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Comment on “Atmospheric ionization by high-fluence, hard spectrum solar proton events and their probable appearance in the ice core archive” by A. L. Melott et al. [2016]

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Comments

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COMMENT

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This article is a companion to *Duderstadt et al.* [2016] doi:10.1002/2015JD023805; *Melott et al.* [2016] doi:10.1002/2015JD024064; and *Sinnhuber* [2016] doi:10.1002/2016JD024950.

Key Points:

- It is necessary to include preexisting stratospheric HNO₃ in an analysis of nitrate deposition from SPEs
- SPE-produced nitrate is negligible compared to the stratospheric background

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Comment on "Atmospheric ionization by high-fluence, hard spectrum solar proton events and their probable appearance in the ice core archive" by A. L. Melott et al.

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1. Introduction

Melott et al. [2016] and *Duderstadt et al.* [2016] are listed as companion papers, although the contents of *Melott et al.* [2016] remained confidential prior to publication. They both study the potential for solar proton events (SPEs) to enhance atmospheric nitric acid (HNO₃) deposition to account for observed nitrate ion spikes in ice cores but reach opposite conclusions. *Melott et al.* [2016] estimate the absolute amount of nitrate produced in the atmosphere by SPEs without considering the substantial preexisting atmospheric column of nitric acid (HNO₃), much of which is in the lower stratosphere. *Duderstadt et al.* [2016] conduct comprehensive chemical transport modeling that includes background HNO₃. This comment addresses these differences and also corrects misrepresentations regarding *Duderstadt et al.* [2016] as referenced by *Melott et al.* [2016] and *Sinnhuber* [2016]. *Melott et al.* [2016] suggest that individual solar proton events (SPEs) are detectable as nitrate ion spikes in ice cores. They use the high fluence, high energy ("hard spectrum") SPE of 23 February 1956 to calculate an enhancement of HNO₃ from the surface to 46 km that is equivalent to a ~120 ng cm⁻² nitrate ion spike observed in the GISP2H ice core. The *Melott et al.* [2016] approach is fundamentally flawed, since it considers only the absolute column burden of SPE-produced nitrate and not the preexisting nitrate in the stratosphere. Modeling studies supported by extensive observations [*Duderstadt et al.*, 2014, 2016, and this comment] show background HNO₃ in the lower and middle stratosphere equivalent to 2000 to 3000 ng cm⁻² nitrate. These high levels of background nitrate must also be included when estimating SPE enhancements to the deposition of nitrate ions that might eventually be preserved in an ice core. The 1956 SPE results in less than a 5% increase in the column burden of atmospheric HNO₃, not large enough to explain the nitrate spike seen in the GISP2H ice core. Even extreme SPE enhancements cannot explain nitrate peaks (typically hundreds of percent increases) observed in the ice record [*Duderstadt et al.*, 2016]. Realistic mechanisms linking nitrate ions in ice cores to SPEs have not been established.

2. Why Preexisting Stratospheric Nitric Acid Cannot be Neglected

In section 1.2, *Melott et al.* [2016] propose that a "fundamentally important difference [between the papers] is that [*Melott et al.*, 2016] examine the total amount of nitrate expected to be produced in the air column [by an SPE] and compare that with ice cores." We agree with this statement and believe that by neglecting background HNO₃, *Melott et al.* [2016] incorrectly approach the question of whether an SPE can create a nitrate spike in polar snow that might be preserved and later observed in an ice core. In contrast, *Duderstadt et al.* [2016] assess the SPE source of nitrate relative to the atmospheric background, resolved vertically as well as in terms of column density. Accounting for preexisting nitrate is essential because the chemical and dynamical processes capable of moving HNO₃ downward from the middle and lower stratosphere into the troposphere, where it is available for deposition to the surface, apply to all HNO₃ molecules regardless of source.

Much of the recent debate regarding the use of nitrate spikes as signatures of SPEs involves whether enhancements of HNO₃ produced through ionization in Earth's atmosphere by an SPE can be rapidly moved

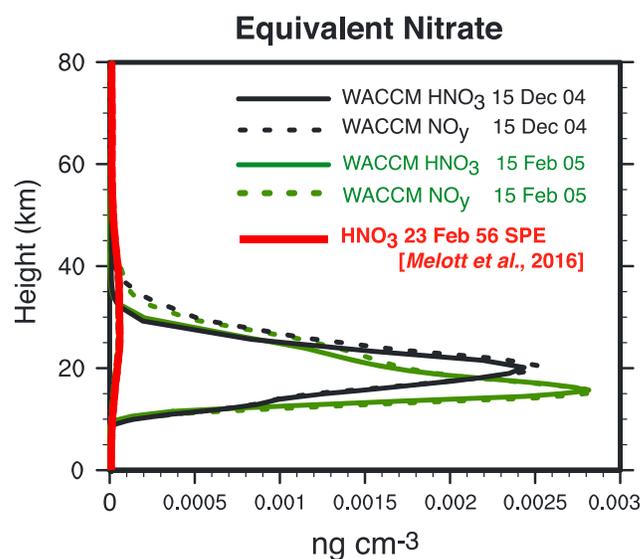


Figure 1. Vertical profiles of equivalent nitrate (NO_3^-) from background (no SPE) WACCM simulations from Duderstadt *et al.* [2016] and the 23 February 1956 SPE of Melott *et al.* [2016]. The profile of nitrate from HNO_3 for the 23 February 1956 SPE is based on the methods of Melott *et al.* [2016] using ionization rates from Usoskin *et al.* [2011] (red). WACCM profiles represent polar vortex averages of HNO_3 (solid) and total NO_y (dashed) for December (black) and February (green). In order to emphasize the overwhelming contribution of background HNO_3 in the lower stratospheric to cumulative column nitrate, as well as to address concerns by Melott *et al.* [2016] over the contribution of polluted anthropogenic plumes to total column densities, we set WACCM values of HNO_3 and NO_y below 8 km to 0 in this figure. Although highly variable, HNO_3 in the WACCM polar troposphere generally ranges from 1×10^{-4} to 3×10^{-4} and NO_y from 1×10^{-4} to 5×10^{-4} , an order of magnitude less than in the lower stratosphere. This figure demonstrates that conclusions presented in Duderstadt *et al.* [2016] involving SPE enhancements to NO_y column densities are independent of tropospheric NO_y and primarily the result of this stratospheric reservoir.

repeating the methods outlined in Melott *et al.* [2016], using Usoskin *et al.* [2011] daily average ionization rates from CRAC:CRIL integrated over 1 day to estimate NO_x production and assuming immediate conversion to HNO_3 . Background HNO_3 in the Arctic lower stratosphere (10 km to 30 km) is almost 2 orders of magnitude more than Melott *et al.* [2016] calculate for the 1956 SPE. By integrating the HNO_3 profile from the 1956 SPE from the surface to ~ 45 km, Melott *et al.* [2016] calculate a cumulative column nitrate density of $\sim 120 \text{ ng cm}^{-2}$, which matches the magnitude of the nitrate spike in the GISP2H core attributed to the 1956 SPE. Note that this spike is roughly a factor of 2 enhancement over the background ice core nitrate [Melott *et al.*, 2016, Figure 4]. In comparison, background WACCM nitrate column densities from 8 km to 45 km (not including minimal tropospheric contributions for reasons explained in Figure 1) are $\sim 2400 \text{ ng cm}^{-2}$ for December and $\sim 2800 \text{ ng cm}^{-2}$ for February. Consequently, an SPE like the 1956 event would increase the column burden of HNO_3 from 0 km to 45 km by only 5%. There is no plausible mechanism to get the HNO_3 SPE enhancement into the snow without also including preexisting HNO_3 . Thus, any SPE-induced ice core enhancement could be no more than $\sim 5\%$, much less than the 100% suggested by Melott *et al.* [2016].

The WACCM profiles in Figure 1 are model derived, but they clearly illustrate the reservoir of HNO_3 that results primarily from the oxidation of nitrous oxide (N_2O) emitted at the surface. Figure 2 compares WACCM profiles of HNO_3 mixing ratios with balloon and satellite measurements, showing that they substantially agree with observations and are accurate within, at worst, a factor of 2. Brakebusch *et al.* [2013] compare WACCM calculations to Microwave Limb Sounder (MLS) observations, showing that WACCM HNO_3 in the lower

downward into the troposphere and then deposited onto the surface of the polar ice sheets in Greenland or Antarctica [e.g., Smart *et al.*, 2014; Wolff *et al.*, 2016; Smart *et al.*, 2016]. Melott *et al.* [2016] suggest that the combination of subsidence within the polar vortex and downward transport due to the formation of nitric acid trihydrate (NAT) particles in polar stratospheric clouds (PSCs) might be capable of moving all of the SPE-derived atmospheric HNO_3 between the surface and 45 km into surface snow within 1–2 months. Smart *et al.* [2014] suggest even shorter transport time scales, including for the 1956 event. But regardless of the rate at which HNO_3 can be transported downward, we emphasize that both subsidence and denitrification of the midstratosphere by downward transport of NAT apply to *all* of the HNO_3 that is present, including preexisting HNO_3 , with no way to selectively transport *only* the newly formed HNO_3 from the SPE.

Figure 1 shows background vertical profiles of HNO_3 and NO_y calculated by the Whole Atmosphere Community Climate Model (WACCM) from the 2004–2005 simulations of Duderstadt *et al.* [2016], averaged over the polar vortex in December and February. The figure also includes the profile of HNO_3 from the 23 February 1956 SPE, determined by

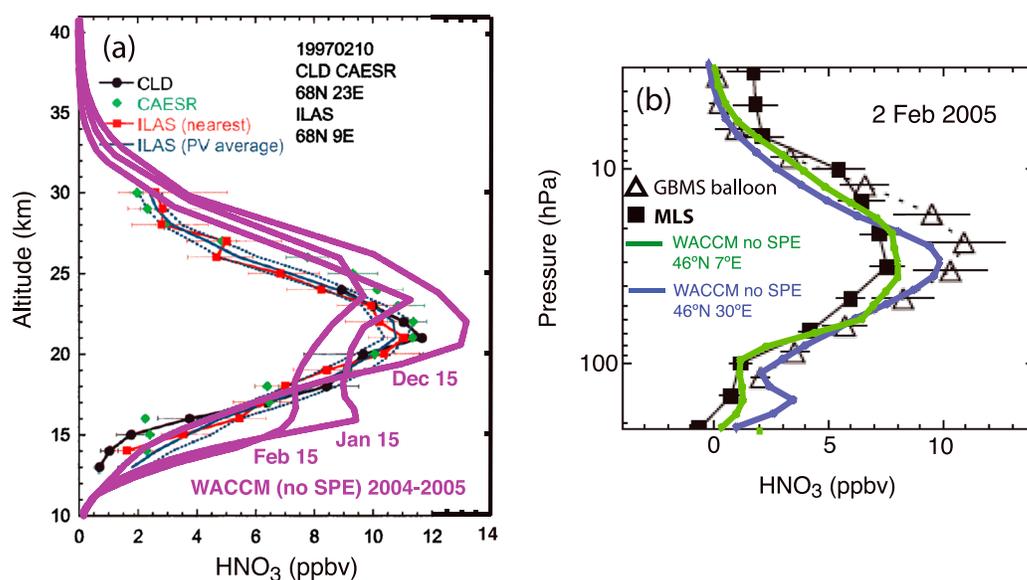


Figure 2. (a) Vertical profiles of HNO₃ mixing ratios from WACCM (purple), balloon-borne measurements (black circles and green diamonds), and ILAS satellite measurements (blue solid lines with dashed lines as standard deviation). Adapted from Koike *et al.* [2000]. (b) Vertical profiles of HNO₃ mixing ratios from WACCM (green and blue), balloon-borne measurements (triangles), and MLS satellite (black squares). MLS and balloon correspond to 46°N, 8°E. All profiles are from 2 February 2005. Adapted from Santee *et al.* [2007].

stratosphere is 10% to 30% higher than MLS observations. Since even a very large SPE cannot significantly increase lower stratospheric HNO₃ above background levels, we stand by our conclusions that SPEs cannot cause nitrate spikes in polar snow or ice cores.

The point can also be made that HNO₃ levels in the stratosphere are likely higher during present times than in 1956 given the increase in anthropogenic sources of N₂O, primarily from agriculture. Atmospheric N₂O increased by ~10% from the 1950s to 2005 (the time of the Duderstadt *et al.* [2016] simulations) and by ~15% since the 1850s [MacFarling Meure *et al.*, 2006]. Reducing background stratospheric HNO₃ from the Duderstadt *et al.* [2016] simulations by 15% results in 0 km to 45 km HNO₃ enhancements from the 1956 SPE of under 6% (only slightly more than the 5% indicated with 2004–2005 background HNO₃). Furthermore, estimates suggest that ~60% of present-day N₂O sources are natural [Intergovernmental Panel on Climate Change, 2013], implying that past levels of stratospheric HNO₃ would remain sufficiently high to support our conclusions, especially given the ~120 year atmospheric lifetime of N₂O.

3. Correcting Misrepresentations by Melott *et al.* [2016] and Sinnhuber [2016]

There are two significant misrepresentations of our work. Melott *et al.* [2016] incorrectly define total NO_y in our WACCM simulations, in the context of concerns about the contribution of tropospheric chemical species such as peroxyacetyl nitrate (PAN) and organic nitrates to total NO_y. In section 1.2, Melott *et al.* [2016] erroneously claim that the “total NO_y present in [the Duderstadt *et al.*, 2016] WACCM model atmospheric reservoir...includes many more species than they list in their definition.” In Duderstadt *et al.* [2016] total NO_y is defined as follows:

$$NO_y = N + NO + NO_2 + NO_3 + 2N_2O_5 + HNO_3 + HO_2NO_2 + ClONO_2 + BrONO_2$$

(We note that nitric oxide, NO, was inadvertently omitted from this list of NO_y species in the Introduction of Duderstadt *et al.* [2016] but is indeed a part of both the NO_x and NO_y families in the WACCM simulations.) The WACCM chemical mechanism used in Duderstadt *et al.* [2016] includes only these listed NO_y species and their reactions and does not include more extensive organic tropospheric chemistry involving PAN and alkyl nitrates. WACCM is initialized using a previously completed climatological simulation and then integrated

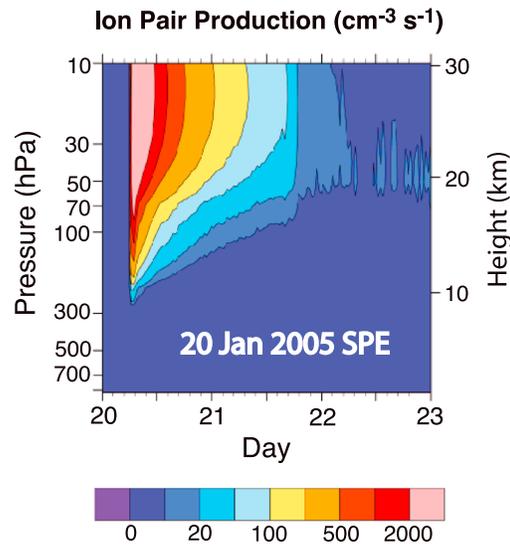


Figure 3. WACCM ion pair production rates ($\text{cm}^{-3} \text{s}^{-1}$) for the 20 January 2005 SPE as a function of altitude (pressure and height) and time (day of the month).

for 4 years to minimize the effects of tropospheric initial conditions. It is clear from Figure 1 that NO_y is overwhelmingly composed of HNO_3 at the altitudes relevant to this discussion. Figure 2 shows how the WACCM predicted HNO_3 compares well with Improved Limb Atmospheric Spectrometer (ILAS) and MLS satellite measurements outside of SPE periods.

The *Melott et al.* [2016] assertion that there is “little to no ionization below 20 km” in our calculations is also inaccurate. *Sinnhuber* [2016] correctly points out that both studies use essentially equivalent methods of calculating atmospheric ionization and subsequent production of nitric oxides but then incorrectly states that “ionization rates in the lowermost stratosphere and troposphere (below ~ 20 km) are higher in the *Melott et al.* [2016] scenario for 1956 than in any of the scenarios shown in *Duderstadt et al.* [2016], therefore leading to more direct production of nitrate there.” Both studies use power law fits (similar to a Band function) to extrapolate to higher energies, *Usoskin et al.* [2010, 2011] CRAC:CRIL yield functions rates to account for the effects of nuclear processes and secondary particles, and *Porter et al.* [1976] and *Rusch et al.* [1981] estimates of NO_x production. Therefore, any major differences in ionization rates and NO_x production should only depend on the solar proton flux at the top of the atmosphere.

4. Conclusions

Figure 3 provides an example of ionization rates from *Duderstadt et al.* [2016] for 20 January 2005, adjusting contour levels to highlight ionization below 20 km. Ion pair production rates below 20 km are in the $100 \text{ s cm}^{-3} \text{ s}^{-1}$, consistent with the observations of *Nicoll and Harrison* [2014] and calculations of *Melott et al.* [2016]. While the 20 January 2005 event in Figure 3 was short lived, our suite of hypothetical events were both amplified and extended in length, representing effects of SPEs with significantly higher fluence and harder spectra than the 1956 SPE. The ionization rates, NO_x production, and equivalent nitrate densities calculated during SPE events in *Duderstadt et al.* [2016] are therefore of the same magnitude or larger than in the *Melott et al.* [2016] study.

Using ice cores and other paleoarchives in conjunction with global climate models to interpret the historical behavior of the Sun remains exciting and promising, especially considering recent progress studying cosmogenic radionuclides [*Beer et al.*, 2012]. However, realistic mechanisms linking nitrate ions in ice cores to SPEs have not been established and nitrate spikes in ice cores cannot provide statistically reliable proxy records of the frequency or magnitude of SPEs because of the many other causes of nitrate variability [e.g., *Legrand and Delmas*, 1986; *Wolff et al.*, 2008, 2012, 2016; *Duderstadt et al.*, 2014, 2016].

The arguments traditionally presented for associating SPEs with nitrate in ice cores rely on selectively choosing spikes that fall near dates of observed historical solar flares, such as the Carrington event of 1859 or neutron monitor enhancements in the 1940s and 1950s [e.g., *Zeller and Dreschhoff*, 1995; *Kepko et al.*, 2009; *Smart et al.*, 2014; *Smart et al.*, 2016]. These selected spikes are then used to extrapolate other nitrate spikes to hypothetical solar storms.

Wolff et al. [2008, 2012, 2016] have convincingly associated nitrate spikes with biomass burning and other tropospheric sources in ice cores that provide a full suite of chemical measurements. In addition, they show that nitrate layers can be explained through the “fixing” of nitrate by sea salt or dust, postdepositional processes, and local meteorology. *Legrand et al.* [1989] and *Legrand and Kirchner* [1990] present results from ice core analyses and two-dimensional modeling studies that come to the same conclusion as

our recent three-dimensional model simulations, namely, that there are no known mechanisms to allow stratospheric enhancements of SPE-produced nitrate to be distinguishable from other sources of nitrate spikes at the surface. These alternative explanations are ignored, with a common theme that any contrary results are based on the wrong measurements at the wrong location at the wrong time [e.g., Laird *et al.*, 1988; Smart *et al.*, 2014, 2016; Melott *et al.*, 2016]. The Melott *et al.* [2016] calculations for the 1956 SPE are representative of the right measurements at the right location at the right time. However, even in this extreme case, the SPE enhancements of HNO₃ in the stratosphere have a negligible effect (~5%) on nitrate column burdens from the surface to 45 km. The hypothetical high-fluence, hard spectra SPEs presented in Duderstadt *et al.* [2016], with larger ionization rates and NO_x production in the lower stratosphere than the 1956 SPE, are also unable to explain nitrate peaks (typically hundreds of percent increases) observed in the ice core record.

Melott *et al.* [2016] study the possibility of producing nitrate peaks from SPEs to the exclusion of the atmospheric background. The authors study only the nitrate contributions that support their conclusion while neglecting all other material in the surrounding medium. It is time to move the search for indicators of solar activity away from nitrate ions: Nitrate ions cannot be used as proxies for individual SPEs in the ice core record. Existing and previous studies that utilize nitrate peaks in the ice core record to identify individual SPEs are flawed.

Acknowledgments

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