- Observations and modelling of increased nitric oxide in the Antarctic polar middle 1
- atmosphere associated with geomagnetic storm driven energetic electron 2
- precipitation 3
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19 **Key Points:**

- NO partial columns over altitudes 65–140 km measured at Halley, Antarctica are on • 20 average 49% higher than SOFIE observations. 21
- NO number density in the Antarctic mesosphere and lower thermosphere is up to 22 3×10^8 cm⁻³ higher in the 2013 winter than the 2014 winter. 23
- Higher mesospheric NO abundance in the 2013 winter is partially explained by increased 24 NO production due to medium energy electrons. 25

26 Abstract

- 27 Nitric oxide (NO) produced in the polar middle and upper atmosphere by energetic particle
- 28 precipitation depletes ozone in the mesosphere and, following vertical transport in the winter
- 29 polar vortex, in the stratosphere. Medium energy electron (MEE) ionization by 30–1000 keV
- 30 electrons during geomagnetic storms may have a significant role in mesospheric NO production.
- 31 However, questions remain about the relative importance of direct NO production by MEE at
- 32 altitudes ~60–90 km versus indirect NO originating from auroral ionization above 90 km. We
- investigate potential drivers of NO variability in the southern-hemisphere mesosphere and lower
 thermosphere during 2013–14. Contrasting geomagnetic activity occurred during the two austral
- winters, with more numerous moderate storms in the 2013 winter. Ground-based millimeter-
- winters, with more numerous moderate storms in the 2015 winter. Ground-based infiniteterwave observations of NO from Halley, Antarctica are compared with measurements by the Solar
- Occultation For Ice Experiment (SOFIE) space-borne spectrometer. NO partial columns over
- the altitude range 65-140 km from the two observational datasets show large day to day
- variability and significant disagreement, with Halley values on average 49% higher than the
- 40 corresponding SOFIE data. SOFIE NO number densities, zonally averaged over geomagnetic
- latitudes -59° to -65° , are up to 3×10^{8} cm⁻³ higher in the winter of 2013 compared to 2014.
- 42 Comparisons with a new version of the Whole Atmosphere Community Climate Model, which
- 43 includes detailed *D*-region ion chemistry (WACCM-SIC) and MEE ionization rates, show that
- the model underestimates NO in the winter lower mesosphere whereas thermospheric
- 45 abundances are too high. This indicates the need to further improve and verify WACCM-SIC
- 46 with respect to MEE ionization, thermospheric NO chemistry, and vertical transport.

47 **1 Introduction**

48 1.1 Background information

- 49 Energetic particle precipitation (EPP) is an important mechanism in the polar middle and upper
- atmosphere, causing ionization in the neutral atmosphere and producing odd nitrogen ($NO_x = NO$
- + NO₂) and odd hydrogen (HO_x = OH + HO₂) (Brasseur & Solomon, 2005; Miranova et al.,
- 52 2015; Sinnhuber et al., 2012). NO_x exists mainly as NO in the thermosphere and upper
- mesosphere, and is converted to NO_2 below 65 km (Solomon et al., 1982). Enhanced
- abundances of these chemical species lead to catalytic destruction of ozone (Jackman &
- 55 McPeters, 2004), perturbing the radiative balance, dynamics, and large-scale circulation patterns
- of the atmosphere. This mechanism potentially links solar variability associated with space
- 57 weather to regional surface climate (e.g. Arsenovic et al., 2016; Baumgartner et al., 2011;
- 58 Semeniuk et al., 2011; Seppälä et al., 2009, 2013).
- 59 The energetic particles, mainly protons and electrons of solar and magnetospheric origin, vary
- 60 widely in energy range and the regions of the atmosphere where they impact, both in
- 61 geographic/geomagnetic coverage and altitude. During solar proton events (SPE's), high fluxes
- of 1–500 MeV protons over the polar caps can greatly enhance NO_x levels directly in the
- 63 stratosphere leading to ozone losses exceeding 60% (Jackman et al., 2009). However, SPE's
- occur sporadically, most often at solar maximum and 1 to 2 years afterwards, and last just a few
- days. At geomagnetic latitudes of 70° – 75° high fluxes of low energy (1–30 keV) auroral
- 66 electrons enter the atmosphere almost continuously and produce abundant nitric oxide (NO) in

the lower thermosphere at 100–120 km, even during low geomagnetic activity (Marsh et al.,
2004).

- 69 During geomagnetic storms, in the subauroral zone at geomagnetic latitudes $\leq 70^{\circ}$, relativistic
- ⁷⁰ electrons (~1–4 MeV) from the radiation belts can reach the lower mesosphere and stratosphere
- (Horne et al., 2005). The effect of these high-energy electrons on the atmosphere is predicted to
- be greatest in the southern hemisphere (SH), pole-ward of the South Atlantic Magnetic Anomaly
- 73 (SAA) region, and during the recovery phase of geomagnetic storms (Horne et al., 2009). At
- ⁷⁴ intermediate energies, medium-energy electron (MEE, ~30–1000 keV) precipitation will increase
- ionization in the polar upper stratosphere and mesosphere at altitudes ~60–90 km (Turunen et al.,
- 76 2009).

77 1.2 Previous studies

78 Satellite-based observations show that MEE precipitation has a direct impact on mesospheric

- chemistry, with the largest hydroxyl (OH) enhancements at altitudes of 70–78 km and
- 80 geomagnetic latitudes ~55°–75° (Andersson et al., 2012; Andersson et al., 2014a; Verronen et
- al., 2011; Zawedde et al., 2016) and ozone perturbed over short timescales (Verronen et al.,
- 2013) and in longer-term variability (Andersson et al., 2014b). The short lifetime of HO_x in the
- middle atmosphere restricts its effect on ozone to the mesosphere. In contrast, while the
- chemical lifetime of NO_x in the sunlit mesosphere and lower thermosphere is typically ~18 h, in
- darkness NO_x can persist for months (Shimazaki, 1984; Solomon et al., 1999). This long
- 86 lifetime allows auroral NO in the lower thermosphere, and mesospheric NO produced directly by
- 87 MEE ionization, to be transported downward inside the polar vortex at high latitudes during
- winter into the stratosphere where it depletes ozone (e.g., Clilverd et al., 2007; Funke et al., 2017; Pandall et al. 2007; Sickind et al. 2000; Sinnhuber et al. 2014)
- 89 2017; Randall et al., 2007; Siskind et al., 2000; Sinnhuber et al., 2014).

90 In the northern hemisphere, sudden stratospheric warmings can result in the breakdown of the

- 91 Arctic wintertime polar vortex and disrupt the downward transport of NO_x. However, in some of
- these events the stratopause and accompanying vortex reforms at higher altitudes, leading to
- pronounced NO descent and NO_x enhancements in the middle atmosphere (e.g., Randall et al.,
- 2009). Descent rates for the SH winter are estimated from first empirical orthogonal function
- 95 mode indices of CO to be constant at 0.16–0.2 km/day below 40 km and increase almost linearly 96 with altitude above 40 km to ~1 km/day at 80 km (Lee et al., 2011). However, the reliability of
- 96 with altitude above 40 km to ~1 km/day at 80 km (Lee et al., 2011). However, the reliability of 97 inferring polar winter mean air-mass descent rates from remote sensing tracer gas measurements
- has been questioned, due to the presence of significant dynamical processes other than vertical
- advection (Ryan et al., 2018). Sheese et al. (2011) determined a proxy NO descent rate in the
- 100 Antarctic mesosphere and lower thermosphere of 3.8 km/day, somewhat larger than mean
- 101 vertical wintertime wind speeds typically presumed to be \sim 1.7 km/day. Meridional circulation
- reversal, which shows large wintertime variability and equatorward flow at 68°S above altitudes
- in the range 80–98 km (Hibbins et al., 2005; Sandford et al., 2010), could provide a barrier
 preventing auroral NO from descending, although diffusion will still disperse NO (Smith et al.,
- 2011). Thus, questions remain as to whether NO produced at high altitudes (>90 km) by
- plentiful lower energy (1–30 keV) electrons, requiring substantial downward transport to reach
- the stratosphere, is more important than NO_x production in the mesosphere by medium and high-
- 108 energy (30 keV to several MeV) electrons (Clilverd et al., 2009).

Observations of NO have been made by the Solar Occultation For Ice Experiment (SOFIE) 109 instrument (Gordley et al., 2009) on board the Aeronomy of Ice in the Mesosphere (AIM) 110 satellite since 14 May 2007. NO volume mixing ratio (VMR) and number density profiles are 111 retrieved over the altitude range 30 km to 149 km with an altitude resolution of approximately 112 2 km. Superposed epoch analysis of SOFIE observations over 2007–2014 by Hendrickx et al. 113 (2015) shows a 27-day solar cycle in EPP NO production down to altitudes in the range 95-114 105 km and initial rapid downward transport to altitudes of 80–85 km followed by slower 115 descent to the lower mesosphere and stratopause (~50 km) at a rate of approximately 1-116 1.2 km/d. Multiple linear regression analysis of observations from SOFIE and the Student Nitric 117 Oxide Explorer (SNOE) showed that geomagnetic activity is the dominant source of short-term 118 NO variability throughout the lower thermosphere at high latitudes whereas in the equatorial 119 region solar radiation is the primary driver (Hendrickx et al., 2017). SOFIE NO observations 120 during a geomagnetic storm in April 2010 have been compared with model calculations 121 incorporating a continuous 1–750 keV electron energy spectrum (Smith-Johnsen et al., 2017). 122 This study indicates that, although NO was produced directly by MEE precipitation down to 123 55 km, variability in mesospheric NO following the storm was mainly due to the indirect effect 124 of downward-transported NO originating from the upper mesosphere at ~ 75 km. Observations 125 by the sub-millimeter radiometer (SMR) on the Odin satellite showed increases in mesospheric 126 NO at 75–90 km about 10 days after recurrent geomagnetic storms during the 2010 austral 127 128 winter, and at all latitudes geographically poleward of 60°S, which were attributed to downward-transported NO in addition to direct MEE production (Kirkwood et al., 2015). 129

130 Continuous ground-based measurements using passive millimeter-wave radiometry (Janssen et

al., 1992) allow the temporal variations of NO and ozone within a localized region of the polar

132 atmosphere to be studied. Observations from Antarctic stations within the SH subauroral region

133 show large short-term enhancements of NO in the upper mesosphere and lower thermosphere

134 (~70–105 km) related to MEE and auroral electron flux increases (Daae et al., 2012; Isono et al.,

135 2014a, 2014b; Newnham et al., 2011, 2013). Mesospheric ozone depletions of 20–70% were

observed above Antarctica during and following a moderate geomagnetic storm (minimum *Dst*

of -79 nT) in late July 2009, indicating that MEE precipitation during these commonplace events

138 may significantly affect middle mesospheric ozone distributions (Daae et al., 2012).

139 Major challenges remain in understanding and quantifying the contribution from MEE ionization to chemical changes in the polar atmosphere. Atmospheric simulations require accurate 140 estimates of precipitating electron fluxes, which are difficult to determine from satellite-based 141 measurements (Rodger et al., 2010). Also, in order to model EPP effects in the polar atmosphere 142 below 90 km it is essential to have a detailed representation of the chemistry of the D-region, 143 where cluster ions dominate and electrons are mostly attached to molecules as negative ions 144 (Brasseur and Solomon, 2005; Sinnhuber et al., 2012; Winkler et al., 2008). Recently, new 145 ion-neutral chemical models have been coupled into the specified dynamics (SD) version of the 146 Whole Atmosphere Community Climate Model (WACCM 4) (Marsh et al., 2013) based on the 147 1-D Sodankylä Ion and Neutral Chemistry (SIC) model (Verronen et al., 2005). The SIC model 148 chemical scheme includes 70 ions, of which 41 are positive and 29 negative, and 34 neutral 149 species with simple vertical transport (molecular and eddy diffusion). WACCM-D (Verronen et 150 al., 2016) includes a D-region ion scheme of 307 reactions of 20 positive ions and 21 negative 151 ions, allowing the 3-D global model to account for substantial HNO₃ enhancements observed in 152

153 the mesosphere at altitudes ~50–80 km after major SPEs (Andersson et al., 2016).

- 154 WACCM-SIC (Kovács et al., 2016) includes a more complete set of ion-neutral reactions from
- the detailed *D*-region ion chemistry in the SIC model while ion-ion recombination reactions are D = D = D = D = D
- included for three major positive ions (NO⁺, H⁺(H₂O)₃, and H⁺(H₂O)₄) and three major negative
- 157 ions $(O_2^-, CO_3^-, and NO_3^-)$.
- 158 1.3 This work

159 Here we study NO in the mesosphere and lower thermosphere above Antarctica during a

- 160 two-year period, 2013–14, close to the maximum of solar cycle 24. Contrasting levels of
- 161 geomagnetic storm activity during the two austral winters and low levels of solar protons make
- this a suitable period to investigate MEE effects on the chemistry of the polar middle
- atmosphere. Ground-based NO measurements using passive millimeter-wave radiometry from
 Halley, Antarctica are compared with satellite observations. The potential causes of significantly
- different levels of winter-time NO in each year are investigated using ancillary atmospheric
- 166 observations and WACCM-SIC simulations which include a representation of MEE ionization.
- 167 Our results provide further evidence in support of other recent studies that identify important
- areas for atmospheric model development and the need for further observational data.

169 The manuscript is organized as follows. Section 2 outlines the geomagnetic conditions during

- 170 2013-14 and determines occurrences of moderate geomagnetic storms. The experimental setups
- for Halley and satellite observations, and the atmospheric model configuration and inputs, are
- described in Section 3. The Halley observations are presented in Section 4.1 and interpreted in
- terms of localized NO production and transport. In Section 4.2 the Halley NO partial columns
- are compared with SOFIE observations covering a defined geomagnetic zonal range
- 175 geographically poleward of 60°S. Possible causes of significant differences between the two sets
- of measurements are suggested. WACCM-SIC simulation results are presented in Section 4.3
- and model NO number densities are compared with SOFIE data in Section 4.4. Potential reasons
- for differences between the model runs and SOFIE observations are discussed in Section 5 and
- areas suggested for future research.

180 2 Geomagnetic Conditions

181 We use disturbance storm time (*Dst*) and Kp indices to characterize geomagnetic conditions

- during 2013–14. The planetary Kp index is widely used in ionospheric and magnetospheric
- 183 studies as a measure of global geomagnetic activity. The Kp index quantifies disturbances in the
- 184 horizontal component of Earth's magnetic field with a quasi-logarithmic integer scale in the
- range 0-9 where Kp > 4 indicates a geomagnetic storm. The *Dst* index is used to assess the
- strength of geomagnetic storms (Yokoyama & Kamide, 1997). During a geomagnetic storm *Dst*
- typically shows a sudden rise, corresponding to the storm sudden commencement, and then
- decreases sharply as the ring current in the magnetosphere intensifies. *Dst* zero crossings and
- subsequent minimum values can indicate the start and magnitude of geomagnetic storms
- 190 respectively.
- 191 The time series of the three-hourly Kp index (available from www.gfz-potsdam.de/en/kp-index)
- and the hourly *Dst* index (available from wdc.kugi.kyoto-u.ac.jp/dstdir) for 2013 and 2014 are
- shown in Figure 1. Periods of increased geomagnetic activity are shown by higher Kp index
- levels. During this 2 yr period 28 moderate geomagnetic storms can be identified where distinct

- Dst zero crossings occur and the Dst index subsequently decreased to below -50 nT. The lowest 195
- 196 Dst index of -132 nT occurred on 17 March 2013. The storm commencement times
- corresponding to Dst index zero crossings for each geomagnetic storm are indicated by brown 197
- vertical lines in Figure 1b. Levels of geomagnetic activity generally lag the solar cycle as 198
- defined by sunspot number and UV irradiance, and geomagnetic storms occur most frequently 199
- during solar maximum and one to two years afterwards. The maximum geomagnetic activity of 200 solar cycle 24 was reached in mid-2015. No major SPE's occurred during 2013–2014. The two 201
- most significant SPE's produced only relatively modest maximum 10 MeV proton fluxes of 202
- 1660 protons \cdot cm⁻²sr⁻¹s⁻¹ on 23 May 2013 and 1033 protons \cdot cm⁻²sr⁻¹s⁻¹ on 9 January 2014, and are 203
- indicated by the blue triangles in Figure 1. Eleven smaller SPE's produced maximum 10 MeV 204
- proton fluxes in the range 14–182 protons cm⁻²sr⁻¹s⁻¹ (a full list of SPE's affecting the Earth 205
- environment is available from ftp.swpc.noaa.gov/pub/indices/SPE.txt). 206
- During 2013 and the first half of 2014 the geomagnetic storms were predominantly driven by 207
- coronal mass ejections (CME's). CME occurrence rate tends to be highest close to solar 208
- maximum (Webb and Howard, 2012), which was in April 2014 for solar cycle 24. Contrasting 209
- geomagnetic activity during the months May-August (indicated by the blue shaded areas in 210
- Figure 1) of the two years under study is more clearly seen in the 31-day smoothed Kp indices 211
- and Dst data. Nine moderate geomagnetic storms occurred during the SH winter-time period in 212
- 2013 compared to only two storms in the 2014 winter, one commencing at the start of the winter 213
- period on 1 May 2014 and the other close to the end on 28 August. 214

3 Experimental Setup & Datasets 215

- 3.1 Halley Observations 216
- 217 Observations were made from the Halley VI research station (75°37'S, 26°15'W, L shell of
- L = 4.7, mean altitude above sea level 50 m), located on the Brunt Ice Shelf in Antarctica. As 218
- shown in Figure 2, Halley is at a geomagnetic latitude of -62°, a suitable location for observing 219
- 220 the effects of MEE and relativistic electron precipitation from the outer radiation belt. In
- winter-time Halley is also typically inside the Antarctic polar vortex which extends from the pole 221
- 222 to at least geographic latitude 60°S and from the thermosphere down to the lower stratosphere
- (Harvey et al., 2004). A combination of atmospheric measurements made at Halley by different 223 instruments, i.e., a millimeter-wave radiometer, a widebeam riometer, and a medium frequency
- 224
- (MF) radar were analyzed for the study period. 225
- Observations of temporal variations in NO abundance during the study period were provided by 226 a ground-based millimeter-wave radiometer (Espy et al., 2006). Atmospheric observations were 227 made at a zenith angle of 60° and azimuthal angle of 163°. Assuming negligible refraction, the 228 radiometer view intercepted altitudes of 65-140 km at horizontal distances in the range 113-229 242 km approximately south of Halley. The radiometer was housed in a customized caboose 230 maintained at a temperature of ~290 K with the atmospheric view through an extruded 231 polystyrene foam vertical window. The window material provided good millimeter-wave 232 233 transmission and thermal insulation properties with minimal snow deposition or degradation under extreme conditions with temperatures as low as -55°C, instantaneous wind speeds in 234 excess of 25 ms⁻¹, and exposure to solar UV radiation. The caboose location \sim 2.5 m above the 235 surface minimized the adverse effects of blowing snow on the millimeter-wave observations. 236

237 During blowing snow conditions, which occur at Halley about 30% of the time during winter, the

- particle number density at heights above 1 m is more than ten times lower than just above the
- surface (Mann et al., 2000) leading to reduced scattering attenuation of the millimeter-wave
- signal. The NO emission line centered at 250.796 GHz, down-converted to ~1350 MHz, was
 measured using a chirp transform spectrometer (Hartogh & Hartmann, 1990; Villanueva &
- Hartogh, 2004; Villanueva et al., 2006) with 14 kHz resolution and 40 MHz bandwidth. Daily
- mean calibrated brightness temperature spectra were calculated from the average of 20.5 h of NO
- 244 observations each day, recorded at 00:30–06:00, 06:30–12:00, 14:00–18:00, and 18:30–23:59
- UTC. NO measurements were made on 508 days between 1 March 2013 and 30 July 2014, i.e.
- 246 98.3% of the total 517 days. Data gaps ranging from a few hours to ~2 days were due to
- 247 electrical power loss resulting in instrument shutdown, or routine maintenance. Limited
- electrical power at Halley station meant that the radiometer could not be operated between 31
- July and the end of 2014.

A widebeam riometer (Little & Leinbach, 1959; Rodger et al., 2012) was used to measure 250 cosmic radio noise absorption at 30 MHz, providing an indication of energetic electron 251 precipitation (EEP). This ground-based instrument receives signal over an angle $\pm 60^{\circ}$ of zenith 252 and probes a ~190–310 km wide cone of the ionosphere directly above Halley station. The 253 region of the atmosphere measured by the riometer overlaps the co-located millimeter-wave 254 radiometer observations. Part of the energy of the cosmic radio noise propagating through the 255 ionosphere is absorbed due to collisions of free ionospheric electrons with neutral atoms. 256 257 Increased atmospheric opacity in the frequency range 15–70 MHz is caused by increased electron concentration in the *D*-region that can arise from EEP. Typically the absorption peaks 258 near 90 km altitude where the product of electron density and neutral collision frequency is 259 largest. The instantaneous changes in cosmic noise absorption (Δ CNA, in dB) for each 24 h 260 period were calculated as the ratio of the measured signal intensity received at the ground to the 261 quiet day curve (QDC) absorption (Krishnaswamy et al., 1985). The QDC characterizes the 262 normal variation in CNA due to sidereal changes in the intensity of cosmic noise entering the 263 atmosphere and background ionospheric absorptions not strongly associated with geomagnetic 264 storms. Daily QDC curves were determined by identifying periods of low geomagnetic activity 265 and applying sidereal time corrections to the corresponding riometer data. The daily mean 266 riometer absorption was calculated for each 24 h period (00:00-23:59 GMT) between 1 March 267 2013 (day 60) and 30 July 2014 (day 211). 268

Daily mean wind speeds in the mesosphere and lower thermosphere for the study period were 269 determined from observations by a MF radar that operated quasi-continuously at Halley from 270 February 2012 until January 2017. Five cross-dipole antennas transmitted pulses in O-mode 271 polarization at 2.7 MHz and 100 kW peak power. The wind structure of the mesosphere was 272 probed using measurements of the radar signal partially-reflected from gradients in electron 273 density within the D-region. The signal scattered by the atmosphere was received by three 274 antennas located above the snow surface and sampled by 24×2 km range gates centered on 275 altitudes from 52 km to 100 km. Horizontal wind profiles were retrieved using the full 276 correlation analysis technique (Briggs, 1984) and averaged to provide daily mean wind speeds. 277

278 3.2 Satellite Observations

In this study we analyzed data from two satellite observing systems: - NOAA Polar Orbiting

Environment Satellites (POES) and the Solar Occultation for Ice Experiment (SOFIE). These instruments provide observations of MEE fluxes and NO vertical profiles respectively.

282 Energetic electron measurements are made by the Medium Energy Proton and Electron Detector (MEPED) (Evans & Greer, 2004; Hendry et al., 2017; Rodger et al., 2010), part of the Space 283 Environment Monitor 2 (SEM-2) instrument package on board the NOAA Polar Orbiting 284 Environment Satellites (POES), which are in high-inclination Sun-synchronous orbits at altitudes 285 286 of ~800-850 km. Here we used data (available from http://www.ngdc.noaa.gov/stp/satellite/poes/dataaccess.html) from the MEPED 0° electron 287 288 telescope, which points radially outwards along the Earth–satellite direction with $\pm 15^{\circ}$ width and provides three channels of energetic electron data: >30 keV (0e1 channel), >100 keV (0e2 289 channel), and >300 keV (0e3 channel). Poleward of geomagnetic latitude 33°, the 0° electron 290 telescope monitors electrons in the bounce loss cone that will enter the Earth's atmosphere. We 291 292 apply a proton correction algorithm (available from the Virtual Radiation Belt Observatory, http://virbo.org) to these data as described in Lam et al. (2010, Appendix A). These corrected 293 data were then used to determine daily mean electron count rates for the >30 keV channel, 294 >100 keV channel, and >300 keV channel (Yando et al., 2011) between L = 3.5 and 5.5. This L-295 shell range covers the extent of the Halley ground-based observations and is equivalent to the 296 geomagnetic latitudes 57–65° and the locations of the inner and mid parts of the outer radiation 297 belt. The daily mean count rates of the >300 keV channel were subtracted from those of the 298 >100 keV channel to estimate the electron count rate (ECR100) for precipitating electrons in the 299 100–300 keV energy range that will deposit the majority of their energy into the atmosphere at 300 altitudes of 70–80 km. Similarly, the daily mean count rates of the >100 keV channel were 301 subtracted from those of the >30 keV channel to estimate the count rate (ECR30) of electrons in 302 the 30–100 keV energy range that will produce strongest ionization in the atmosphere at \sim 75– 303

304 110 km.

305 We used NO vertical profiles from the Solar Occultation for Ice Experiment (SOFIE) (Gordley et

al., 2009) on the Aeronomy of Ice in the Mesosphere (AIM) satellite. During the observation

period 2013–mid 2014 SOFIE made 15 sunrise and sunset occultation measurements each day in

308 the SH. NO profiles are retrieved from measurements of the 5.32 μ m absorption band and cover

the altitude range 30–149 km with height resolution of approximately 2 km. The methods

described in Hendrickx et al. (2015), and estimated uncertainties from Gómez-Ramírez et al.

(2013), were used to determine daily mean zonal average NO number density profiles over the

312 geomagnetic latitude range -59° to -65° and geographically poleward of 60° S from processed

313 SOFIE data (version 1.3, available from sofie.gats-inc.com).

314 3.3 Model Simulations

For this study, atmospheric calculations were performed using WACCM-SIC as described in

316 Kovács et al. (2016). The model was used in specified dynamics mode, nudged up to ~0.79 hPa

317 toward the Modern-Era Retrospective Analysis for Research and Application (MERRA)

reanalysis of NASA's Global Modelling and Assimilation Office (Rienecker et al., 2011), and

transitioning linearly above this level to a free running atmosphere. The simulations followed

- the reference chemistry climate model (REF-C1SD) forcing scenario from the SPARC 320
- 321 Chemistry Climate Model Initiative (Eyring et al., 2013). Solar fluxes were from the Naval
- Research Laboratory (NRLSSI v.1) empirical solar model and vary daily, while the parametrized 322
- 323 auroral forcing varied with the daily Kp index. The model was run with enhanced eddy diffusion
- rate (Prandtl number 2) which improves representation of trace species concentrations in the 324
- mesosphere and lower thermosphere (Garcia et al., 2014; Smith, 2012). The global model 325 simulation data were output at 88 pressure levels from the surface to 5.96×10^{-6} hPa (~140 km
- 326
- altitude) and at a horizontal resolution of $1.9^{\circ} \times 2.5^{\circ}$ (latitude \times longitude). Daily mean NO 327 number density profiles for 2013-14 were calculated using WACCM-SIC data at model grid
- 328 points within the geomagnetic latitude range -59° to -65° and geographically poleward of 60° S to
- 329
- match the selected sampling of the SOFIE observations used in this study. 330
- Two WACCM-SIC runs were performed, a 'no MEE' run using the standard parametrization for 331
- auroral electron precipitation in WACCM, and a 'MEE' run in which the auroral mechanism was 332
- supplemented with MEE ionization. The methodology for calculating MEE ionization rates was 333
- similar to that described in Orsolini et al. (2018). This method is based on direct satellite 334
- 335 measurements by the MEPED instrument rather than the proxy-based parametrizations (e.g., van
- de Kamp et al., 2016; Matthes et al., 2017) developed as part of the long-term solar forcing 336
- dataset recommended for the sixth phase of the Coupled Model Intercomparison Project 337
- 338 (CMIP6). However, different from Orsolini et al. (2018), we changed the energy range from 50-2000 keV to 30-1000 keV to be consistent with the CMIP6 recommendation. We also used an 339
- improved method by Fang et al. (2010) to calculate the atmospheric ionization rates. 340
- WACCM-SIC provided the model atmosphere that was used in the ionization rate calculations. 341
- For MEE ionization rate estimation we used electron fluxes observed by the 0° MEPED 342
- telescope. Measurements in the three electron channels >30 keV (0e1 channel), >100 keV (0e2 343
- channel), and >300 keV (0e3 channel) with values $<250 \text{ cm}^{-2} \text{ s}^{-1} \text{ sr}^{-1}$, approaching the minimum 344 detectable flux (~100 el·cm⁻² s⁻¹), were set to zero. Similarly all electron observations around
- 345 the SAA and when the MEPED P7 omni-directional detector reports >36 MeV protons were 346
- excluded. Electron observations from each integral channel were combined from all operational 347
- POES instruments by zonally averaging the measurements in geomagnetic coordinates with 3 h 348
- time resolution and 0.5 L resolution over L = 2.25-9.75, which encompasses the outer radiation 349
- belt. It has previously been shown that power laws are an accurate representation of the EEP 350
- flux spectrum, i.e., through a comparison of high energy resolution DEMETER electron flux 351
- observations with POES MEPED measurements (Whittaker et al., 2013). Hence, we fitted a 352
- power-law spectrum to the three 0° electron telescopes (i.e. 0e1 channel, 0e2 channel, and 0e3 353
- channel) to obtain the energy spectral gradient (k) for the precipitating electrons. 354

The power-law fitted EEP parameters were then used to determine ionization rates assuming the 355 EEP had a differential power-law flux spectrum covering the energy range 30–1000 keV using 356 168 logarithmically spaced bins. The ionization rate calculation was based on a continuously-357 slowing-down approximation and a normalized energy dissipation distribution function for 358 electrons (Rees, 1989). A prior WACCM simulation provided daily zonal mean neutral 359 background data for the ionization rate calculation. The Fang et al. (2010) parameterization of 360 atmospheric ionization by isotropically precipitating monoenergetic (100 eV to 1 MeV) electrons 361 was used. Ionization rates were calculated with 3 h time resolution for each of the L-shell bins 362 (latitudes), after the differential electron fluxes were integrated over pitch angles 0-80° and 363

azimuth angles 0–360° assuming an isotropic angular distribution. The L shell-dependent

ionization rates were then converted to geomagnetic latitude and, with the assumption ofuniformity on magnetic longitude, projected onto the WACCM grid points.

367 **4 Results**

368 4.1 Radiometer NO partial columns

Figure 3a shows a 12 MHz section of the daily mean brightness temperature spectrum for 2 July 369 370 2013 (day 183), centered on the NO emission at 250.796 GHz. A smoothly-varying baseline of ~73 K has been subtracted from the atmospheric spectrum by fitting a 4-term polynomial to the 371 data excluding the region within ± 1.5 MHz of the NO peak. The baseline contains broadband 372 components of the atmospheric spectrum including the water vapor continuum and the wings of 373 pressure-broadened ozone lines. The root-mean-square (RMS) noise of the spectrum is 33 mK. 374 The observed NO emission line is fitted to single Gaussian and single Lorentzian curves, with 375 376 the best fit results shown in Figure 3a. The observed-minus-fit residuals (Figure 3b) for the Gaussian curve (coefficient of determination, $R^2 = 0.87$) are at the RMS noise level whereas for 377 the Lorentzian curve ($R^2 = 0.86$) the residual signal exceeds the noise level in the line wings. 378 The full-width half-maximum of the Gaussian fit is 503(11) kHz. This indicates that thermal, 379 Doppler-broadened NO emission from altitudes above ~ 65 km dominates the observed signal, as 380 was found in measurements from Syowa station, Antarctica during 2012-13 (Isono et al., 2014a, 381 2014b). 382

Gaussian curves were fitted to all observed daily mean spectra where the maximum baseline 383 brightness temperature was below 120 K, corresponding to atmospheric transmittance higher 384 than 0.95. The spectrum baselines were modeled as described above by selecting either a 2-, 3-, 385 or 4-term polynomial or a sine curve to achieve the best fit. Daily mean NO partial column 386 densities above ~65 km were determined from the integrated intensities of the NO emission line 387 brightness temperature using the method described in Isono et al. (2014b). The upper range of 388 the NO partial column is estimated to be 140 km since thermal-broadened emission from NO 389 molecules above this altitude makes a negligibly small contribution to the measured integrated 390 intensities. The integrated intensities were determined from the area under each fitted Gaussian 391 curve, with uncertainties estimated from the 95% confidence bounds, i.e. ± 2 standard deviations 392 393 (σ) , of each fit. Rather than assuming a constant atmospheric temperature for the column density estimation we use the mean daily temperature calculated over altitude range 65–140 km from 394 SD-WACCM data. 395

Figure 4a shows the time series of observed daily mean NO partial columns for altitudes above 396 65 km. Large day-to-day variability in the partial columns can be attributed to short-term NO 397 production and transport. Abrupt increases in mesospheric and lower thermospheric NO 398 coincide with occurrences of moderate geomagnetic storms and high riometer absorption (Figure 399 400 4b), which indicates increased ionisation at ~75–90 km above Halley. The 31-day moving averages smooth the short-term variability of NO abundances and riometer absorption, enabling 401 longer-term seasonal variations during 2013–14 to be seen more clearly. During both years NO 402 shows strong seasonal variability with substantially higher partial columns during the austral 403 winter months May–August (indicated by the blue shaded areas). At this high latitude (76°S), 404 during winter the middle and upper atmosphere remains in near darkness for long periods (Figure 405

406 4c). Very low levels of solar illumination are present in the atmosphere 90 km above Halley

- when solar elevation is $\leq -20^\circ$, which is for a maximum ~14 h at winter solstice. During austral
- summer solar elevation is $\ge 0^\circ$ in the mesosphere during a 70 d period from 1 November to 9
- 409 February (day numbers 305 to 406). Throughout the 2013–14 austral summer, despite increased
- ionisation as indicated by riometer absorption, NO partial columns were low due to photolysis
 losses exceeding production in the mesosphere and lower thermosphere. However, high levels
- of NO occurred during the early part of 2013 when production associated with a series of
- 412 of No occurred during the early part of 2015 when production associated with a series of 413 closely-spaced moderate geomagnetic storms overcomes losses in the sunlit atmosphere. The
- 414 lowest *Dst* index (-132 nT) of 2013–14 occurred on 17 March 2013 (day number 76) during a
- 415 coronal mass ejection-driven storm (Søraas et al., 2017). Higher values of NO partial column are
- 416 observed during the 20 days following this event.
- 417 A particularly striking feature in the observed NO is the difference between the two winter
- periods. Although NO partial columns are similar during late autumn and the start of winter in
- both years, during the first half (May–June) of the 2013 winter the partial columns continue to
- 420 increase and by mid-winter are up to 1.0×10^{15} cm⁻² higher than at the corresponding time in
- 421 2014. During 2013 the partial columns reach maximum values either side of mid-winter whereas
- in 2014 the highest daily mean values are at the start of winter, shortly after the geomagnetic
- storm on 1 May 2014. For both winters, increased NO generally coincides with the occurrences
- 424 of geomagnetic storms and higher riometer absorption.
- 425 The potential roles of atmospheric transport and dynamics in adding complexity to the NO partial column variations, by redistributing NO, are indicated by the Halley MF radar wind speed 426 data shown in Figure 4d-g. Although the zonal and meridional winds show large day-to-day 427 variability, distinctly different patterns of mesospheric wind speed and direction are observed for 428 the two winters. Eastward winds typically develop during late autumn (April) at altitudes of 60-429 90 km above Halley and strengthen as the winter-time polar vortex becomes established. In 430 2013 the strong early winter-time zonal winds weakened around solstice before strengthening 431 432 again in the latter part of the winter, whereas in the 2014 winter initially strong eastward winds above ~70 km decreased after solstice. The strongest eastward winds, and dips in wind speed 433 during both winters, coincided with observed variations in NO partial column. During the 2014 434 winter the strongest eastward winds appeared at 70-80 km at the same time as the second peak in 435 NO and declined in strength as the NO partial column decreased. Throughout the 2013 winter 436 meridional winds were predominantly equatorward (i.e. northward) at altitudes above ~80 km 437 and poleward below ~80 km. The meridional winds showed the opposite behaviour in the first 438 half of the 2014 winter with light poleward winds above ~75 km and strong equatorward winds 439 below ~75 km. Averaged over the altitude range 65–90 km, the 31-day smoothed meridional 440 winds were close to zero throughout both winters. Within the measurement uncertainty there is 441 some indication of light poleward winds in the second half of the 2013 winter whereas during 442 July 2014 the upper mesospheric wind strengthened slightly in a predominantly equatorward 443
- 444 direction.

445 4.2 Comparison of radiometer and SOFIE NO partial columns

446 The daily mean NO partial column densities from the ground-based radiometer measurements at

- Halley are compared in Figure 5 with those calculated by integrating NO number densities
- observed by SOFIE over altitudes 65–140 km within the geomagnetic latitude range -59° to -65°

and geographically poleward of 60°S. Although Figure 5a shows that the general pattern of NO
 variability is similar for the two datasets there are significant differences between the

- 450 variability is similar for the two datasets there are significant differences between the 451 measurements (Figure 5b). The largest differences, with Halley partial columns up to
- 452 1.0×10^{15} cm⁻² higher than the SOFIE values in early 2013 and either side of the 2013 winter
- solstice, coincide with increased NO and geomagnetic storm activity.

The overlapping Halley ground-based radiometer and SOFIE observations in 2013–14 are

- 455 compared further using reduced major axis regression in which the SOFIE and Halley
- 456 observations are switched as regressors. The linear least squares fits are weighted by the inverse
- of the variance (i.e. $1/\sigma^2$) for individual NO partial column measurements. The linear regression analyses with the SOFIE observations as regressors, and the Halley data as regressors, are shown
- 459 in Figures 5c and 5d respectively. Although there is moderate correlation (coefficient of
- determination, $R^2 = 0.86$) between the datasets the regression analyses shows rather poor overall
- 461 agreement. Reduced χ^2 values are 35 and 469 respectively for the fits using SOFIE and Halley
- data as regressors. For the latter regression the best-fit straight line is biased towards the smaller
 SOFIE NO partial columns which have lower uncertainty, i.e. higher weighting. The geometric
- 463 SOFIE NO partial columns which have lower uncertainty, i.e. higher weighting. The geometric 464 mean of the two slopes is 1.49 (i.e. Halley NO = $\sqrt{1.16 \times (1/0.52)} \times$ SOFIE NO). The Halley
- 464 mean of the two slopes is 1.49 (i.e. Halley NO = $\sqrt{1.16 \times (1/0.52)} \times \text{SOFIE NO}$). The Halley 465 NO partial columns are therefore on average 49% higher than those calculated from the SOFIE
- 466 dataset.

467 Day-to-day differences in NO partial column could arise due to the different sampling of the

- atmosphere by the two instruments and underestimation of the measurement and data analysis
- uncertainties. The radiometer makes near-continuous local observations whereas the satellite
- data are from solar occultations within the specified geomagnetic zonal range geographically
- poleward of 60°. Further investigations, ideally with a longer time series of observations than is
- used in this study, are needed to establish whether NO production in the polar mesosphere and
- lower thermosphere is enhanced above the Halley region of Antarctica.
- The SOFIE daily mean NO number density time series in Figure 6 shows short-term NO
 production by auroral electron and MEE ionization associated with geomagnetic storms. The
 NO variability is seen at all altitudes above ~65 km but is largest in the lower thermosphere and
- upper mesosphere. NO number density reaches higher values during the 2013 winter with the
- 477 appendices of the second reaches angle in values during the 2015 whiter with the 478 2×10^8 cm⁻³ isopleth descending to ~82 km, 10 km lower than for the following winter. The
- 1×10^8 cm⁻³ isopleth descends to at least 65 km in 2013, ~15 km lower than in 2014.
- 480 4.3 WACCM-SIC model simulation results
- Figure 7 shows the daily mean NO number densities from the WACCM-SIC model simulations
- 482 for the MEE scenario, calculated for the geomagnetic latitude range -59° to -65° and
- 483 geographically poleward of 60°S during 2013–14. Compared to the SOFIE observations (Figure
- 6) the model simulation shows less short-term NO variability in the mesosphere and lower
- thermosphere, but the observed longer-term seasonal variability is reproduced with NO number
- density increasing at altitudes below 100 km in winter-time. Differences between the MEE and
- 487 no MEE model runs are shown in Figure 7b where ΔNO , the absolute difference in NO number
- density, is NO number density (MEE) NO number density (no MEE). Mesospheric NO
- number density is generally higher in the 'MEE' run, by up to 3.5×10^7 cm⁻³ compared to the 'no

490 MEE' run at altitudes in the range ~55–90 km where MEE ionization by 30–1000 keV electrons

is expected to drive NO production. For the 'MEE' run the MEE ionization rates in the model

decrease at altitudes above ~90 km, with lower direct MEE NO production to augment the

493 auroral, Kp-driven NO production that dominates in the lower thermosphere. Thus the electron

494 forcing in the two model runs is essentially identical above ~90 km.

The daily mean and 31-day smoothed POES-derived count rates for 30–100 keV electrons

496 (ECR30) and 100–300 keV electrons (ECR100) are shown in Figure 8. These data further

highlight the large differences in MEE forcing during the two years, in particular during the

winter periods with much higher MEE fluxes observed in 2013. The NO partial columns and

number density from the observations and, to a certain extent in the model simulations, increasewhen sustained high MEE count rates occur.

500 when sustained high when count rates occur.

501 The differences between the two WACCM-SIC runs are very similar to those reported for

502 WACCM simulations over decadal timescales (Andersson et al., 2018) in which 30–1000 keV

EEP was introduced using an Ap index-driven model (van de Kamp, 2016), rather than the

electron observation-based estimates of MEE ionization used in this study. For the polar SH

(geographic latitude range 60° – 90° S) the Andersson et al. (2018) model calculations show the

⁵⁰⁶ largest relative increases in NO_x during the summer, exceeding 200% at altitudes \sim 75–90 km. ⁵⁰⁷ During mid-winter the Ap index-driven MEE ionization increased average mesospheric NO_x by

508 over 20%.

509 4.4 Comparison of observed NO number density with model simulations

The SOFIE observations and WACCM-SIC simulation results are compared in Figure 9, which 510 shows NO number density at 10 km intervals from 60 km to 110 km after applying a 31-day 511 moving average to each of the three datasets. Smoothing reveals the general long-term and 512 seasonal differences between the data-sets by removing the large day-to-day differences between 513 the two model runs arising from short-term NO variability. The largest differences between the 514 smoothed 'MEE' and 'no MEE' model data are at 60 km, 70 km, and 80 km during the 2013 515 winter with the smoothed 'MEE' NO number density up to 2.7×10^7 cm⁻³ higher. At higher 516 altitudes the results for the two model runs are very similar due to the electron forcing in the two 517 model runs being essentially identical above ~90 km. The best agreement between the SOFIE 518 observations and 'MEE' model data is at 80 km, although the model doesn't reproduce observed 519 NO number density increases during the first half of each winter. The modeled NO number 520 density reaches a maximum close to mid-winter in 2013, higher than is reached in 2014. The 521 observed winter-time NO at 80 km and below is almost always higher than in the 'MEE' model 522 run. At 60 km the observed NO number density is up to 0.8×10^8 cm⁻³ higher than the model in 523 both years at mid-winter. However, at altitudes in the range 90–110 km this discrepancy 524 switches round with modeled NO number density generally higher than is observed, and up to 525 1.9×10^8 cm⁻³ higher than the observations close to mid-winter. This suggests that the auroral 526 forcing in WACCM-SIC could be too high, or that the rate of downward transport of NO 527 produced in the lower thermosphere is too low in the model. 528

529 **5 Discussion**

530 Our WACCM-SIC calculations combine, for the first time in a 3-D global atmospheric model,

the most detailed representation of *D*-region ion-neutral chemistry with MEE ionization rates

estimated from electron flux observations. By including these additional components in the

simulations, modeled NO number density in the mesosphere is increased, and there is closer
 agreement with observations for the upper mesosphere (altitudes ~70–90 km). However, there

- remain significant quantitative differences between modeled NO distributions and those
- observed during 2013–14, in particular for the lower mesosphere (~50–70 km) and lower
- thermosphere (\geq 90 km). Various possible factors are discussed which could produce these
- discrepancies between the observations and model results. These factors include the derivation
- and accuracy of the used MEE ionization rates, the characterization of NO downward transport
- 540 in the model, and uncertainties in lower thermospheric NO production mechanisms.

541 The MEE ionization rates used in the simulations are based on a model of 30–1000 keV

energetic electron precipitation constructed using observations from the POES MEPED satellite

during 2013–14. POES observations in and around the SAA are seriously affected by proton

contamination (Rodger et al., 2013), that cannot be readily removed or corrected, and these

regional data are not included in the zonally-averaged model. The SAA corresponds to the drift

loss cone region where electron fluxes into the atmosphere are expected to be considerably
 higher. This could result in an underestimation of MEE ionization rates, perhaps by a factor 2–3,

547 higher. This could result in an underestimation of MEE ionization rates, perhaps by a factor

in the simulations over a large region of the SH mesosphere.

549 The Prandtl number (Pr) is the ratio of momentum diffusivity to thermal diffusivity, which

affects atmospheric transport and NO distributions. The eddy diffusion coefficient (Kzz) in

551 WACCM is a product of the gravity wave drag parameterization (Garcia et al., 2007) and is

- 552 proportional to the gravity wave drag and inversely proportional to the Prandtl number. Our
- 553 WACCM-SIC model simulations were run with enhanced Kzz, produced by setting Pr to 2. A
- control run with Pr = 4 reduced mesospheric NO VMR throughout the two-year period 2013–14,
- as expected due to weaker downwards transport using the standard eddy diffusion rate, but also
- slightly decreased thermospheric NO. Setting the Prandtl number below the recommended value
- of 2 increased mesospheric NO in our WACCM-SIC simulations, producing better agreement
- between the modeled and observed data for both winters and also increased thermospheric NO abundance.
- 5(0 Hondrighty at al. (2018) compared 7 years (2007, 2015) f COETE NO. 1

Hendrickx et al. (2018) compared 7 years (2007–2015) of SOFIE NO observations in the SH
 with simulations performed by the standard version of WACCM incorporating specified

with simulations performed by the standard version of WACCM incorporating specified dynamics. SD-WACCM includes a Kp-driven auroral electron parametrization but lacks the

dynamics. SD-WACCM includes a Kp-driven auroral electron parametrization but lacks the specific *D*-region ion-neutral chemistry and MEE precipitation that are in WACCM-SIC.

specific *D*-region ion-neutral chemistry and MEE precipitation that are in WACCM-SIC.
 However, above the mesopause MEE precipitation has a negligible effect and, similar to our

- 565 findings using WACCM-SIC, their modelled NO concentrations in the lower thermosphere are
- almost a factor 2 higher than observations. Hendrickx et al. (2018) suggest the differences
- 567 between their observations and model simulations could be attributed, at least in part, to
- ⁵⁶⁸ uncertainties and challenges in determining reaction rates and branching ratios in several NO
- reactions involving excited state ($N(^2D)$) and ground state ($N(^4S)$) nitrogen. In the standard
- parameterization in WACCM (Jackman et al., 2005; Marsh et al., 2007) an ion pair produces
- 571 1.25 N atoms with branching ratios of 0.55 $N(^4S)$ and 0.70 $N(^2D)$. However, as pointed out by

- 572 Hendrickx et al. (2018), other recommended values of the $N(^{2}D)$ branching ratio range from 0.50
- to 0.60 (Solomon et al., 1982; Yonkers et al., 2013). Our simulations use a different
- 574 parameterization from standard WACCM, with the detailed and verified mechanisms
- 575 implemented in WACCM-SIC (Kovács et al., 2016) based on comprehensive analysis and
- revision of the *D*-region chemistry in the SIC model using updated rate coefficients (Pavlov,
- 577 2014; Verronen et al., 2016). However, the significant discrepancies found between modelled
- and observed NO using either standard WACCM or WACCM-SIC indicate that further studies
- 579 may be needed to verify the reaction parameterizations for the critical pathways that impact
- 580 mesospheric and lower thermospheric NO production and loss.

581 6 Conclusions

- NO in the mesosphere and lower thermosphere above Antarctica has been studied during a
- two-year period, 2013–14, close to solar maximum. Contrasting levels of geomagnetic storm
- activity occurred during the two austral winters, with nine moderate geomagnetic storms
- (minimum *Dst* index \leq -50 nT) during May–August in 2013 compared to just one storm at the
- start and one close to the end of the corresponding period in 2014. The geomagnetic storms
- caused energetic electron precipitation into the polar middle atmosphere, driving NO production
- in the mesosphere and lower thermosphere. Energetic electron measurements by the 0° electron telescope on the POES SEM-2 MEPED instrument over L = 3.5-5.5 (geomagnetic latitudes
- $\sim 57^{\circ}-65^{\circ}$), corrected for proton contamination, show much higher count rates for 30–300 keV
- 591 electrons during the 2013 winter compared to 2014.
- 592 Ground-based measurements from Halley, Antarctica (L = 4.7, geomagnetic latitude -62°) of
- 593 daily mean NO partial column densities at altitudes above ~65 km using passive millimeter-wave
- radiometry show significant differences (up to 1.0×10^{15} cm⁻² higher for the Halley
- 595 measurements) compared to satellite observations over 65–140 km by the SOFIE instrument.
- The differences in partial column could be due to higher NO abundance in the region of the
- 597 Antarctic mesosphere and lower thermosphere above Halley and underestimated measurement
- ⁵⁹⁸ uncertainties. Short-term increases in mesospheric and lower thermospheric NO, observed by
- both instruments, coincided with moderate geomagnetic storm occurrences, increases in
 ionization at ~75–90 km observed by the Halley riometer, and increased MEPED electron count
- rates. During the 2013 winter, NO number density was up to 3×10^8 cm⁻³ higher than in the
- 602 corresponding period of 2014, suggesting greater MEE production directly in the mesosphere
- and lower thermosphere in 2013. However, radar measurements show distinctly different
- ⁶⁰⁴ behavior of the zonal and meridional mesospheric wind components above Halley, in particular
- after mid-winter in the two years. This contrast in winter-time horizontal winds indicates
- differing localized dynamical conditions that, if present over a more widespread region of the SH
- 607 polar middle atmosphere, could also potentially affect NO distributions.
- 608 WACCM-SIC simulations show that including full *D*-region ion-neutral chemistry and estimates
- 609 of MEE ionization in the 3-D model increases calculated NO number density in the high-latitude
- 610 SH winter mesosphere by up to 3.5×10^7 cm⁻³. However, the model still significantly
- underestimates NO in the winter-time mesosphere, whereas lower thermospheric levels are much
- higher than observed. This underestimation of mesospheric NO abundance could be resolved by
- 613 increasing MEE ionization rates in the model to boost direct NO production at 55–90 km or more
- 614 efficient transport of NO from the lower thermosphere to the lower mesosphere. Our results

- 615 provide further evidence in support of other recent studies that identify the need to further refine
- our understanding of MEE processes in the polar middle atmosphere. The impact of
- uncertainties in branching and ionization rates and vertical transport parametrizations on
- modeled NO distributions needs to be further investigated and further observational data for NO_x
- and HO_x species are needed to verify and develop the models.

620 Acknowledgments

- This work was supported in part by the UK Natural Environment Research Council (Grant
- References NE/J022187/1 and NE/J02077X/1) and the New Zealand Marsden Fund. A. S. was
- supported by the Academy of Finland (Project nos. 258165 and 265005). The work of P. T.
- Verronen and M. E. Andersson was supported by the Academy of Finland (Project no. 276926 -
- 625 SECTIC: Sun-Earth Connection Through Ion Chemistry). L. M. was supported by the Swedish
- Research Council under contract 621-2012-1648. D. R. M. was supported in part by NASA
- 627 Living With a Star grant NNX14AH54G. The National Center for Atmospheric Research
- 628 (NCAR) is sponsored by the U.S. National Science Foundation (NSF). We thank Christoph
- 629 Larndorfer, William Clark, David Maxfield, Jonas Ekstedt, and Paul Breen for supporting the
- observations at Halley, Antarctica. We thank Anne K. Smith for providing the SD-WACCM
- data and Martyn Chipperfield for helpful discussions. Aaron Hendry is acknowledged for
- 632 providing computer code (GEO2CGM) to facilitate the conversion from spherical geographic
- coordinates to spherical corrected geomagnetic coordinates. Data from the WACCM-SIC runs
- are archived at the University of Leeds. Observational datasets from Halley, Antarctica are
- available from the UK Polar Data Centre (https://www.bas.ac.uk/data/uk-pdc/).

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Figure 1. Time series of (a) 3-hourly Kp index and (b) hourly *Dst* index for 2013–14. In (a) the green vertical bars are for Kp \leq 3, the yellow bars are 3 < Kp \leq 4, and the red bars are Kp > 4. The brown vertical lines in (b) indicate the occurrences of moderate geomagnetic storms and the blue triangles show the times of maximum proton flux for the two largest SPE's. The shaded light blue areas indicate the months May–August. Note that the 3-hourly Kp index and hourly *Dst* index, and the 31-day smoothed data, are plotted on different scales shown by the left- and right-hand axes respectively.

Figure 2. Map of the southern hemisphere and Antarctica poleward of geographic latitude 60°S showing the location of Halley station (75°37'S, 26°15'W). The three red solid and dashed lines show the geomagnetic latitudes $\Lambda = -59^\circ$, $\Lambda = -62^\circ$, and $\Lambda = -65^\circ$, calculated for 1 January 2013 and an altitude of 90 km using the IGRF-12 internal field model (Thébault et al., 2015). Only the area between the dashed line ($\Lambda = -59^\circ$) and the dash-dotted line ($\Lambda = -65^\circ$) is considered in this study.

Figure 3. (a) Halley radiometer daily mean NO observation for 2 July 2013 (day 183), Gaussian
and Lorentzian line-fits, (b) observed minus Gaussian line-fit residual, and (c) observed minus
Lorentzian line-fit residual.

Figure 4. Overview of observations from Halley station, Antarctica in 2013–14:- (a) radiometer
daily mean and 31-day smoothed NO partial column density for altitudes above ~65 km, (b)
daily mean and 31-day smoothed 30 MHz widebeam riometer absorption, (c) diurnal variation in
solar elevation (SE) angle calculated for an altitude of 90 km above Halley, where time is UTC,
(d) MF radar zonal winds (+ve = eastwards), (e) 31-day smoothed MF radar zonal winds

- averaged over 65-90 km, (f) MF radar meridional winds (+ve = northwards), and (g) 31-day 981
- 982 smoothed MF radar meridional winds averaged over 65–90 km. The shaded light blue areas in
- (a), (b), (e), and (g) indicate the months May–August. The brown vertical lines in (b) indicate 983
- the occurrences of moderate geomagnetic storms and the blue triangles show the times of 984 maximum proton flux for the two largest SPE's during 2013–14. For the MF radar data in (e) 985
- and (g) the shaded areas are the 95% confidence intervals (±2 standard deviations) of the 31-day 986
- smoothed winds. Note that the riometer daily mean absorption and the 31-day smoothed data in 987
- panel (b) are plotted on different scales shown by the left- and right-hand axes respectively. 988

Figure 5. (a) Time series of daily mean Halley radiometer and SOFIE NO partial column density 989 over the altitude range 65-140 km, (b) differences between the observed partial column 990 densities, and (c, d) linear least squares regression analyses for the observed partial column 991 densities with SOFIE and Halley data respectively as regressors and the red lines showing the 992

993 best-fit lines. Error bars are $\pm 1\sigma$.

Figure 6. Time series of SOFIE daily mean NO number density during 2013–14. The dataset is 994 for satellite observations within the geomagnetic latitude range -59° to -65° and geographically 995 poleward of 60°S. The dotted, solid, and dot-dashed lines show isopleths at 5×10^7 cm⁻³, 996 1×10^8 cm⁻³, and 2×10^8 cm⁻³ of the 11-day smoothed NO number density. The white panels 997 998 indicate gaps in data coverage.

- 999 **Figure 7**. Time series of daily mean NO number density profiles during 2013–14, for the
- geomagnetic latitude range -59° to -65° and geographically poleward of 60°S, from WACCM-1000
- SIC simulations (a) including MEE ionization and (b) differences between the two model runs. 1001 In (a) the dotted, solid, and dot-dashed lines show isopleths at 5×10^7 cm⁻³, 1×10^8 cm⁻³, and 1002
- 2×10^8 cm⁻³ of the 11-day smoothed NO number density. 1003

Figure 8. Daily mean and 31-day smoothed POES count rates during 2013–14 for (a) 30– 1004 1005 100 keV electrons (ECR30) and (b) 100-300 keV electrons (ECR100). The POES data are between L = 3.5 and 5.5, equivalent to geomagnetic latitudes 57°–65°. The shaded light blue 1006 areas indicate the months May–August. Note that the daily mean and 31-day smoothed electron 1007 1008 count rates are plotted on different scales, shown by the left- and right-hand axes respectively.

1009 Figure 9. Comparison of 31-day smoothed SOFIE NO number density observations and the corresponding model data from WACCM-SIC runs with, and without, MEE ionization. The data 1010 are at discrete 10 km levels descending from 110 km to 60 km. Observation and model data are 1011 restricted to the geomagnetic latitude range -59° to -65° and geographically poleward of 60°S. 1012 1013 Error bars on the SOFIE data are $\pm 1\sigma$. The shaded light blue panels indicate the months Mav-1014 August.

Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7.



Figure 8.



Figure 9.

