

*Jackman et al.*, [2009] show an increase in upper stratospheric  $\text{NO}_y$  (mostly  $\text{NO}_x$ ),  
430 exceeding 1000% for several days after the Nov 9 SPE, followed by the prolonged  
downward transport of enhanced  $\text{NO}_y$  during the weeks and months following the event,  
exceeding 20% at 30 km during January and February. Model calculations of  $\text{HO}_x$  and  $\text{O}_3$   
presented in this paper are also consistent with *Jackman et al.* [2008; 2009].

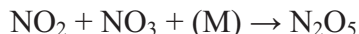
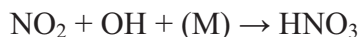
Figure 5 shows a comparison of  $\text{NO}_2$  from WACCM with POAM III (Polar Ozone  
435 and Aerosol Measurement) satellite measurements within the Arctic vortex. Descriptions  
of the POAM III data along with methods for determining the edge of the polar vortex for  
Figure 5a are provided in *Randall et al.* [2002], *Harvey et al.* [2002], and *Randall et al.*  
[2007]. Scaled potential vorticity (sPV) is used to identify the location of the vortex for  
the WACCM results, consistent with the analysis throughout this paper. Magnitudes of  
440  $\text{NO}_2$  simulated by WACCM are similar to observations by POAM III, with background  
levels 1 to 3 ppbv between 30 and 40 km during November, increasing substantially in  
early February. The WACCM simulations do a better job capturing levels of  $\text{NO}_2$  during  
December and January when including SPEs. Favorable comparisons for  $\text{NO}_x$  and  $\text{O}_3$   
have also been made among WACCM simulations and available satellite measurements  
445 for more recent SPEs, including MIPAS observations of the October 2003 “Halloween”  
SPEs [*Jackman et al.*, 2008; *Jackman et al.*, 2009; *Funke et al.*, 2011] and MIPAS, MLS,  
and ACE-FTS observations for the January 2005 SPE [*Jackman et al.*, 2011].

Simulations using global models other than WACCM to study SPEs similar in  
magnitude to this study also show enhancements of  $\text{NO}_x$  and reductions of  $\text{O}_3$  in the  
450 stratosphere during the months following each event [e.g., *Semeniuk et al.*, 2005;  
*Paivarinta et al.*, 2013]. *Calisto et al.* [2012] use the SOCOL (ECHAM4+MEZON)

model to study how a hypothetical extremely large SPE (the August 1972 SPE scaled to fluences associated with the 1859 Carrington Event) would impact the atmosphere if it occurred during a contemporary solar maximum. The short-term enhancements of HO<sub>x</sub> (10 ppbv) and NO<sub>x</sub> (200 ppbv) exceed the 9 November SPE WACCM simulations. However, longer-term increases in NO<sub>x</sub> (10%) and decreases in O<sub>3</sub> (20-40%) in the stratosphere are comparable to the 9 November SPE WACCM simulations, likely attributable to solar radiation variations between fall and winter. While the SOCOL simulation of the extreme SPE results in significant depletion of total column O<sub>3</sub> (20 DU), the WACCM simulations of the 9 November SPE show a vortex-averaged decrease reaching only 5 DU by late January, with reductions up to 10 DU occurring sporadically in the center of the vortex.

### 3.3. Modeled Conversion of NO<sub>x</sub> to NO<sub>y</sub> and the Downward Transport of NO<sub>y</sub>

As NO<sub>x</sub> descends within the stratosphere, oxidation reactions convert NO<sub>x</sub> into other NO<sub>y</sub> species, primarily through the following pathways:



(where NO<sub>3</sub> is produced from NO<sub>2</sub> reactions with O and O<sub>3</sub>)

These products of NO<sub>x</sub> oxidation are of particular interest because of their role in nitrate ion deposition. Background NO<sub>y</sub> densities peak in the lower stratosphere, where a reservoir of HNO<sub>3</sub> accumulates from the oxidation of nitrous oxide (N<sub>2</sub>O) emitted at the

475 surface. The WACCM simulations presented in this paper strive to answer whether or not  
the  $\text{NO}_y$  enhancements resulting from the oxidation of SPE  $\text{NO}_x$  can descend and persist  
within this background pool of  $\text{NO}_y$  in the lower stratosphere at levels high enough to be  
detected at the surface. Note that WACCM does not include reactions involving hydrated  
cluster ions, which have also been implicated in the production of  $\text{HNO}_3$  at altitudes over  
480 35 km [*Kawa et al.*, 1995; *Verronen et al.*, 2008; *Kvissel et al.*, 2012].

Figure 6 presents vortex-averaged  $\text{NO}_y$  within the stratosphere from November  
through March. Figure 6a shows  $\text{NO}_y$  in simulations without SPEs, depicting the  
subsidence of air within the polar vortex during winter. Figure 6b shows the  
corresponding downward transport of SPE  $\text{NO}_y$  enhancements within the stratosphere.  
485 By late January there is a thin layer ( $\sim 5$  km) of 5 to 10 ppbv SPE-enhanced  $\text{NO}_y$  around  
30 km. SPE enhancements continue through March, remaining at altitudes well above 20  
km. Figure 6a clearly identifies a background pool of  $\text{NO}_y$  in the lower stratosphere (10  
to 15 ppbv), an order of magnitude larger than typical values in the middle stratosphere (1  
to 4 ppbv) and troposphere (less than 1 ppbv). While downward transport is best studied  
490 using mole ratios or mixing ratios (measures of composition that are independent of  
density), it is nonetheless important to draw attention to the exponential decrease in  
atmospheric density with height. A background level of 15 ppbv  $\text{NO}_y$  at 50 hPa ( $\sim 20$  km)  
contains a factor of 10 more molecules than 15 ppbv of SPE-enhanced  $\text{NO}_y$  at 5 hPa ( $\sim 35$   
km). Figure 6c emphasizes that  $\text{NO}_y$  background number densities peak below 20 km.  
495 The challenge remains explaining how a thin SPE-produced layer averaging 5 to 10 ppbv  
 $\text{NO}_y$  at 30 km might be detected at the surface given the thick background pool of 10  
to 15 ppbv  $\text{NO}_y$  in the thermally stable lower stratosphere.

As a means of estimating the maximum potential for enhanced deposition of nitrogen at the surface as a result of the 9 November SPE, Figure 6d shows vortex-averaged  $\text{NO}_y$  total column densities from model simulations with SPEs (blue) and without SPEs (red).  
500 Vertical column densities are integrated over each model surface grid, and vortex averages are calculated using latitudes and longitudes where sPV values on the 500 K isentropic surface ( $\sim 20$  km) are greater than  $1.4 \times 10^{-4} \text{ s}^{-1}$ . Figure 6e provides similar model results for column densities integrated above 30 km. A large relative increase in column densities above 30 km reflects significant SPE enhancement of  $\text{NO}_y$ . However, the absolute magnitude of the stratospheric SPE-induced  $\text{NO}_y$  enhancement is small compared to the total column density of  $\text{NO}_y$ . There is a general increase in total column density of  $\text{NO}_y$  throughout winter. However, vortex-averaged SPE enhancements of total column  $\text{NO}_y$  remain below 5%, with enhancements never exceeding 20% at any location  
505 within the vortex (not shown). In contrast, nitrate peaks in snow and ice show enhancements 4 to 5 times background levels, significantly greater than the maximum potential for SPE enhancement suggested by column densities of  $\text{NO}_y$ .

The fact that the increase in  $\text{NO}_y$  in the atmospheric column is on average less than 5% (and a maximum of 20% locally) challenges the theory of SPEs being responsible for spurious peaks in nitrate deposited at the surface. However, it does not rule out the  
515 possibility of longer-term trends in nitrate resulting from solar activity. For example, although *Palmer et al.* [2001] do not find a correlation between nitrate spikes and individual solar events in ice cores sampled at Law Dome, Antarctica, a statistical analysis reveals an 11% enhancement of nitrate during the 3 to 14 months following solar  
520 events, consistent with the total column nitrate enhancement calculated in this study.



### 3.4. Modeled Partitioning of $\text{NO}_y$

An analysis of individual  $\text{NO}_y$  species within WACCM helps to identify precursors to nitrate ions deposited to the surface. The majority of  $\text{NO}_y$  above 40 km is in the form of  $\text{NO}_x$ , while  $\text{HNO}_3$  is the principal  $\text{NO}_y$  species below 30 km. Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) becomes significant in the 30 to 40 km layer.  $\text{HO}_2\text{NO}_2$  is primarily of importance in the troposphere. Other  $\text{NO}_y$  species such as chlorine nitrate ( $\text{ClONO}_2$ ), bromine nitrate ( $\text{BrONO}_2$ ), and nitrate radical ( $\text{NO}_3$ ) are small in comparison.

Figure 7a-d presents vortex-averaged WACCM simulation results of  $\text{HNO}_3$  including: background levels from WACCM simulations without SPEs, enhancements from SPEs, SPE enhancements of column densities integrated over the total atmospheric column, and SPE enhancements of column densities above 30 km. Throughout late December and most of January, SPE enhancements of  $\text{HNO}_3$  do not exceed 1 ppbv, levels much lower than the 10 ppbv background pool of  $\text{HNO}_3$  at 20 km. The largest SPE enhancements of  $\text{HNO}_3$  occur from 20 to 30 km during late January through early March, peaking under 3 ppbv and remaining small in comparison to background values. Vortex-averaged total column densities of  $\text{HNO}_3$  show little change as a result of SPEs, and local enhancements only occasionally reach 2 to 3% within the polar vortex (not shown). The most significant SPE enhancements of  $\text{HNO}_3$  occur above 30 km but have little impact on total column density.

The model calculates an increase in  $\text{N}_2\text{O}_5$  throughout the stratosphere as a result of SPEs (Figures 7e-h), with most of the enhancement occurring from 30 to 40 km. In contrast to  $\text{HNO}_3$ , the model shows significant enhancements (up to 40%) of vortex-

averaged  $\text{N}_2\text{O}_5$  total column density during the months after the 9 November event. Local  
545  $\text{N}_2\text{O}_5$  total column densities are enhanced by over 100% in the center of the vortex during  
late December and January (not shown).  $\text{N}_2\text{O}_5$  makes up only 5% of total column  $\text{NO}_y$ . In  
order for total column  $\text{N}_2\text{O}_5$  enhancements to explain nitrate spikes at the surface, there  
would need to be a mechanism involving preferential deposition of  $\text{N}_2\text{O}_5$  over  $\text{HNO}_3$ . To  
the authors' knowledge, no such mechanism has been suggested in the literature. In  
550 addition, *Jackman et al.* [2008] and *Funke et al.*, [2011] emphasize that WACCM SPE-  
enhanced  $\text{N}_2\text{O}_5$  is larger than levels from satellite measurements, hypothesizing the need  
to include water cluster ion reactions in WACCM to convert  $\text{NO}_3$  to  $\text{HNO}_3$  in order to  
simulate lower  $\text{N}_2\text{O}_5$  values [e.g., *Solomon et al.*, 1981; *Lopez-Puertes et al.*, 2005]. This  
additional  $\text{HNO}_3$ , however, would not significantly impact the variability of nitrate at the  
555 surface, since  $\text{N}_2\text{O}_5$  comprises such a small percentage of total column  $\text{NO}_y$ .

### 3.5. Modeled Deposition of $\text{NO}_y$

Several mechanisms allow nitrogen in the atmosphere to deposit as nitrate ions to  
surface snow. Dry deposition involves gas phase and particulate nitrogen species sticking  
560 to the surface snow in the absence of precipitation. Wet deposition removes nitrate as  
 $\text{HNO}_3$  (and to a lesser extent  $\text{HO}_2\text{NO}_2$ ) is taken up by falling snow by means of in-cloud  
nucleation scavenging and below-cloud impaction scavenging. Nitrate deposition can  
also result from the uptake of  $\text{HNO}_3$  by polar stratospheric clouds (PSCs), heterogeneous  
conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  on PSCs, and subsequent gravitational settling of cloud  
565 particles to the troposphere.

Although background levels of  $\text{NO}_y$  are large in the lower stratosphere, thermal stability inhibits mixing across the tropopause. In the absence of stratospheric intrusions, denitrification by gravitational settling of PSC particles is the most likely mechanism for upper atmospheric nitrate to reach the troposphere. WACCM relies on an equilibrium approach to calculate the amount of  $\text{HNO}_3$  condensed on polar stratospheric clouds, which in turn determines the radii and settling velocities of these aerosols (see supporting information in *Kinnison et al.* [2007]). Although heterogeneous reactions in WACCM occur on PSCs composed of supercooled ternary solutions (STS), nitric acid trihydrate (NAT), and water-ice [*Kinnison et al.*, 2007; *Lamarque et al.*, 2012; *Wegner et al.*, 2013], condensed nitrogen is limited to STS and NAT aerosols in WACCM, with gravitational settling occurring only for NAT particles because of their larger radii. Once settling and advection bring condensed  $\text{HNO}_3$  to the troposphere, it may be removed from the modeled atmosphere via wet deposition.

Denitrification through cloud sedimentation is not as common in the Arctic as in the Antarctic, where temperatures are low enough to allow PSC particles to grow to larger masses. Although PSCs and denitrification have been observed in the Arctic during years when the polar vortex is strong [e.g, *Waibel et al.*, 1999; *Kondo et al.*, 2000; *Santee et al.*, 2000; *Fahey et al.*, 2001; *Popp et al.*, 2001], the winter of 2000-2001 exhibits neither a consistently strong vortex nor low temperatures (see Figure 1 from *Manney et al.* [2006]). In addition, observations show significant re-nitrification in the Arctic as increasing temperatures in the lower stratosphere and troposphere cause nitrogen from PSCs to re-enter the gas phase [*Dibb et al.*, 2006].

Nonetheless, for completeness, it is useful to consider model-calculated PSCs when examining maximum potential nitrate deposition from the stratosphere. WACCM  
590 calculates the presence of all three types of PSCs over the Arctic during winter 2000-2001, with STS and NAT particles most abundant in mid-January and ice clouds briefly present when stratospheric temperatures reach a minimum. Figure 8 presents vortex-averaged vertical temperatures, vortex-averaged condensed nitrate as NAT particles (the most relevant PSC leading to denitrification in WACCM), and condensed nitrate as NAT  
595 PSCs for 5 January 2001 (a representative day when PSCs are significant). Although results are given for simulations with SPEs, differences in temperature from simulations without SPEs are negligible and can be attributed to computational noise. WACCM temperatures drop below 200 K during January, reaching a minimum of 194 K at 20 km.

Condensed NAT in the form of PSCs peaks above 15 km during January, contributing  
600 50% of total column  $\text{HNO}_3$  on 5 January 2001. However, NAT radii are small (median radii less than 1.5 microns) and the modeled flux of nitrate never extends below 17 km, as temperatures exceed 200 K and condensed nitrate ions re-enter the gas phase before reaching the troposphere. The impact of solar proton events on simulated vortex-averaged total column condensed NAT as PSCs is less than 0.2%, with local maximum  
605 enhancements of 1 to 3%. The limited impact of SPEs on nitrate in the form of NAT PSCs is consistent with the limited SPE enhancement of total  $\text{HNO}_3$  presented in Figure 7. As a comparison to Antarctic simulations where temperatures are lower, NAT and ice PSCs are prevalent, and stratospheric denitrification has been observed to be significant, Howeverm *Jackman et al.* [1990] calculate only a 10.6% maximum SPE enhancement of  
610 nitrate deposition following the August 1972 SPE event over Antarctica. In summary, it

is unlikely that SPE-enhanced denitrification could account for the 4 to 5 fold nitrate spikes observed in Greenland surface snow.

Enhanced nitrate from the lower stratosphere descends into the troposphere not only through the gravitational settling of PSCs but also from dynamics associated with  
615 stratosphere-troposphere exchange. Given the minimal SPE enhancement of  $\text{NO}_y$  in the lower stratosphere, downward transport of SPE-enhanced  $\text{NO}_y$  through isolated tropopause folds and stratospheric intrusions could still not explain the magnitude of observed nitrate ion spikes.

In spite of WACCM's inability to calculate enhancements of  $\text{NO}_y$  from the 9  
620 November 2000 SPE large enough to explain surface spikes in nitrate ions, it is nonetheless worthwhile to examine how closely WACCM's calculations of nitrate deposition resemble observations. Summertime estimates of the  $\text{NO}_3^-$  inventory presented by *Bergin et al.* [1995] attribute 93% of deposition to snow, 6% to fog and 1% to dry  
625 deposition. The strong stability of the wintertime surface layer would suggest that dry deposition plays an even less significant role during the time period considered in this study.

WACCM treats wet deposition in the troposphere as a first order loss rate from the gas phase, with precipitation rates and cloud cover derived from MERRA meteorological fields. During each time step, WACCM calculates how much of a given gas will be  
630 incorporated into aerosols within each grid box and removes this amount from the grid box concentration that is passed to the next time step. While re-evaporation and desorption are included within a given time step, WACCM does not archive and propagate the soluble ion species nor account for subsequent aqueous reactions. The

following analysis assumes that all loss from the gas phase in the tropospheric grid  
635 column ends up in precipitated water at the end of each half-hour time step. This analysis  
estimates the potential enhancement of nitrate at the surface by wet deposition within the  
entire vertical tropospheric column, most likely an overestimate especially when  
precipitation levels are minimal.

Figure 9 shows estimates for nitrate deposition resulting from the wet deposition of  
640  $\text{HNO}_3$  in WACCM directly over Summit both with and without SPEs. The method of  
calculating modeled wet deposition instantaneously from the entire atmospheric column  
is useful for determining the maximum potential deposition of nitrate but will tend to  
over-estimates nitrate deposition, as is apparent in the different scales on the left and right  
vertical axes. This variation in magnitude is confounded by a coarse grid model  
645 resolution that is unable to represent the spatial variability caused by blowing or drifting  
snow, local accumulation and ablation, or sporadic fog and rime at the surface. Instead,  
our interest lies in identifying whether or not the model can capture the relative  
variability associated with the measured nitrate ions. Indeed, the model does capture  
relative peaks in nitrate on 23 November, 14 December, and 24 January corresponding to  
650 the nitrate ion spikes of interest in this study observed in surface snow on 22-24  
November, 13 December, and 25 January. We present results for simulations with and  
without SPEs for completeness, noting that differences are negligible (never exceeding  
0.2%), once again supporting the conclusion that enhanced nitrate concentrations on  
these days are not related to SPEs.

655

### 3.6. Alternative Explanations for Nitrate Spikes

The WACCM simulations provide evidence that nitrate spikes not readily accounted for by soluble ion correlations may nonetheless be related to tropospheric sources. Figure 10 shows the time evolution of vertical profiles of  $\text{NO}_x$  and  $\text{HNO}_3$  above Summit from November through January. Elevated  $\text{NO}_x$ , with a lifetime on the order of days, indicates relatively fresh pollution sources.  $\text{HNO}_3$ , a product of  $\text{NO}_x$  oxidation with a lifetime on the order of months, is more characteristic of aged plumes. WACCM calculates enhanced  $\text{NO}_x$  and  $\text{HNO}_3$  in the lower troposphere during 22-24 November. High levels of  $\text{NO}_x$  in the middle to upper troposphere occur around 14 December. Elevated levels of both  $\text{NO}_x$  and  $\text{HNO}_3$  are present in the lower to middle troposphere on 25 January.

Figure 11 presents isobaric maps of  $\text{NO}_x$  and  $\text{NO}_y$  from WACCM, identifying polluted continental plumes corresponding to vertical enhancements above Summit. Figure 11a depicts  $\text{NO}_x$  at 800 hPa (~1.5 km) in the lower troposphere above the marine boundary layer one day prior to each nitrate ion spike not attributable to tropospheric sources. Figure 11b shows  $\text{NO}_y$  plots at 500 hPa (~3.5 km) on days coinciding with these nitrate ion spikes. Overlaid vectors indicate the direction and intensity of winds. The WACCM simulations show pollution from Europe reaching Summit on 22 November, with a polluted plume from North America also evident to the south. The middle panels in Figure 11 provide a snapshot of a polluted plume traveling from North America at low altitudes on 13 December and aloft over Greenland on 14 December. At altitudes above 5 km (not shown in Figure 11), higher wind speeds steer this plume directly over Summit, consistent with elevated levels of  $\text{NO}_x$  in Figure 10. The simulations show transport of  $\text{NO}_x$  from Europe on 24 January, with a broad region of enhanced  $\text{NO}_y$  over Greenland on 25 January. These model simulations of continental plumes suggest that nitrate spikes

680 in surface snow during these time periods are more likely the result of continental anthropogenic pollution than SPEs.

#### 4. Conclusions

This study screens a two-year data set of daily measurements of ions in surface snow at Summit, Greenland from 2000 to 2001 for known tropospheric sources in the search for evidence of solar proton events in nitrate records. WACCM modeling simulations examine transport, chemistry, and deposition during three specific time periods when correlations between nitrate and other soluble ions are inconsistent with tropospheric sources. The model calculations confirm that solar proton events significantly impact  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{O}_3$  levels in the mesosphere and stratosphere during the weeks and months after the major 9 November 2000 solar proton event. However, there is never a time during the simulation when SPE-enhanced  $\text{NO}_y$  within the atmospheric column is large enough to account for the observed nitrate peaks in surface snow.

We see no convincing evidence that SPEs are related to impulsive nitrate spikes in surface snow at Summit in the winter of 2000 to 2001 but suggest that spikes not readily accounted for by soluble ion correlations are the result of deposition from polluted plumes originating in North America and Europe. This conclusion is particularly compelling for recent centuries when anthropogenic emissions are capable of modifying atmospheric composition on a global scale.

700 The limited SPE enhancement of total column  $\text{NO}_y$  (5% vortex-averaged and 20% local maxima) leads us to conclude that impulsive spikes of nitrate ions at the surface are unlikely to result from SPEs similar in magnitude to the 9 November 2000 SPE. It would



be worthwhile, however, to consider how large an event would be necessary to produce nitrate ion levels at the surface discernible from tropospheric sources as well as the  
705 likelihood of such events given the limits of solar flare energy [*Aulanier et al.*, 2013]. The association of nitrate ion levels with solar activity on centennial (Gleissberg) and millennial timescales also remains of interest [e.g., *Motizuki et al.*, 2009; *Traversi et al.*, 2012; *Ogurtsov and Oinonen*, 2014].

A promising alternative to nitrate ions in the search for proxies for historical SPEs  
710 remains the study of cosmogenic radionuclides such as Carbon-14 ( $^{14}\text{C}$ ) and Beryllium-10 ( $^{10}\text{Be}$ ) [*Steinhilber et al.*, 2012]. Measurements of the cosmogenic radionuclide Beryllium-7 ( $^7\text{Be}$ ) are available from Summit from 1997-1998, 2000-2002, and 2003-present [Dibb, 2007]. Although too short-lived to serve as a historical proxy, measurements and model comparisons of  $^7\text{Be}$  following recent SPEs would provide  
715 insight into vertical transport and deposition processes, paving the way for modeling studies involving longer-lived cosmogenic radionuclides in the context of solar particle events.

Although this study could not definitively link surface observations with solar energetic protons impacting the upper atmosphere, WACCM results once again point to  
720 significant impacts of SPEs on the middle and upper atmospheric concentrations of  $\text{HO}_x$ ,  $\text{NO}_x$ , and  $\text{O}_3$ , adding to the growing collection of satellite observations and modeling experiments that strive to clarify perturbations in the chemistry, radiation budget, and dynamics of the atmosphere resulting from solar variability. The quest for an alternate proxy to nitrate for studying solar activity through history remains compelling,

725 particularly with regard to protecting technological infrastructure, understanding climate,  
and validating predictive models for space weather.

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735 **References**

- Aulanier, G., P. Démoulin, C. J. Schrijver, M. Janvier, E. Pariat, and B. Schmieder (2013), The standard flare model in three dimensions II. Upper limit on solar flare energy, *Astron. Astrophys.*, 549(A66), doi:10.1051/0004-6361/201220406.
- 740 Barnard, L., M. Lockwood, M. A. Hapgood, M. J. Owens, C. J. Davis, and F. Steinhilber (2011), Predicting space climate change, *Geophys. Res. Lett.*, 38(16), doi:10.1029/2011GL048489.
- 745 Bartels-Rausch, T. et al. (2012), Relationship between snow microstructure and physical and chemical processes, *Atmos. Chem. Phys. Discuss.*, 12, 30409–30541, doi:10.5194/acpd-12-30409-2012.
- Bergin, M. H., J.-L. Jaffrezo, C. I. Davidson, J. E. Dibb, S. N. Pandis, R. Hillamo, W. 750 Maenhaut, H. D. Kuhns, and T. Makela (1995), The contributions of snow, fog, and dry deposition to the summer flux of anions and cations at Summit, Greenland, *J. Geophys. Res.*, 100(D8), 16275–16288, doi:10.1029/95JD01267.
- 755 Brakebusch, M., C. E. Randall, D. E. Kinnison, S. Tilmes, M. L. Santee, and G. L. Manney (2013), Evaluation of Whole Atmosphere Community Climate Model simulations of ozone during Arctic winter 2004-2005, *J. Geophys. Res. Atmos.*, 118, 2673–2688, doi:10.1002/jgrd.50226.
- 760 Burkhart, J. F., M. Hutterli, R. C. Bales, and J. R. McConnell (2004), Seasonal accumulation timing and preservation of nitrate in firn at Summit, Greenland, *J. Geophys. Res.*, 109, D19302, doi:10.1029/2004JD004658.
- 765 Calisto, M., P. T. Verronen, E. Rozanov, and T. Peter (2012), Influence of a Carrington-like event on the atmospheric chemistry, temperature and dynamics, *Atmos. Chem. Phys.* 12(18), 8679–8686, doi:10.5194/acp-12-8679-2012.
- COESA (1976), U.S. Standard Atmosphere, 1976, U.S. Government Printing Office, Washington, D.C.
- 770 Computational and Information Systems Laboratory (2012), Yellowstone: IBM iDataPlex System (University Community Computing), Boulder, CO: National Center for Atmospheric Research, <http://n2t.net/ark:/85065/d7wd3xhc>.
- 775 Crutzen, P. J., I. S. A. Isaksen, and G. C. Reid (1975), Solar proton events - Stratospheric sources of nitric oxide, *Science*, 189(4201), 457–459, doi:10.1126/science.189.4201.457.
- 780 Damiani, A., M. Storini, C. Rafanelli, and P. Diego (2010), The hydroxyl radical as an indicator of SEP fluxes in the high-latitude terrestrial atmosphere, *Adv. Space Res.*, 46(9), 1225–1235, doi:10.1016/j.asr.2010.06.022.

Dibb, J. E. (2007), Vertical mixing above Summit, Greenland: Insights into seasonal and high frequency variability from the radionuclide tracers  $^7\text{Be}$  and  $^{210}\text{Pb}$ , *Atmos. Environ.*, 41(24), 5020–5030, doi:10.1016/j.atmos.env.2006.12.005.

785 Dibb, J. E., and M. Fahnstock (2004), Snow accumulation, surface height change, and firn densification at Summit, Greenland: Insights from 2 years of in situ observation, *J. Geophys. Res.*, 109, D24113, doi:10.1029/2003JD004300.

790 Dibb, J. E., and J.-L. Jaffrezo (1997), Air-snow exchange investigations at Summit, Greenland: An overview, *J. Geophys. Res.*, 102(C12), 26795–26807, doi:10.1029/96JC0230.

795 Dibb, J.E., and S.I. Whitlow (1996), Recent climate anomalies and their impact on snow chemistry at South Pole, 1987-1994, *Geophys. Res. Lett.*, 23(10), 1115–1118, doi:10.1029/96GL01039.

Dibb, J. E., R. W. Talbot, and M. H. Bergin (1994), Soluble acidic species in air and snow at Summit, Greenland, *Geophys. Res. Lett.*, 21(15), 1627–1630, doi:10.1029/94GL01031.

800 Dibb, J. E., R. W. Talbot, S. I. Whitlow, M. C. Shipham, J. Winterle, J. McConnell, and R. Bales (1996), Biomass burning signatures in the atmosphere and snow at Summit, Greenland: An event on 5 August 1994, *Atmos. Environ.*, 30(4), 553–561, doi:10.1016/1352-2310(95)00328-2.

805 Dibb, J. E., R. W. Talbot, J. W. Munger, D. J. Jacob, and S.-M. Fan (1998), Air-snow exchange of  $\text{HNO}_3$  and  $\text{NO}_y$  at Summit, Greenland, *J. Geophys. Res.*, 103(D3), 3475–3486, doi:10.1029/97JD03132.

810 Dibb, J. E., M. Arsenault, M. C. Peterson, and R. E. Honrath (2002), Fast nitrogen oxide photochemistry in Summit, Greenland snow, *Atmos. Environ.*, 36(15), 2501-2511, doi: 10.1016/S1352-2310(02)00130-9.

815 Dibb, J. E., R. W. Talbot, E. M. Scheuer, G. Seid, M. A. Avery, and H. B. Singh (2003), Aerosol chemical composition in Asian continental outflow during the TRACE-P campaign: Comparison with PEM-West B, *J. Geophys. Res.*, 108(D21), 8815, doi:10.1029/2002JD003111.

820 Dibb, J. E., E. Scheuer, M. Avery, J. Plant, and G. Sachse (2006), In situ evidence for renitrication in the Arctic lower stratosphere during the polar aura validation experiment (PAVE), *Geophys. Res. Lett.*, 33, L12815, doi:10.1029/2006GL026243.

825 Dibb, J. E., S. I. Whitlow, and M. Arsenault (2007), Seasonal variations in the soluble ion content of snow at Summit, Greenland: Constraints from three years of daily surface snow samples, *Atmos. Environ.*, 41(24), 5007–5019, doi:10.1016/j.atmosenv.2006.12.010.

Dreschhoff, G.A. M., and E. J. Zeller (1990), Evidence of individual solar proton events in Antarctic snow, *Sol. Phys.*, *127*(2), 333-346, doi:10.1007/BF00152172.

830 Dunkerton, T. J., and D. P. Delisi (1986), Evolution of potential vorticity in the winter stratosphere of January-February 1979, *J. Geophys. Res.*, *91*(D1), 1199–1208, doi:10.1029/JD091iD01p01199.

835 Emmons, L. K. et al. (2010), Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, *3*, 43–67, doi:10.5194/gmd-3-34-2010.

840 Fahey, D. W. et al. (2001), The detection of large HNO<sub>3</sub>-containing particles in the winter Arctic stratosphere, *Science*, *291*(5506), 1026–1031, doi:10.1126/science.1057265.

Fibiger, D. L., M. G. Hastings, J. E. Dibb, and L. G. Huey (2013), The preservation of atmospheric nitrate in snow at Summit, Greenland, *Geophys. Res. Lett.*, *40*(13), 3484–3489, doi:10.1002/grl.50659.

845 Funke, B. et al. (2011), Composition changes after the “Halloween” solar proton event: the High Energy Particle Precipitation in the Atmosphere (HEPPA) model versus MIPAS data intercomparison study, *Atmos. Chem. Phys.*, *11*(17), 9089–9139, doi:10.5194/acp-11-9089-2011.

850 Garcia, R. R., D. R. Marsh, D. E. Kinnison, B. A. Boville, and F. Sassi (2007), Simulation of secular trends in the middle atmosphere, 1950–2003, *J. Geophys. Res.*, *112*, D09301, doi:10.1029/2006JD007485.

855 Granier, C., A. Guenther, J.-F. Lamarque, A. Mieville, J. F. Muller, J. Olivier, J. Orlando, J. Peters, G. Petron, G. Tyndall, S. Wallens (2005), POET, a database of surface emissions of ozone precursors, <http://www.aero.jussieu.fr/projet/ACCENT/POET.php>, GEIA/ACCENT database.

860 Grannas, A. M., et al. (2007), An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, *7*(16), 4329–4373, doi: 10.5194/acp-7-4329-2007.

Gray, L. J. et al. (2010), Solar influences on climate, *Rev. Geophys.*, *48*, RG4001, doi:10.1029/2009RG000282.

865 Harvey, V. L., R. B. Pierce, T. D. Fairlie, and M. H. Hitchman (2002), A climatology of stratospheric polar vortices and anticyclones, *J. Geophys. Res.*, *107*(D20), 4442, doi:10.1029/2001JD001471.

870 Honrath, R. E., M. C. Peterson, S. Guo, J. E. Dibb, P. B. Shepson, and B. Campbell (1999), Evidence of NO<sub>x</sub> production within or upon ice particles in the Greenland snowpack, *Geophys. Res. Lett.*, *26*(6), 695–698, doi: 10.1029/1999GL900077.

875 Horowitz, L. W. et al. (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, *108*(D24), 4784, doi:10.1029/2002JD002853.

880 Huff, D. M., P. L. Joyce, G. J. Fochesatto, and W. R. Simpson (2011), Deposition of dinitrogen pentoxide,  $N_2O_5$ , to the snowpack at high latitudes, *Atmos. Chem. Phys.*, *11*, 4929–4938, doi:10.5194/acp-11-4929-2011.

885 Jackman, C. H., J. E. Frederick, and R. S. Stolarski (1980), Production of odd nitrogen in the stratosphere and mesosphere: An intercomparison of source strengths, *J. Geophys. Res.*, *85*(C12), 7495–7505, doi:10.1029/JC085iC12p07495.

890 Jackman, C. H., A. R. Douglass, R. B. Rood, R. D. McPeters, and P. E. Meade (1990), Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, *J. Geophys. Res.*, *95*(D6), 7417–7428, doi:10.1029/JD095iD06p07417.

895 Jackman, C. H., M. T. Deland, G. J. Labow, E. L. Fleming, D. K. Weisenstein, M. K. W. Ko, M. Sinnhuber, and J. M. Russell (2005), Neutral atmospheric influences of the solar proton events in October–November 2003, *J. Geophys. Res.*, *110*, A09S27, doi:10.1029/2004JA010888.

900 Jackman, C. H. et al. (2008), Short- and medium-term atmospheric constituent effects of very large solar proton events, *Atmos. Chem. Phys.*, *8*(3), 765–785, doi:10.5194/acp-8-765-2008.

905 Jackman, C. H., D. R. Marsh, F. M. Vitt, R. R. Garcia, C. E. Randall, E. L. Fleming, and S. M. Frith (2009), Long-term middle atmospheric influence of very large solar proton events, *J. Geophys. Res.*, *114*, D11304, doi:10.1029/2008JD011415.

910 Jackman, C. H. et al. (2011), Northern Hemisphere atmospheric influence of the solar proton events and ground level enhancement in January 2005, *Atmos. Chem. Phys.*, *11*(13), 6153–6166, doi:10.5194/acp-11-6153-2011.

Kahl, J. D., D. A. Martinez, H. Kuhns, C. I. Davidson, J.-L. Jaffrezo, and J. M. Harris (1997). Air mass trajectories to Summit, Greenland: A 44-year climatology and some episodic events. *J. Geophys. Res.*, *102*(C12), 26861–26875, doi:10.1029/97JC00296.

915 Kawa, S. R., J. B. Kumer, A. R. Douglass, A. E. Roche, S. E. Smith, F. W. Taylor, and D. J. Allen (1995), Missing chemistry of reactive nitrogen in the upper stratospheric polar winter, *Geophys. Res. Lett.*, *22*(19), 2629–2632, doi:10.1029/95GL02336.

Kepko, L., H. Spence, D. F. Smart, and M. A. Shea (2009), Interhemispheric observations of impulsive nitrate enhancements associated with the four large ground-

level solar cosmic ray events (1940–1950), *J. Atmos. Sol-Terr. Phys.*, 71(17-18), 1840–1845, doi:10.1016/j.jastp.2009.07.002.

920

Kinnison, D. E. et al. (2007), Sensitivity of chemical tracers to meteorological parameters in the MOZART-3 chemical transport model, *J. Geophys. Res.*, 112, D20302, doi:10.1029/2006JD007879.

925

Kondo, Y., H. Irie, M. Koike, and G. E. Bodeker (2000), Denitrification and nitrification in the Arctic stratosphere during the winter of 1996–1997, *Geophys. Res. Lett.*, 27(3), 337–340, doi:10.1029/1999GL011081.

930

Kvissel, O.-K., Y. J. Orsolini, F. Stordal, I. S. A. Isaksen, and M. L. Santee (2012), Formation of stratospheric nitric acid by a hydrated ion cluster reaction: Implications for the effect of energetic particle precipitation on the middle atmosphere, *J. Geophys. Res.*, 117, D16301, doi:10.1029/2011JD017257.

935

Lamarque, J.-F. et al. (2012), CAM-chem: description and evaluation of interactive atmospheric chemistry in the Community Earth System Model, *Geosci. Model Dev.*, 5(2), 369–411, doi: 10.5194/gmd-5-369-2012.

940

Legrand, M., and M. De Angelis (1996), Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, 101(D2), 4129–4145, doi:10.1029/95JD03296.

945

Legrand, M. R., and R. J. Delmas (1986), Relative contributions of tropospheric and stratospheric sources to nitrate in Antarctic snow, *Tellus B*, 38(3-4), 236–249, doi:10.1111/j.1600-0889.1986.tb00190.x.

Legrand, M. R., and S. Kirchner (1990), Origins and variations of nitrate in south polar precipitation, *J. Geophys. Res.*, 95(D4), 3493–3507, doi:10.1029/JD095iD04p03493.

950

Legrand, M. R., F. Stordal, I. S. A. Isaksen, and B. Rognerud (1989), A model study of the stratospheric budget of odd nitrogen, including effects of solar cycle variations, *Tellus B*, 41B(4), 413–426, doi:10.1111/j.1600-0889.1989.tb00318.x.

955

Legrand, M., M. De Angelis, T. Staffelbach, A. Neftel, and B. Stauffer (1992), Large perturbations of ammonium and organic acids content in the summit-Greenland Ice Core. Fingerprint from forest fires?, *Geophys. Res. Lett.*, 19(5), 473–475, doi:10.1029/91GL03121.

960

Legrand, M., A. Léopold, and F. Dominé (1996), Acidic gases (HCl, HF, HNO<sub>3</sub>, HCOOH, and CH<sub>3</sub>COOH): a review of ice core data and some preliminary discussions on their air-snow relationships, *Chemical exchange between the atmosphere and polar snow*, edited by E. W. Wolff and R. C. Bales, 19–43, Springer-Verlag, Berlin, Germany.



- 965 López-Puertas, M., B. Funke, S. Gil-López, T. von Clarmann, G. P. Stiller, M. Höpfner,  
S. Kellmann, H. Fischer, and C. H. Jackman (2005), Observation of NO<sub>x</sub> 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.
- 970 Manney, G. L., M. L. Santee, L. Froidevaux, K. Hoppel, N. J. Livesey, and J. W. Waters  
(2006), EOS MLS observations of ozone loss in the 2004-2005 Arctic winter, *Geophys.  
Res. Lett.*, L04802, doi:10.1029/2005GL024494.
- 975 Marsh, D. R., R. R. Garcia, D. E. Kinnison, B. A. Boville, F. Sassi, S. C. Solomon, and K.  
Matthes (2007), Modeling the whole atmosphere response to solar cycle changes in  
radiative and geomagnetic forcing, *J. Geophys. Res.*, *112*, D23306,  
doi:10.1029/2006JD008306.
- 980 Marsh, D. R., M. J. Mills, D. E. Kinnison, J.-F. Lamarque, N. Calvo, and L. M. Polvani  
(2013), Climate change from 1850 to 2005 simulated in CESM1(WACCM), *J. Climate*,  
*26*(19), 7372–7391, doi:10.1175/JCLI-D-12-00558.1.
- 985 Mayewski, P. A., W. B. Lyons, M. J. Spencer, M. S. Twickler, C. F. Buck, and S.  
Whitlow (1990), An ice-core record of atmospheric response to anthropogenic sulphate  
and nitrate, *Nature*, *346*, 554–556, doi:10.1038/346554a0.
- 990 McCracken, K. G., G. A. M. Dreschhoff, E. J. Zeller, D. F. Smart, and M. A. Shea  
(2001a), Solar cosmic ray events for the period 1561-1994: 1. Identification in polar ice,  
1561-1950, *J. Geophys. Res.*, *106*(A10), 21585–21598, doi:10.1029/2000JA000237.
- 990 McCracken, K. G., G. A. M. Dreschhoff, D. F. Smart, and M. A. Shea (2001b), Solar  
cosmic ray events for the period 1561-1994: 2. The Gleissberg periodicity, *J. Geophys.  
Res.*, *106*(A10), 21599–21609, doi:10.1029/2000JA000238.
- 995 Motizuki, Y. et al. (2009), An Antarctic ice core recording both supernovae and solar  
cycles, *arXiv*, *0902*, 3446, preprint at <http://arXiv.org/abs/0902.3446>.
- 1000 National Research Council, (2008), Severe space weather events-understanding societal  
and economic impacts: A Workshop Report, The National Academies Press, Washington,  
DC.
- 1005 National Research Council (2012), The effects of solar variability on Earth's climate: A  
workshop report, The National Academies Press, Washington, DC.
- 1005 The NCAR Command Language (Version 6.1.1) [Software] (2013), Boulder, Colorado:  
UCAR/NCAR/CISL/VETS, <http://dx.doi.org/10.5065/D6WD3XH5>.
- Neale, R. B., J. Richter, S. Park, P. H. Lauritzen, S. J. Vavrus, P. J. Rasch, and M. Zhang  
(2013), The mean climate of the Community Atmosphere Model (CAM4) in forced SST

- and fully coupled experiments, *J. Climate*, 26, 5150–5168, doi:  
1010 <http://dx.doi.org/10.1175/JCLI-D-12-00236.1>.
- Neu, J. L., and M. J. Prather (2012), Toward a more physical representation of precipitation scavenging in global chemistry models: cloud overlap and ice physics and their impact on tropospheric ozone, *Atmos. Chem. Phys.*, 12(7), 3289–3310,  
1015 doi:10.5194/acp-12-3289-2012.
- Ogurtsov, M. G. and M. Oinonen (2014), Evidence of the solar Gleissberg cycle in the nitrate concentration in polar ice, *J. Atmos. Sol-Terr. Phys.*, 109, 37–42, doi:  
10.1016/j.jastp.2013.12.017.
- 1020 Päivärinta, S.-M., A. Seppälä, M. E. Andersson, P. T. Verronen, L. Thölix, and E. Kyrölä (2013), Observed effects of solar proton events and sudden stratospheric warmings on odd nitrogen and ozone in the polar middle atmosphere, *J. Geophys. Res. Atmos.*, 118, 6837–6848, doi:10.1002/jgrd.50486.
- 1025 Palmer, A. S., T. D. Van Ommen, M. A. J. Curran, and V. Morgan (2001), Ice-core evidence for a small solar-source of atmospheric nitrate, *Geophys. Res. Lett.*, 28(10), 1953–1956, doi:10.1029/2000GL012207.
- 1030 Popp, P. J. et al. (2001), Severe and extensive denitrification in the 1999-2000 Arctic winter stratosphere, *Geophys. Res. Lett.*, 28(15), 2875–2878, doi:10.1029/2001GL013132.
- Porter, H. S., C. H. Jackman, and A. E. S. Green (1976), Efficiencies for production of atomic nitrogen and oxygen by relativistic proton impact in air, *J. Chem. Phys.*, 65, 154–  
1035 167, doi:10.1063/1.432812.
- Randall, C. E. et al. (2002), Validation of POAM III NO<sub>2</sub> measurements, *J. Geophys. Res.*, 107(D20), 4432, doi:10.1029/2001JD001520.
- 1040 Randall, C. E. et al. (2005), Stratospheric effects of energetic particle precipitation in 2003-2004, *Geophys. Res. Lett.*, 32, L05802, doi:10.1029/2004GL022003.
- Randall, C.E., V. L. Harvey, C. S. Singelton, S. M. Bailey, P. F. Bernath, M. Codrescu, H. Nakajima, and J. M. Russell III, (2007) Energetic particle precipitation effects on the Southern Hemisphere stratosphere in 1992-2005, *J. Geophys. Res.*, 112, D08308,  
1045 doi:10.1029/2006JD007696.
- Randall, C. E., V. L. Harvey, D. E. Siskind, J. France, P. F. Bernath, C. D. Boone, and K. A. Walker (2009), NO<sub>x</sub> descent in the Arctic middle atmosphere in early 2009, *Geophys. Res. Lett.*, 36, L18811, doi:10.1029/2009GL039706.
- 1050 Rasch, P. J., N. M. Mahowald, and B. E. Eaton (1997), Representations of transport, convection, and the hydrologic cycle in chemical transport models: Implications for the

- 1055 modeling of short-lived and soluble species, *J. Geophys. Res.*, *102*(D23), 28127–28138, doi:10.1029/97JD02087.
- Rienecker, M. M. et al. (2011), MERRA: NASA's Modern-Era Retrospective Analysis for Research and Applications, *J. Climate*, *24*(14), 3624–3648, doi:10.1175/JCLI-D-11-00015.1.
- 1060 Riley, P. (2012), On the probability of occurrence of extreme space weather events, *Space Weather*, *10*, S02012, doi:10.1029/2011SW000734.
- 1065 Röthlisberger, R., M. Bigler, M. Hutterli, S. Sommer, B. Stauffer, H. G. Junghans, and D. Wagenbach (2000), Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environ. Sci. Technol.*, *34*(2), 338–342, doi:10.1021/es9907055.
- 1070 Röthlisberger, R. et al. (2002), Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes, *Ann. Glaciol.*, *35*, 209–216, doi:10.3189/172756402781817220.
- 1075 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*(7), 767–774, doi:10.1016/0032-0633(81)90048-9.
- 1080 Santee, M. L., G. L. Manney, N. J. Livesey, and J. W. Waters (2000), UARS Microwave Limb Sounder observations of denitrification and ozone loss in the 2000 Arctic late winter, *Geophys. Res. Lett.*, *27*, 3213–3216, doi:10.1029/2000GL011738.
- 1085 Savarino, J., and M. Legrand (1998), High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core, *J. Geophys. Res.*, *103*(D7), 8267–8279, doi:10.1029/97JD03748.
- Schrijver, C. J. et al. (2012), Estimating the frequency of extremely energetic solar events, based on solar, stellar, lunar, and terrestrial records, *J. Geophys. Res.*, *117*, A08103, doi:10.1029/2012JA017706.
- 1090 Semeniuk, K., J. C. McConnell, and C. H. Jackman (2005), Simulation of the October–November 2003 solar proton events in the CMAM GCM: Comparison with observations, *Geophys. Res. Lett.*, *32*, L15S02, doi:10.1029/2005GL022392.
- 1095 Shea, M. A., D. F. Smart, K. G. McCracken, G. A. M. Dreschhoff, and H. E. Spence (2006), Solar proton events for 450 years: The Carrington event in perspective, *Adv. Space Res.*, *38*(2), 232–238, doi:10.1016/j.asr.2005.02.100.
- Sigg, A., K. Fuhrer, M. Anklin, T. Staffelbach, and D. Zurmühle (1994), A continuous analysis technique for trace species in ice cores, *Environ. Sci. Technol.*, *28*(2), 204–209, doi:10.1021/es00051a004.

- 1100 Smart, D. F., and M. A. Shea (1994), Geomagnetic cutoffs: A review for space dosimetry applications, *Adv. Space Res.*, *14*(10), 787–796, doi:10.1016/0273-1177(94)90543-6.
- 1105 Solomon, S., D. W. Rusch, J. C. Gerard, 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.*, *29*(8), 885–893, doi:10.1016/0032-0633(81)90078-7.
- 1110 Steinhilber, F. et al. (2012), 9,400 years of cosmic radiation and solar activity from ice cores and tree rings, *Proceedings of the National Academy of Sciences*, *109*(16), 5967–5971, doi:10.1073/pnas.1118965109.
- 1115 Sturm, M., and C. S. Benson (1997), Vapor transport, grain growth and depth-hoar development in the subarctic snow, *J. Glaciol.*, *43*(143), 42–59.
- Taylor, K. E., R. J. Stouffer, and G. A. Meehl (2012), An overview of CMIP5 and the experiment design, *Bull. Amer. Meteor. Soc.*, *93*(4), 485–498, doi:10.1175/BAMS-D-11-00094.1.
- 1120 Traversi, R., I. G. Usoskin, S. K. Solanki, S. Becagli, M. Frezzotti, M. Severi, B. Stenni, and R. Udisti (2012), Nitrate in polar ice: A new tracer of solar variability, *Sol. Phys.*, *280*, 237–254, doi:10.1007/s11207-012-0060-3.
- 1125 van der Werf, G. R., J. T. Randerson, L. Giglio, G. J. Collatz, P. S. Kasibhatla, and A. F. Arellano Jr. (2006), Interannual variability in global biomass burning emissions from 1997 to 2004, *Atmos. Chem. Phys.*, *6*, 3423–3441, doi:10.5194/acp-6-3423-2006.
- 1130 Verronen, P. T., B. Funke, M. López-Puertas, G. P. Stiller, T. von Clarmann, N. Glatthor, C.-F. Enell, E. Turunen, and J. Tamminen (2008), About the increase of HNO<sub>3</sub> in the stratopause region during the Halloween 2003 solar proton event, *Geophys. Res. Lett.*, *35*, L20809, doi:10.1029/2008GL035312.
- 1135 Vitt, F. M., and C. H. Jackman (1996), A comparison of sources of odd nitrogen production from 1974 through 1993 in the Earth's middle atmosphere as calculated using a two-dimensional model, *J. Geophys. Res.*, *101*(D3), 6729–6739, doi:10.1029/95JD03386.
- 1140 Waibel, A. E. et al. (1999), Arctic ozone loss due to denitrification, *Science*, *283*(5410), 2064–2069, doi:10.1126/science.283.5410.2064.
- 1145 Wegner, T., D. E. Kinnison, R. R. Garcia, and S. Solomon (2013), Simulation of polar stratospheric clouds in the specified dynamics version of the Whole Atmosphere Community Climate Model, *J. Geophys. Res. Atmos.*, *118*, 4991–5002, doi:10.1002/jgrd.50415.

- Weller, R., D. Wagenbach, M. Legrand, C. Elsässer, X. Tian-Kunze, and G. König-Langlo (2011), Continuous 25-yr aerosol records at coastal Antarctica – I: inter-annual variability of ionic compounds and links to climate indices, *Tellus B*, 63, 901–919, doi: 10.1111/j.1600-0889.2011.00542.x.
- 1150 Whitlow, S., P. Mayewski, J. Dibb, G. Holdsworth, and M. Twickler (1994), An ice-core-based record of biomass burning in the Arctic and Subarctic, 1750-1980, *Tellus B*, 46(3), 234–242, doi:10.1034/j.1600-0889.1994.t01-2-00006.x.
- 1155 Wolff, E. W., A. E. Jones, S. J.-B. Bauguitte, and R. A. Salmon (2008), The interpretation of spikes and trends in concentration of nitrate in polar ice cores, based on evidence from snow and atmospheric measurements, *Atmos. Chem. Phys.*, 8(18), 5627–5634, doi:10.5194/acp-8-5627-2008.
- 1160 Wolff, E. W., M. Bigler, M. A. J. Curran, J. E. Dibb, M. M. Frey, M. Legrand, and J. R. McConnell (2012), The Carrington event not observed in most ice core nitrate records, *Geophys. Res. Lett.*, 39, L08503, doi:10.1029/2012GL051603.
- 1165 Zeller, E. J., and B. C. Parker (1981), Nitrate ion in Antarctic firn as a marker for solar activity, *Geophys. Res. Lett.*, 8(8), 895–898, doi:10.1029/GL008i008p00895.
- Zeller, E. J., and G. A. M. Dreschhoff (1995), Anomalous nitrate concentrations in polar ice cores—Do they result from solar particle injections into the polar atmosphere? *Geophys. Res. Lett.*, 22, 2521–2524, doi:10.1029/95GL02560.
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## Figures and Figure Captions

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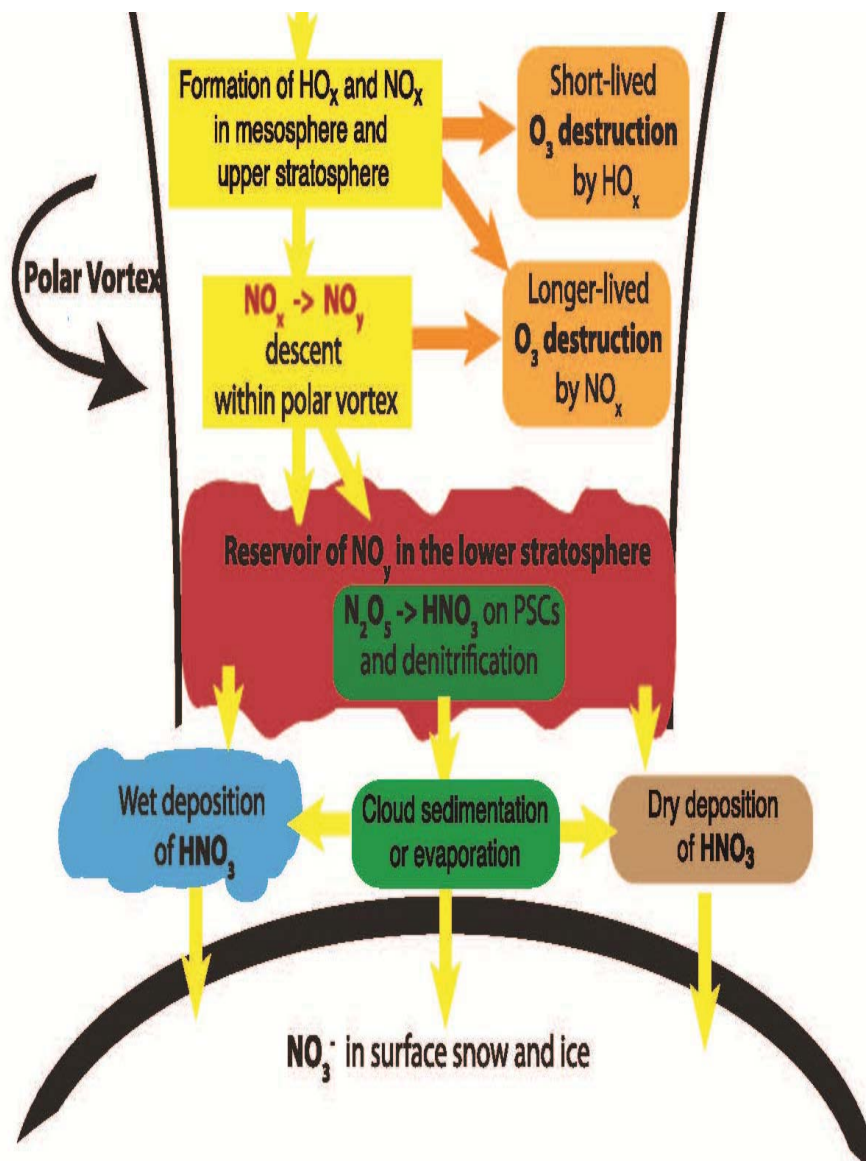


Figure 1. Schematic diagram of processes involved with nitrate deposition from solar energetic protons.

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## Soluble Ions in Surface Snow at Summit

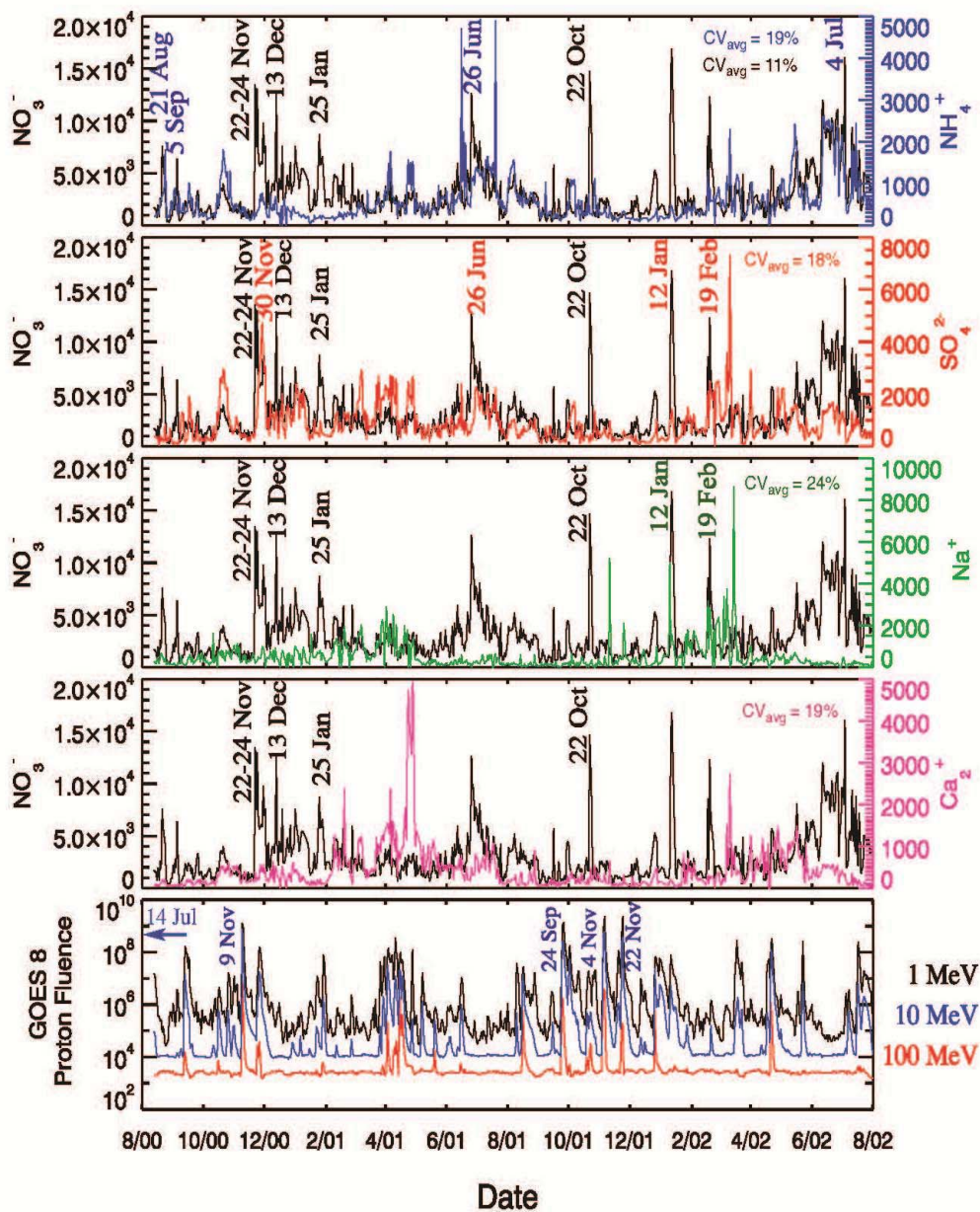
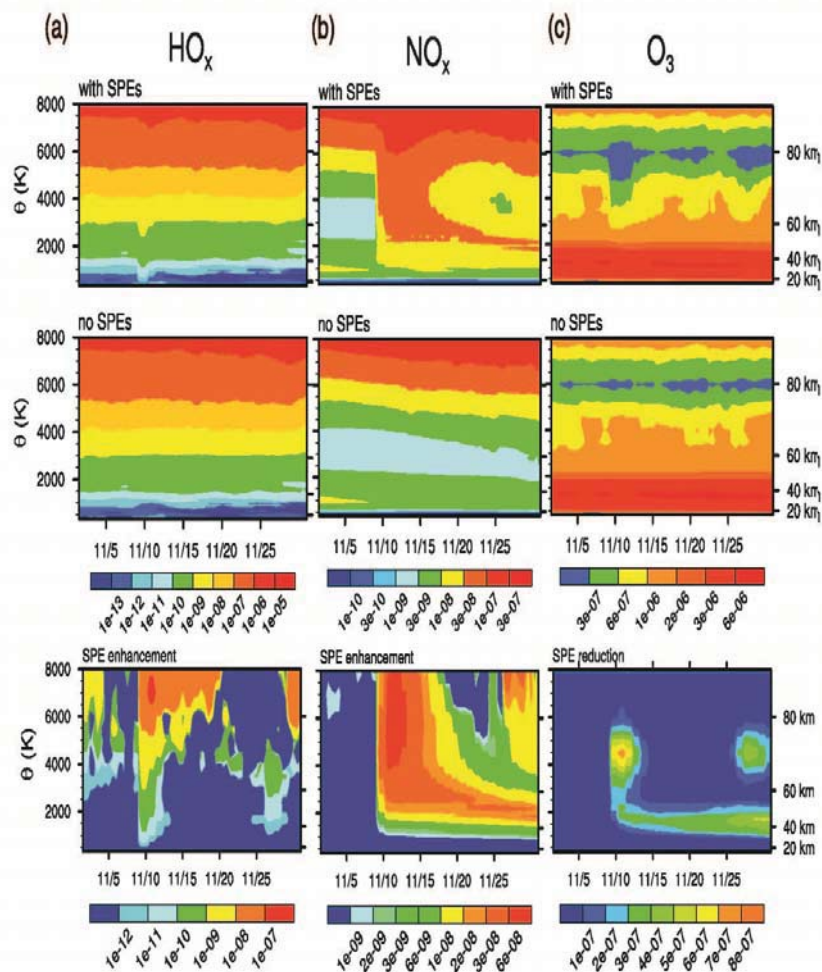


Figure 2. Daily measurements of ion content (nmol/kg) in surface snow at Summit, Greenland from August, 2000 to August, 2002 [Dibb et al., 2007]. Concurrent peaks of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Na}^+$ , and  $\text{NO}_3^-$  and  $\text{Ca}_2^+$  are dated by color for source identification. Nitrate spikes dated in black represent enhancements not readily attributable to tropospheric sources. Average coefficient of variation ( $\text{CV}_{\text{avg}}$ ) indicates the spread among three simultaneous snow samples used to calculate each daily average, representing the major source of error. The lower graph identifies major SPE events in the context of daily solar proton fluxes from GOES-8 in protons/( $\text{cm}^2$ -day-sr) (NOAA at <http://www.swpc.noaa.gov/>).



1195 Figure 3. Time evolution of the vertical structure for WACCM vortex-averaged a)  $\text{HO}_x$ ,  
 b)  $\text{NO}_x$ , and c)  $\text{O}_3$  during the weeks following the 9 Nov 2000 event (mole ratios). The  
 vertical scale is represented by potential temperature ( $\theta$ ), left, and approximate  
 geopotential height ( $Z$ ), right. Top: with SPEs. Middle: no SPEs. Bottom:  $\text{HO}_x$   
 1200 SPE enhancement ( $\text{HO}_x$  with SPEs –  $\text{HO}_x$  no SPEs),  $\text{NO}_x$  enhancement ( $\text{NO}_x$  with SPEs –  
 $\text{NO}_x$  no SPEs), and  $\text{O}_3$  reduction ( $\text{O}_3$  no SPEs –  $\text{O}_3$  with SPEs).



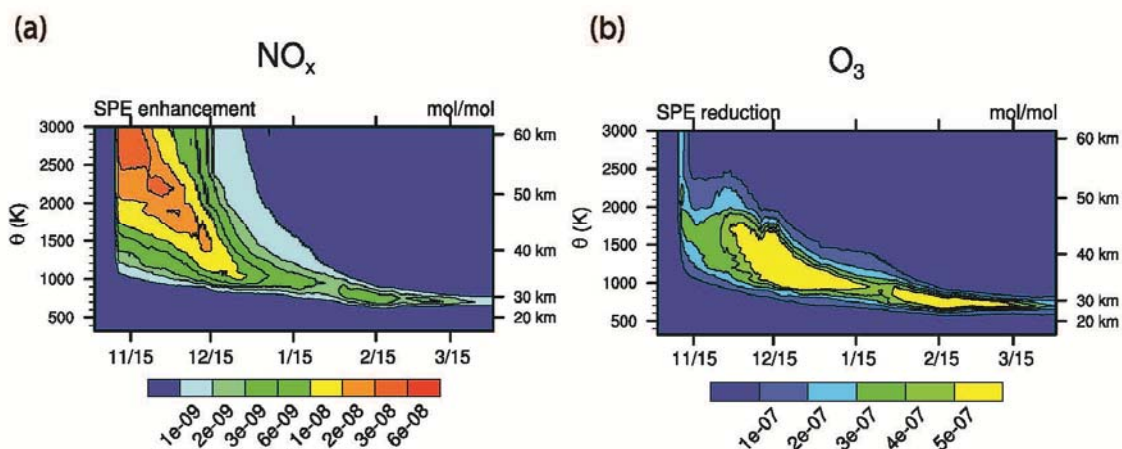


Figure 4. Time evolution of the vortex-averaged a) enhancement of NO<sub>x</sub> and b) reduction O<sub>3</sub> from November through March (mole ratios).

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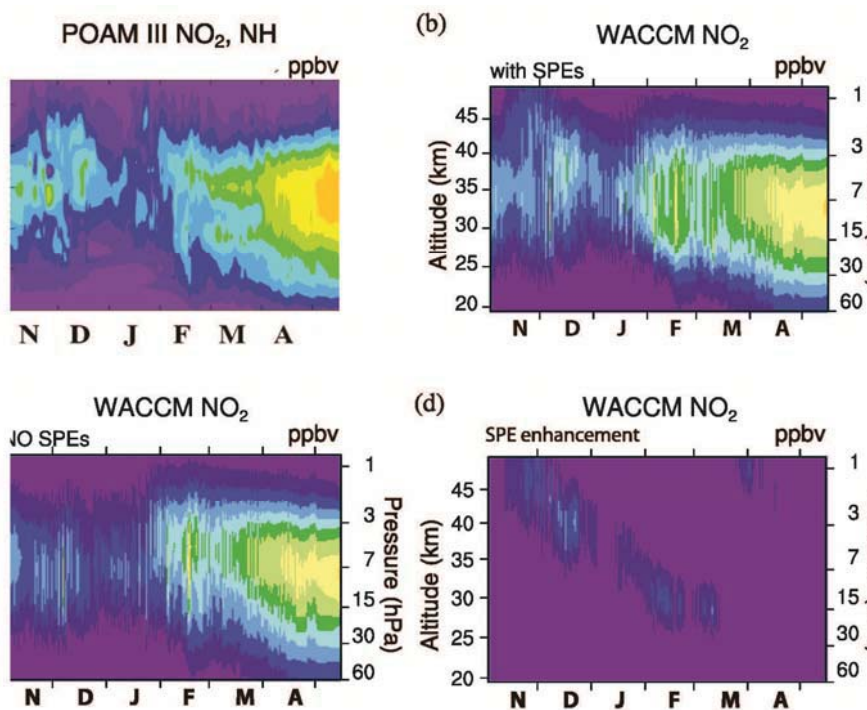
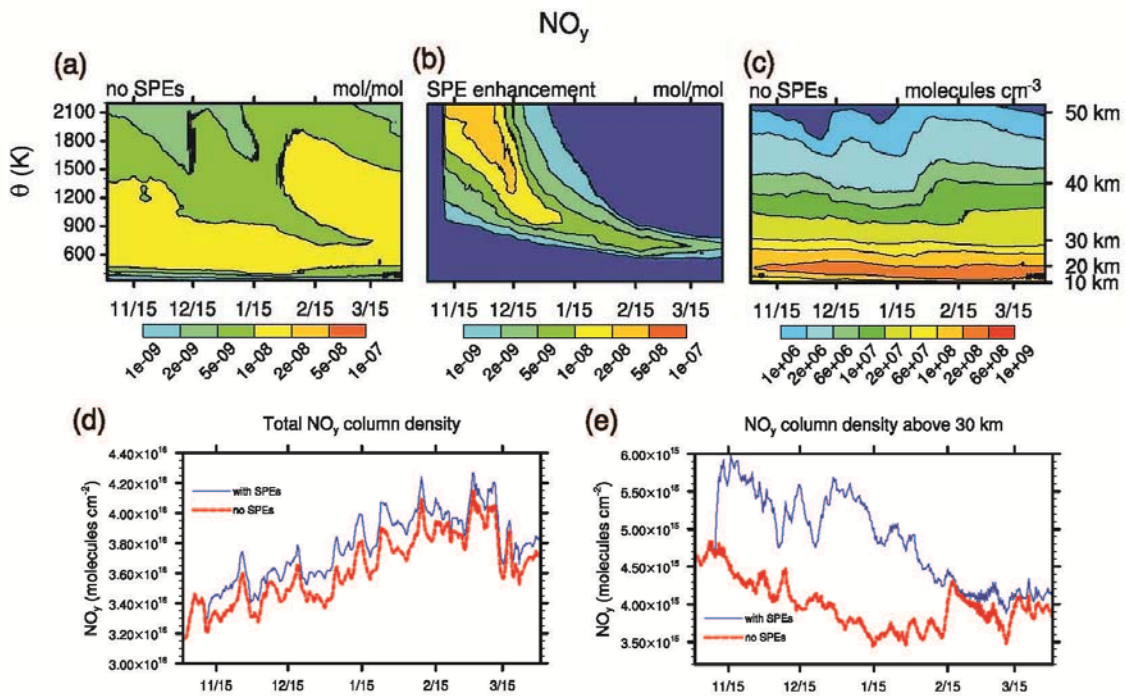


Figure 5. Comparison of WACCM NO<sub>2</sub> with POAM III satellite observations: a) POAM III observations, b) WACCM with SPEs, c) WACCM without SPEs, d) WACCM SPE enhancements (units in ppbv). WACCM results are linearly interpolated and smoothed for clarity during periods when satellite measurements are outside the WACCM polar vortex defined according to  $sPV > 1 \times 10^{-4} \text{ s}^{-1}$ .

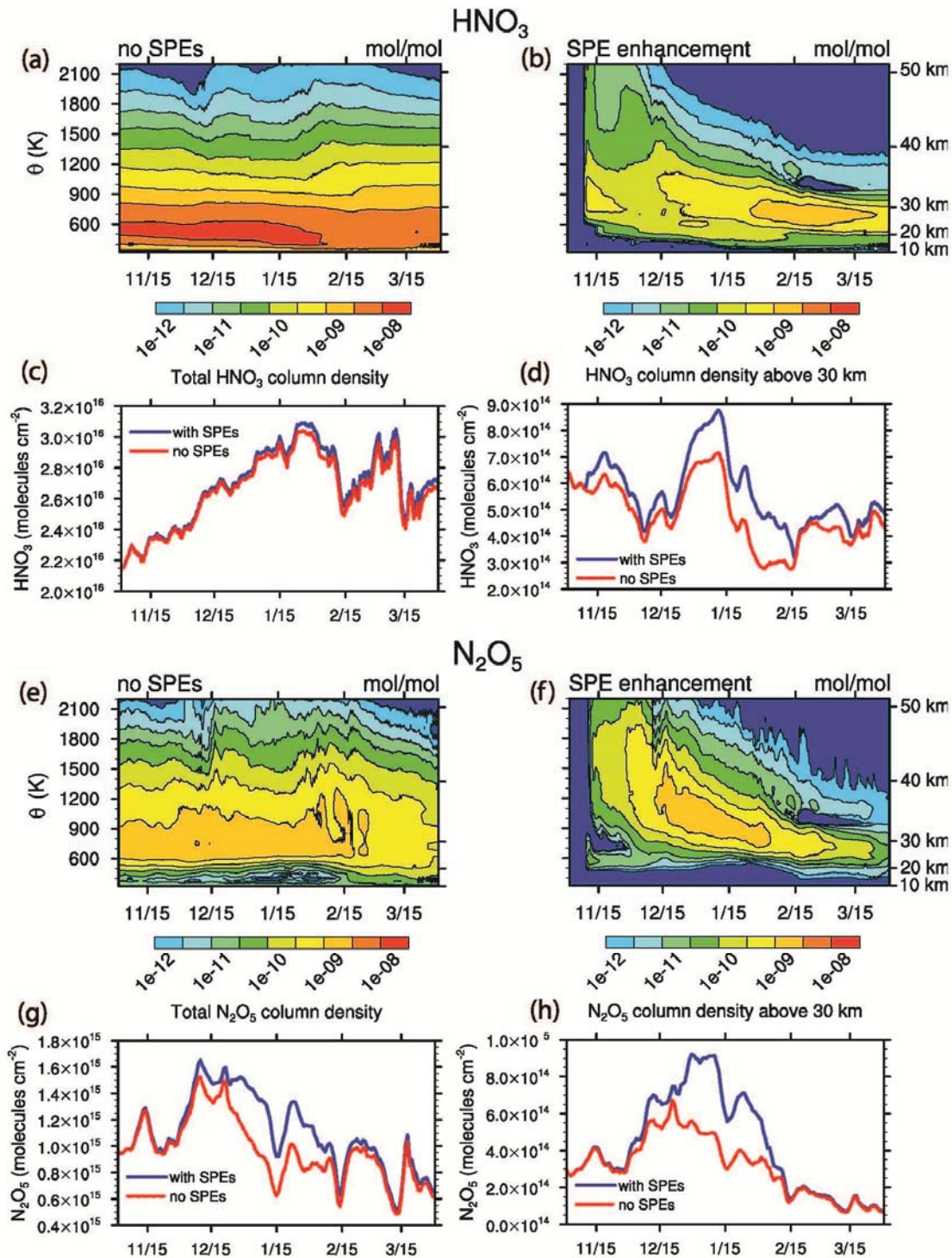
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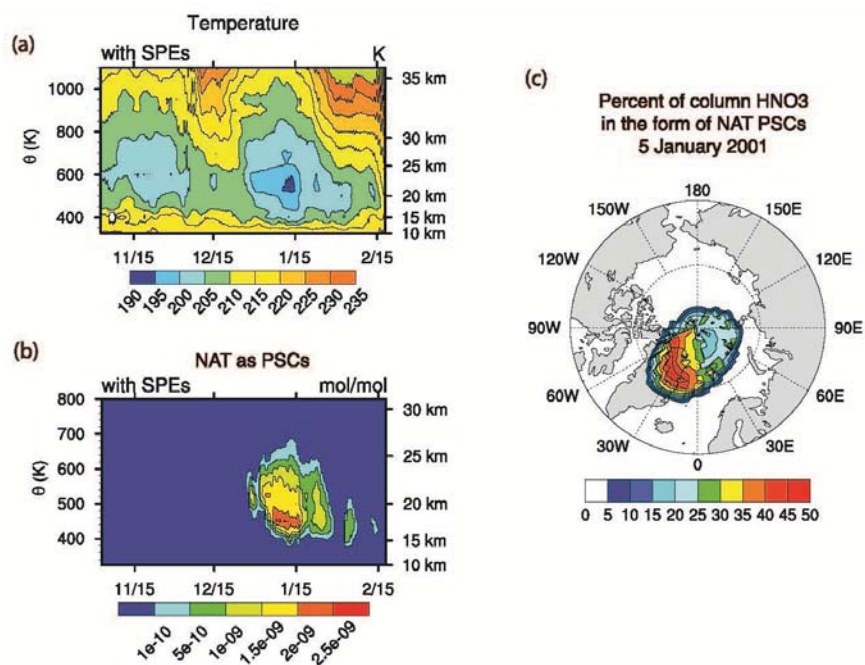
Figure 6. WACCM vortex-averaged NO<sub>y</sub>: a) no SPEs (mole ratios), b) SPE enhancement (mole ratios), c) no SPEs (number density), d) column densities (molecules cm<sup>-2</sup>) integrated throughout the total atmosphere with SPEs (blue) and no SPEs (red), and e) column densities (molecules cm<sup>-2</sup>) integrate from 30 km to the top of the atmosphere with SPEs (blue) and no SPEs (red).



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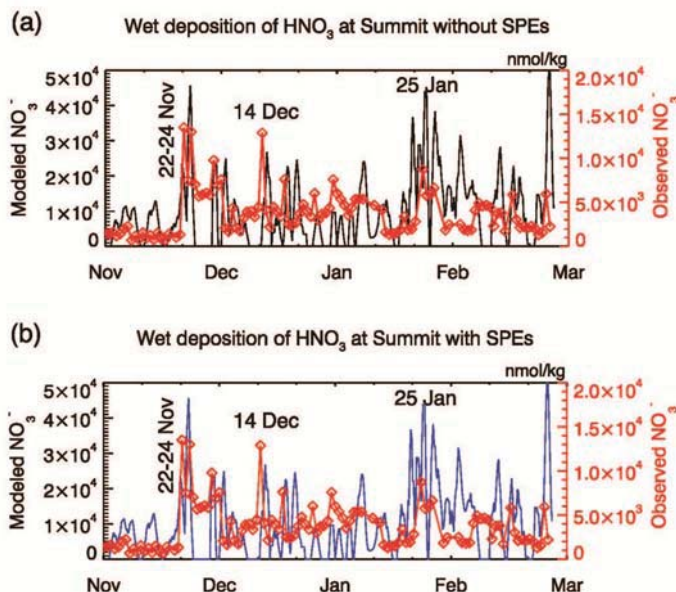
Figure 7. Time evolution of WACCM vortex-averages: a) background HNO<sub>3</sub> (no SPEs), b) SPE enhancement of HNO<sub>3</sub> (HNO<sub>3</sub> with SPEs – HNO<sub>3</sub> no SPEs), c) total column density of HNO<sub>3</sub>, d) column density of HNO<sub>3</sub> above 30 km, e) background N<sub>2</sub>O<sub>5</sub> (no SPEs), f) SPE enhancement of N<sub>2</sub>O<sub>5</sub> (N<sub>2</sub>O<sub>5</sub> with SPEs – N<sub>2</sub>O<sub>5</sub> without SPEs), g) total column density of N<sub>2</sub>O<sub>5</sub>, h) column density of N<sub>2</sub>O<sub>5</sub> above 30 km.

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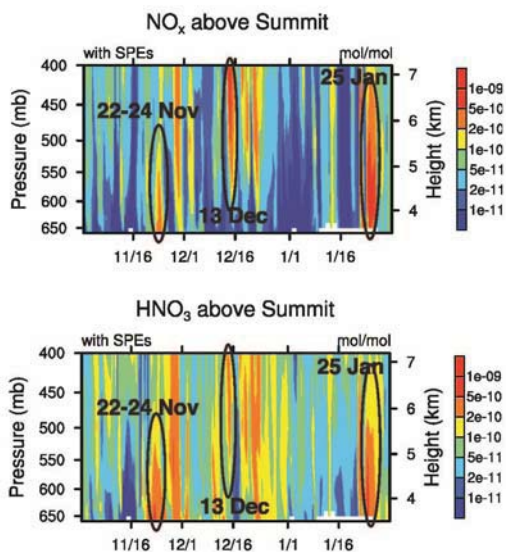
1235 Figure 8. WACCM vortex-averaged vertical profiles for a) temperature (K) and b) condensed nitrate as nitric acid trihydrate (NAT) PSC particles (mole ratios). c) Vortex-averaged percent of total column NAT in the form of PSCs with respect to total gas plus condensed phase  $\text{HNO}_3$ . Although results are from simulations with SPEs, differences with respect to no SPE simulations are negligible.

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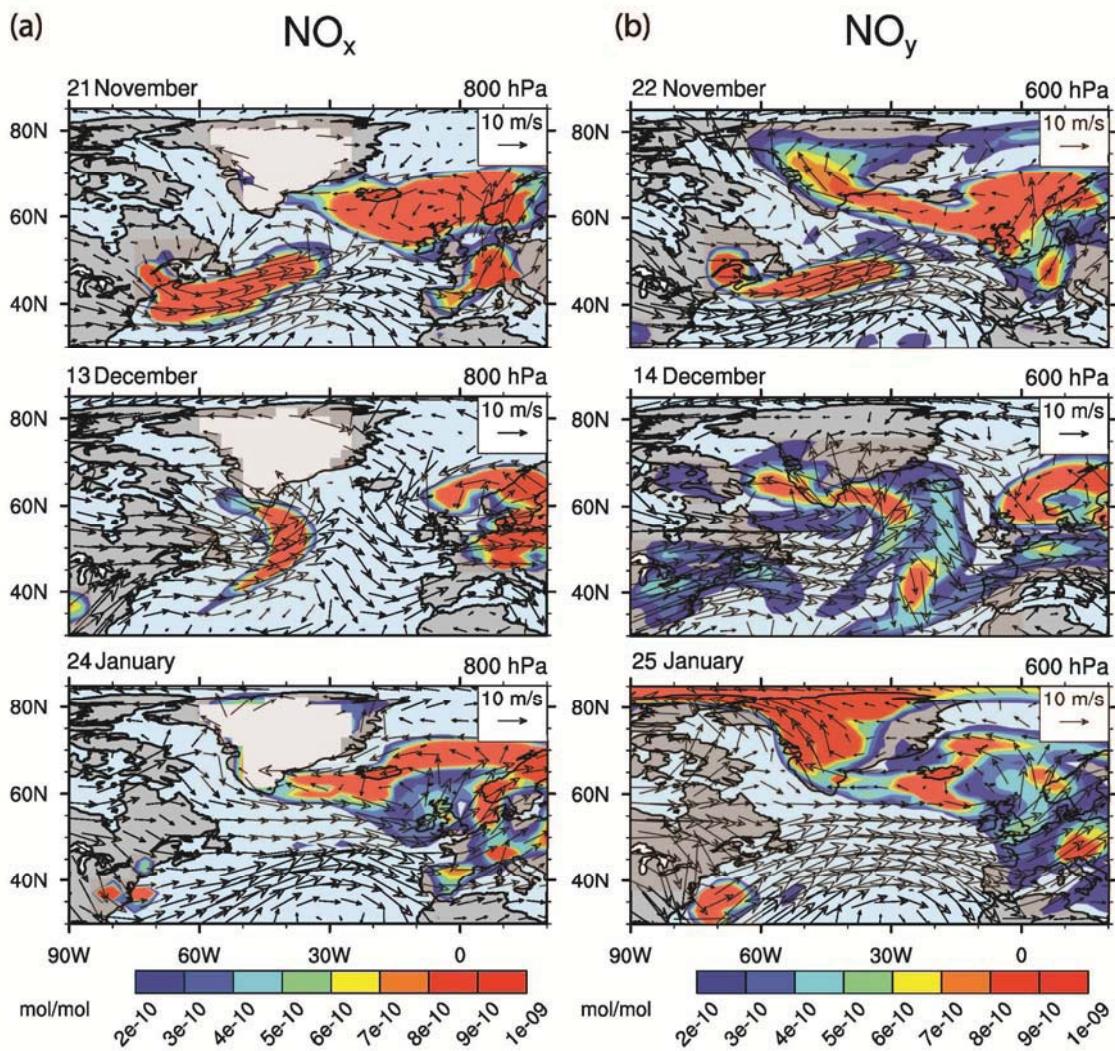
Figure 9. Estimates of nitrate from wet deposition at Summit, Greenland during the 2000-2001 winter ( $\text{nmol/kg}$ ). The blue and black lines along with the left axes present the concentration of nitrogen resulting from the loss of  $\text{HNO}_3$  in precipitation throughout the atmospheric column during the WACCM simulations a) with SPEs and b) without SPEs. The red lines and right axes refer to measurements of  $\text{NO}_3^-$  in daily samples of surface snow.



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Figure 10. WACCM time evolution of the vertical profile of a)  $\text{NO}_x$  and b)  $\text{HNO}_3$  above Summit, Greenland. Recall that Summit is located 3.2 km above sea level with surface pressures from 660-680 hPa. Peak  $\text{NO}_x$  and  $\text{HNO}_3$  are circled during time periods where surface snow measurements indicate nitrate ion spikes uncorrelated with other ions.

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1260 Figure 11. Transport of polluted continental plumes simulated by WACCM prior to nitrate ion spikes in Summit snow on 22-24 November, 14 December, and 25 January. a)  $\text{NO}_x$  at 800 hPa ( $\sim 1.5$  km) on 21 November, 13 December, and 24 January. The white region over Greenland indicates surface elevations above 800 hPa. b)  $\text{NO}_y$  at 600 hPa ( $\sim 3.5$  km) on 22 November, 14 December, and 25 January. Wind vectors are overlaid on both plots to indicate the travel direction of the polluted plumes.

