- 1 Constraining N₂O emissions since 1940 using firn air isotope measurements in
- 2 both hemispheres
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18 Abstract

 N_2O is currently the 3rd most important anthropogenic greenhouse gas in terms of radiative 19 20 forcing and its atmospheric mole fraction is rising steadily. To quantify the growth rate and its causes over the past decades, we performed a multi-site reconstruction of the atmospheric 21 22 N₂O mole fraction and isotopic composition using new and previously published firn air data 23 collected from Greenland and Antarctica in combination with a firn diffusion and 24 densification model. The multi-site reconstruction showed that while the global mean N₂O mole fraction increased from (290 \pm 1) nmol mol⁻¹ in 1940 to (322 \pm 1) nmol mol⁻¹ in 2008 the 25 isotopic composition of atmospheric N₂O decreased by (-2.2 ± 0.2) % for $\delta^{15}N^{av}$, (-1.0 ± 0.3) 26 % for δ^{18} O, (-1.3±0.6) % for δ^{15} N^{α}, and (-2.8±0.6) % for δ^{15} N^{β} over the same period. The 27 28 detailed temporal evolution of the mole fraction and isotopic composition derived from the 29 firn air model was then used in a two-box atmospheric model (comprising a stratospheric and

30 a tropospheric box) to infer changes in the isotopic source signature over time. The precise 31 value of the source strength depends on the choice of the N₂O lifetime, which we choose to be 123_{10}^{+29} a. The average isotopic composition over the investigated period is $\delta^{15}N^{av}$ = 32 (-7.6 ± 0.8) ‰ (vs. air-N₂) δ^{18} O = (32.2\pm0.2) ‰ (vs. VSMOW) for δ^{18} O, δ^{15} N^{α} = (-3.0±1.9) 33 % and $\delta^{15}N^{\beta} = (-11.7 \pm 2.3) \%$. $\delta^{15}N^{av}$ and $\delta^{15}N^{\beta}$ show some temporal variability while for 34 35 the other signatures the error bars of the reconstruction are too large to retrieve reliable temporal changes. Possible processes that may explain trends in ¹⁵N are discussed. The ¹⁵N 36 site-preference (= $\delta^{15}N^{\alpha} - \delta^{15}N^{\beta}$) provides evidence for a shift in emissions from 37 denitrification to nitrification, although the uncertainty envelopes are large. 38

39 **1** Introduction

The rise of nitrous oxide (N₂O) since pre-industrial times contributes significantly to radiative forcing (Forster et al., 2007). Over the past four decades, the N₂O mole fraction has increased by 0.25 % per year, reaching 324 nmol mol⁻¹ in 2011 (Ciais et al., 2013). Therefore, the understanding of the biogeochemical cycle of N₂O is important for a reliable assessment of future climate change. In addition, the destruction of N₂O in the stratosphere provides an important source of nitrogen oxides (NO_x), which contribute to stratospheric ozone depletion (Ravishankara et al., 2009; Crutzen, 1979; McElroy et al., 1971).

47 Natural sources of N₂O are microbial processes in soils and oceans, which produce N₂O during nitrification and denitrification (Bouwman et al., 2013; Loescher et al., 2012; Santoro 48 49 et al., 2011; Galloway et al., 2004; Pérez et al., 2001; Yung and Miller, 1997; Kim and Craig, 50 1993). The increase of N₂O since pre-industrial times (hereafter referred to as 51 "anthropogenic" increase) has been attributed largely to increased microbial production, 52 resulting from the increased use of nitrogen fertilizers in agriculture. Industry (especially 53 nylon production) and fossil fuel combustion present a smaller contribution to the anthropogenic source (Davidson, 2009; Kroeze et al., 1999; Mosier et al., 1998). N₂O is 54 55 primarily destroyed in the stratosphere via UV photolysis (90 %) and reactions with excited 56 oxygen atoms (10 %) (Minschwaner et al., 1993), with a minor N₂O fraction removed by 57 surface sinks (Syakila, 2010).

Estimates of the total N₂O source strength from various bottom-up and top-down studies suggest a mean value of roughly 17 Tg a^{-1} N equivalents at present. However, the range in both approaches is large, especially for bottom-up estimates, which range between 8.5 and 27.7 Tg a^{-1} N, whereas top-down estimates range between 15.8 and 18.4 Tg a^{-1} N (Potter et 62 al., 2011 and references therein). Besides the total source strength, the contributions of 63 individual source processes are also poorly constrained. Due to the long steady-state lifetime 64 of N₂O in the atmosphere (123_{-19}^{+29} a; SPARC Lifetimes Report 2013), temporal and spatial 65 gradients are small, making it difficult to resolve localised sources.

66 Measurements of the isotopic composition of N₂O may help to constrain the atmospheric N₂O budget. The N₂O molecule is linear (NNO) and the two N atoms are chemically 67 distinguishable as a consequence they tend to attain different isotopic compositions. Beyond 68 oxygen (δ^{18} O, δ^{17} O) and average δ^{15} N^{av} ("bulk") signatures, N₂O also displays site specific 69 ¹⁵N isotopic information. Site preference ($\delta^{15}N^{sp}$) is defined as the difference in $\delta^{15}N^{av}$ 70 between the central (2, μ or α) and terminal position (1, τ or β) of N atoms in N₂O (Kaiser, 71 2002; Brenninkmeijer and Röckmann, 2000; Yoshida and Toyoda, 1999), i.e. $\delta^{15}N^{sp} = \delta^{15}N^{\alpha}$ – 72 $\delta^{15}N^{\beta}$. For consistency with many recent publications in the field, we here adopt the 73 74 nomenclature from Yoshida and Toyoda (1999), α and β , for the two positions.

75 The different sources and sinks of N₂O are associated with characteristic fractionation 76 processes leading to different isotope ratios. For example, microbial sources emit N₂O that is depleted in ¹⁵N and ¹⁸O relative to the tropospheric background. N₂O that returns from the 77 78 stratosphere after partial photochemical removal is enriched in both heavy isotopes (Yoshida 79 and Toyoda, 2000; Rahn and Wahlen, 1997; Yung and Miller, 1997; Kim & Craig, 1993). Stratospheric N₂O also has a high ¹⁵N site-preference compared to tropospheric N₂O. The 80 81 observed enrichment is caused by kinetic isotope fractionation in the stratospheric sink 82 reactions (Kaiser et al., 2006; 2002; Park et al., 2004; Röckmann et al., 2001; Yoshida and 83 Toyoda, 2000; Rahn et al., 1998).

The multi-isotope signature of N_2O adds useful constraints on its budget. In particular, when the isotopic composition of tropospheric N_2O is combined with the fractionation during its removal in the stratosphere, the isotopic composition of the global average source can be determined (Ishijima et al., 2007; Bernard et al., 2006; Röckmann et al., 2003; Kim and Craig, 1993).

The temporal variations of the N_2O isotopic composition are difficult to quantify on a short timescale because of its long residence time in the atmosphere. Longer time scales can be reconstructed by using air trapped in Arctic and Antarctic firn and ice which provides a natural archive of past atmospheric composition. The firn phase is the intermediate stage between snow and glacial ice, which constitutes the upper 40-120 m of the accumulation zone

94 of ice sheets. Within the firn, air exchanges relatively freely in the upper layers and with the 95 overlying atmosphere (convective zone). With increasing depth the air pores shrink in size due to firn compaction, and air mixes primarily via slow diffusion in the diffusive zone. At 96 97 densities larger than ≈ 815 kg m⁻³, air is permanently trapped in closed bubbles in the ice and 98 totally isolated from the atmosphere. The precise age range of air that can be retrieved from 99 polar firn between the surface and bubble close-off depends on site specific characteristics 100 like temperature, accumulation rate and porosity and typically ranges from several decades to 101 120 years.

102 For N₂O, a number of studies have reported isotope measurements from different Arctic and 103 Antarctic firn drilling sites showing a steady decrease of the heavy isotope content of N₂O 104 over the past decades (Park et al., 2012; Ishijima et al., 2007; Bernard et al., 2006; Röckmann 105 et al., 2003; Sowers et al., 2002). A more recent study by Park et al. (2012) attempted to 106 reconstruct the long-term trends in N₂O isotopic compositions and its seasonal cycles to 107 further distinguish between the influence of the stratospheric sink and the oceanic source at 108 Cape Grim, Tasmania, demonstrating that isotope measurements can help in the attribution 109 and quantification of surface sources in general.

110 Taking into account the long atmospheric lifetime of N₂O and the fact that both hemispheres 111 are well mixed on annual timescales, it is reasonable to assume that the results from these 112 studies are representative for the global scale. However care needs to be taken because small differences in the diffusivity profiles of the firn column lead to large effect on the isotope 113 114 signature (Buizert et al., 2012). Interestingly, for atmospheric methane (CH₄), another important greenhouse gas, a recent multi-site analysis of its carbon isotopic composition 115 116 showed large differences among reconstructions from different sites (Sapart et al., 2013). In 117 particular, firn fractionation effects related to diffusion and gravitational separation and their 118 implementation in models (Buizert et al., 2012) have large effects on the reconstructed 119 signals. Small differences in the diffusivity profiles of the firn column lead to large effects on 120 the isotope signatures. Therefore, more robust results may be obtained by combining isotope 121 information from a number of different sites in a multi-site reconstruction, including a critical 122 evaluation of diffusivity profiles.

Here we combine new N_2O isotope measurements from the NEEM site in Greenland with previously published firn air N_2O isotope records from 4 different sites from Greenland and Antarctica to reconstruct records of the N_2O isotopic composition over the last 70 years. We use the multi-gas firn transport model developed by the Laboratoire de Glaciologie et Géophysique de l'Environnement and Grenoble Image Parole Signal Automatique (LGGE-GIPSA) to obtain an atmospheric scenario that is constrained by and consistent with all individual sites (Allin et al., 2015; Witrant et al., 2012; Wang et al., 2012; Rommelaere et al., 130 1997). We then use an isotope mass balance model to infer the changes in the isotopic signature of the N₂O source over time to investigate possible changes in the source mix.

132 2 Materials and Methods

133 **2.1 Firn air Sampling**

134 New firn air samples added in this study to the total dataset were collected in 2008 and 2009 during the firn campaign (Buizert et al., 2011) as part of the North Eemian Ice Drilling 135 programme (NEEM) in Greenland (77.45° N 51.06° W). These data are combined with 136 137 existing firn air data from four other sites. Information on the locations is provided in Table 1. The firn air collection procedure is described in detail by Schwander et al. (1993). Here a 138 brief description is presented. Essentially a borehole is drilled in the firn to a certain depth and 139 then the firn air sampling device is inserted into the borehole. The device consists of a 140 141 bladder, a purge line and a sample line. When the sampling device reaches the desired depth 142 the bladder is inflated to seal the firn hole and isolate the air below the bladder from the 143 overlying atmosphere, and air is pumped out from the pore space below the bladder. 144 Continuous online CO₂ concentration measurements are performed to verify that no contamination with contemporary air occurs during the extraction procedure. After the 145 contaminating air has been pumped away, firn air is collected in stainless steel, glass or 146 147 aluminium containers.

148 2.2 N₂O isotope analysis

The firn air samples from NEEM are analyzed for N_2O isotopocules at the Institute for Marine and Atmospheric research Utrecht (IMAU). The N_2O mole fraction and isotopic composition are measured using continuous flow isotope ratio mass spectrometry (IRMS). The method is described in detail by Röckmann et al. (2003b). Here only a brief summary is given. The firn air sample (333 mL) is introduced into the analytical system at a flow rate of 50 mL/min for 400 s. After CO₂ is removed chemically over Ascarite, N₂O and other condensable substances are cryogenically preconcentrated. After cryo-focusing the sample the 156 remaining traces of CO₂ and other contaminants are removed on a capillary GC column 157 (PoraPlot Q, 0.32 mm i.d., 25 m). The column is separated into a pre-column and an 158 analytical column. This set-up eliminates interferences from other atmospheric compounds 159 that have much longer retention times. Finally the sample is transferred to the IRMS via an 160 open split interface. For the new NEEM samples reported here, each firn air sample has been 161 measured five times. Before and after each sample we measured five aliquots of air from a reference cylinder with known isotopic composition and mole fraction for calibration 162 163 purposes.

 $\delta^{15}N^{av}$ values are reported with respect to Air-N₂ while $\delta^{18}O$ refers to Vienna Standard Mean 164 165 Ocean Water (VSMOW). As laboratory reference gas we used an atmospheric air sample with an N₂O mole fraction of 318 nmol mol⁻¹ and δ values of (6.4±0.2) ‰ for δ^{15} N^{av} vs. Air-N₂, 166 (44.9±0.4) % for δ^{18} O vs. VSMOW. The intramolecular δ^{15} N^{av} values of the air standard are 167 $\delta^{15}N^{\alpha} = (15.4 \pm 1.2)$ ‰ and $\delta^{15}N^{\beta} = (-2.7 \pm 1.2)$ ‰. The calibration of the intramolecular 168 distribution follows Toyoda and Yoshida (1999). Typically the 1σ standard deviations of 169 replicate sample measurements are 0.1 % for $\delta^{15}N^{av}$, 0.2 % for $\delta^{18}O$ and 0.3 % for $\delta^{15}N^{\alpha}$ and 170 $\delta^{15} N^{\beta}$. 171

172 **2.3 Modelling trace gas transport in firn**

In firn air, the interstitial gas is not yet isolated in closed-off bubbles, so diffusion processes and gravitational separation alter mole fractions and isotope ratios over time. Thus, firn air measurements cannot be used directly to derive the atmospheric history of trace gas signatures. Over time, atmospheric compositional changes are propagated downwards into the firn based on the diffusivity of the atmospheric constituent in question. Firn air diffusion models take these effects into account and thereby allow reconstruction of changes in the atmospheric composition from the firn profile.

In this study we use the LGGE-GIPSA firn air transport model to reconstruct the temporal
evolution of N₂O mole fraction and isotopic composition from the measured firn profiles
(Allin et al., 2015; Witrant et al., 2012; Wang et al., 2012; Rommelaere et al., 1997).

183 In the "forward version" of LGGE-GIPSA, a physical transport model uses a historic 184 evolution of atmospheric N_2O mole fractions to calculate the vertical profiles of mole 185 fractions in firm. For the isotopocules, further simulations are performed separately to 186 calculate their respective vertical profiles. Important parameters needed to constrain the 187 model are the site temperature, accumulation rate, depth of the convective layer and close-off depth, together with profiles of firn density and effective diffusivity. The latter parameter is 188 189 determined as a function of depth for each firn-drilling site by modelling the mole fractions in 190 firn for trace gases with well known atmospheric histories (Buizert et al., 2012; Witrant et al., 191 2012; Rommelaere et al., 1997; Trudinger et al., 1997). A multi-gas constrained inverse method (Witrant et al., 2012) is used to calculate the effective diffusivity of each site for each 192 193 specific gas. It is noteworthy that diffusivity is not constrained equally well at all sites 194 because different sets of constraints (e.g. number of available reference gases) are used at 195 different sites and because of different depth resolutions.

A Green-function approach, as presented by Rommelaere et al. (1997) and used for halocarbon trend reconstruction by Martinerie et al. (2009), with an extension for isotopic ratios and revised to take into account the scarcity of the measurements (Allin et al., 2015; Witrant and Martinerie, 2013; Wang et al., 2012) is used to assign a mean age and age distribution to a certain depth.

- 201 Due to the long N₂O residence time in the atmosphere, the global variability of the isotopic 202 composition of N₂O is very small and no significant variations between individual background locations have been detected so far (Kaiser et al., 2003). In particular, the isotope 203 204 ratio difference between northern and southern hemisphere tropospheric air is expected to be only -0.06 % (based on an interhemispheric mole fraction gradient of 1.2 nmol mol⁻¹ [Hirsch 205 206 et al. 2006] and isotope ratio difference of -15 ‰ between average source and average 207 tropospheric isotopic delta value). These differences are within the uncertainties of the firn air 208 measurements used here and therefore the data from the northern and southern hemisphere are 209 combined into a single dataset without including an interhemispheric gradient.
- With the multi-site reconstruction method, we used the measurements from six firn air drillings at five sites (NEEM-09, NEEM-EU-08, BKN-03, NGRIP-01_{Bernard}, DC-99, DML-98) to constrain our model and determine a set of atmospheric reconstructions that fits all sites. Data from Ishijima et al. (2007) and Sowers et al. (2002) [NGRIP-01_{Ishijima} and SP-01, SP-95 respectively] were not included in our multi-site reconstruction because no data for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ were published for those sites. These datasets were used for independent validation of $\delta^{15}N^{av}$ and $\delta^{18}O$.
- To quantify the isotope fractionation due to diffusion and gravitational settling within the firn, a forward firn transport model simulation was carried out with a realistic N_2O mole fraction

- scenario (based on the Law Dome record, MacFarling Meure et al., 2006), but with a constant isotopic N₂O history. This allows determining the role of transport isotope fractionation occurring in the firn, in the absence of isotopic changes in the atmosphere. The results are used to subtract the firn fractionation effects from the measured signals, which can then be used to assess the atmospheric history. Compared to the signal, the effect of firn fractionation is minor for $\delta^{15}N^{av}$, but important for $\delta^{18}O$ especially at the lower accumulation rates in the Southern Hemisphere (see Appendix A).
- The deepest firn data from each site provide constraints furthest back in time and the oldest air samples that are included in the inversion are from the DML-98 and DC-99, which extend the reconstruction of atmospheric N_2O back to the early 20th century (Röckmann et al., 2003). At the same time, the correction for isotopic fractionation in firn is most uncertain for the deepest samples, where strong differences between individual firn air models have been reported (Buizert et al., 2012).

232 **2.4 Scaling of different data sets**

At present, no international reference materials for the isotopic composition of N₂O exist. 233 Kaiser et al. (2003) and Toyoda et al. (1999) linked the isotopic composition of N₂O in 234 tropospheric air to the international isotopes scales for nitrogen isotopes (Air-N₂) and oxygen 235 isotopes (either VSMOW or Air-O₂). Our measurements are linked to a standard gas cylinder 236 of tropospheric air with known N₂O mole fraction and isotopic composition based on the 237 scale of Kaiser et al. (2003) for $\delta^{15}N^{av}$ and $\delta^{18}O$ values and Yoshida and Toyoda (1999) for 238 position dependent ¹⁵N values. However, the reference air cylinder used for the calibration 239 240 was exhausted and had to be replaced three times over the years in which the different 241 measurement that we combine in this study were performed. Although the cylinders were carefully compared, the long-time consistency of the isotope scale could not be guaranteed 242 243 because long-time isotope standards are not available. In fact, analysis of the data from the 244 convective zone for the different sites, show small but significant differences from the 245 temporal trends that are well established from previously published data from the German Antarctic Georg von Neumayer station for 1990 to 2002 (Röckmann and Levin; 2005). The 246 linear trends reported in that paper are (-0.040±0.003) ‰ a⁻¹ for δ^{15} N^{av}, (0.014±0.016) ‰ a⁻¹ 247 for $\delta^{15}N^{\alpha}$, (-0.064±0.016) ‰ a⁻¹ for $\delta^{15}N^{\beta}$ and (-0.021±0.003) ‰ a⁻¹ for $\delta^{18}O$. Since they were 248 derived from direct air samples (unaffected by firn fractionation), these trends can be used as 249

250 a reference to re-scale the different firn air results from different dates. To do so, data from the diffusive zone ($\rho < 815$ kg m⁻³) for each individual site were scaled to one reference site, 251 DC-99, taking into account the temporal differences in sampling and the model-assigned 252 253 mean age of the firn air samples (see below). DC-99 was chosen as reference site because it 254 has most measurements in the diffusive zone. Also, the precision of these measurements was 255 high because high volume cylinders were available from which many measurements could be 256 performed and averaged. To test the sensitivity to the choice of reference site, we repeated the re-scaling using NEEM-09 as reference, which generated almost identical results within 257 258 uncertainty bars (Appendix C).

The average difference between the samples from the diffusive zone at a given site and the interpolated DC-99 results was compared to the expected temporal trend between the sampling date of each station and DC-99, using the temporal trends established by Röckmann and Levin (2005), as shown in the equations below. The effect of this scaling is that the temporal trend in the past decade is effectively forced to follow the atmospheric measurements at Neumayer station (Röckmann and Levin, 2005).

After re-scaling the firn isotopic data we detected some individual data points that clearly deviated from the general trends. These were considered outliers, because they exceeded the 2σ error, and were removed from the dataset. All of these values are site-specific ¹⁵N values, specifically the following, were excluded: NEEM-EU-08 hole depth -4.9 m, -34.72 m, -61.95 m and -74.5 m, and NEEM-09 hole depth 1.0 m, 0.2 m and -69.4 m.

The mole fraction data that can be obtained from the NEEM air isotope measurements were substituted with more precise measurements of N_2O mole fraction by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) the Institute of Environmental Physics, University of Heidelberg (IUP), the Centre of Ice and Climate, University of Copenhagen (CIC) and National Oceanic and Atmospheric Administration (NOAA). In this way we combine all available N_2O mole fraction data narrow the uncertainty envelope but do not affect the trend.

²⁷⁷The mole fraction data were scaled to the most recent international scale, NOAA-2006A from278the CSIRO scale or the NOAA-2000 scale. Conversion of the NOAA-2000 data to the279NOAA-2006A scale is done using a conversion factor available by National Oceanic and280Atmospheric281(http://www.esrl.noaa.gov/gmd/ccl/scales/N2O scale.html). Converting from the CSIRO to

the NOAA-2006A scale, though, requires the reference cylinder details, which were not available. Instead we used a trend scenario, based on the CSIRO atmospheric scale combined with Law Dome data and assuming a constant interhemispheric gradient. This trend scenario was then compared with the data provided on NOAA-2006A scale, and a polynomial fit was generated, which was then used to convert the data to the NOAA-2006A scale. All results presented in the next section are based on the scaling procedure and removal of the outliers as described above (Appendix B).

289 2.5 Global N₂O (isotope) budget calculations

The tropospheric budget is controlled by N_2O emissions from natural and anthropogenic sources at the surface and by the exchange between troposphere and stratosphere. A simple two-box model is used to quantitatively understand the emissions and the budget changes of N_2O . The model consists of a tropospheric N_2O reservoir (index T) into which N_2O is emitted from natural (E_{nat}) and anthropogenic (E_{anth}) sources. N_2O is then transported to the stratosphere (index S) where part of it is destroyed by photochemical reactions (L), and the remainder returns from the stratosphere to the troposphere (F_{exch}).

297 The change in the tropospheric N_2O reservoir is given by the following mass balance 298 equations (Allin et al, 2015):

299
$$n_{\rm T} \frac{d\chi_{\rm T}}{dt} = E_{\rm nat} + E_{\rm anth} - F_{\rm exch}(\chi_{\rm T} - \chi_{\rm S})$$
 (1)

$$300 \quad n_{\rm S} \frac{d\chi_{\rm S}}{dt} = F_{\rm exch}(\chi_{\rm T} - \chi_{\rm S}) - L \tag{2}$$

where *n* is the amount of air and χ_s and χ_T are the mole fractions of N₂O in the stratosphere and troposphere respectively. Annual fluxes between the two reservoirs, F_{exch}, are calculated based on previous estimates (Appenzeller et al., 1996; Holton et al., 1990) and given in Table 3. The loss due to stratospheric sink is determined by:

$$305 \qquad L = \frac{n_{T}\chi_{T} + n_{S}\chi_{S}}{\tau} \tag{3}$$

306 where τ is the atmospheric lifetime of 123_{-19}^{+29} a.

307 The isotopic budgets are calculated by simply multiplying the reservoir sizes with the 308 corresponding δ values of the different flux terms:

309
$$n_{\rm T} \frac{d\chi_{\rm T}\delta_{\rm T}}{dt} = E_{\rm nat}\delta_{\rm nat} + E_{\rm anth}\delta_{\rm anth} + F_{\rm exch}(\chi_{\rm S}\delta_{\rm S} - \chi_{\rm T}\delta_{\rm T})$$
 (4)

310
$$n_{\rm S} \frac{d\chi_{\rm S} \delta_{\rm S}}{dt} = F_{\rm exch} (\chi_{\rm T} \delta_{\rm T} - \chi_{\rm S} \delta_{\rm S}) - L \delta_{\rm L}$$
(5)

Separating the l.h.s in two terms and substituting eq. 1 and 2 into eq. 4 and 5 yields the finalisotope equations:

313
$$n_{\rm T} \frac{d\delta_{\rm T}}{dt} = \frac{E_{\rm nat}}{\chi_{\rm T}} (\delta_{\rm nat} - \delta_{\rm T}) + \frac{E_{\rm anth}}{\chi_{\rm T}} (\delta_{\rm anth} - \delta_{\rm T}) + \frac{F_{\rm exch}\chi_{\rm S}}{\chi_{\rm T}} (\delta_{\rm S} - \delta_{\rm T})$$
(6)

314
$$n_{\rm S} \frac{d\delta_{\rm S}}{dt} = \frac{F_{\rm exch}\chi_{\rm T}}{\chi_{\rm S}} (\delta_{\rm T} - \delta_{\rm S}) - \frac{L}{\chi_{\rm S}} \varepsilon_{\rm L}$$
(7)

where $\delta_{\rm T}$ is either $\delta^{15} {\rm N}^{\rm av}$, $\delta^{18} {\rm O}$, $\delta^{15} {\rm N}^{\alpha}$, $\delta^{15} {\rm N}^{\beta}$ from the multi-site reconstruction as shown below. $\delta_{\rm nat}$ and $\delta_{\rm anth}$ is the isotopic composition of the natural and anthropogenic N₂O source, respectively (our target quantity). $\varepsilon_{\rm L}$ is the apparent Rayleigh fractionation factor associated with stratospheric destruction.

319 $\delta_{\rm S}$ is also not known, but can be calculated using the analogue from Röckmann et al. (2003) 320 by employing the observed apparent Rayleigh fractionation in the stratosphere ($\varepsilon_{\rm app}$) (Table 321 3). Based on this, the relative isotope ratio difference between the stratosphere and the 322 troposphere can be calculated by:

323
$$\delta_{\rm S} = \left[(\delta_{\rm T} + 1) \left(\frac{\chi_{\rm S}}{\chi_{\rm T}} \right)^{\varepsilon_{\rm app}} - 1 \right] \tag{8}$$

Here, we used the average ε_{app} of all lowermost stratospheric measurements from Kaiser et al. (2006) (Table 3). Note that slightly different fractionations ε_{app} have been used in previous studies by Rahn and Wahlen (2000), Röckmann et al. (2001) and Park et al. (2012; 2004). The sensitivity of the results to these differences will be examined below.

Furthermore we assume that the N₂O lifetime and ε_{app} remained constant from pre-industrial time to 2008, thus the annual sink strength can be scaled down from its current value at χ_T = 322 nmol mol⁻¹ to the pre-industrial level of $\chi_{T,pi}$ =270 nmol mol⁻¹ and the relative enrichment of stratospheric N₂O relative to tropospheric N₂O described by Eq. 8 remains constant over time. The effect of changing the N₂O lifetime is also examined below.

Our model approach assumes that during the pre-industrial period only natural emissions occurred without any anthropogenic input. After the industrialization (\approx 1750) any increase in the emissions is considered to be due to anthropogenic input while natural emissions remain constant. Hence, the temporal change in isotopic composition is formally due to the increase in one single "anthropogenic" source only, which may in reality also contain a naturalcomponent.

339 **2.6** Uncertainty estimation using random scenarios

The precision of the calculated N₂O emissions (E_{nat} , E_{anth}) depends primarily on the precision of the atmospheric reconstruction of the N₂O mole fraction (χ_T). However, taking random histories within the uncertainty envelope provided by the firn air reconstruction is not adequate to quantify the uncertainty of the atmospheric N₂O reconstruction: the year-to-year variability of N₂O is constrained by the N₂O lifetime in the troposphere. Possible realistic N₂O scenarios are scenarios that are within the confidence intervals provided by the atmospheric reconstructions, and that have realistic year-to-year variability.

Mathematically, this can be represented by an uncertainty variance covariance matrix **B**, where the diagonal elements (variances) are the yearly uncertainties on the atmospheric N₂O mole fractions, and the off-diagonals are the covariances of the uncertainties of different years. The covariance between the uncertainty on the reconstruction in one year *i* and the uncertainty in another year *j* is defined as:

352
$$cov(i,j)=r_{i,j}\sigma_i\sigma_j$$
 (9)

353
$$r_{i,j} = f(|i-j|)$$
 (10)

The correlation $(r_{i,j})$ is maximum between two consecutive years, and decreases as the time difference increases.

We generated an ensemble of 50 random realistic N_2O scenarios within the uncertainty envelope of the firn atmospheric N_2O reconstruction constrained by the covariance matrix **B**. For each of these atmospheric N_2O scenarios, we calculated the corresponding N_2O emission time series. The range of emissions from these scenarios then provides a realistic estimate for the uncertainty in N_2O emissions.

We carried out the same analysis for the different N₂O isotopocules: for each isotopocule (δ value), we generated a covariance matrix \mathbf{B}^{δ} , constrained by the uncertainty ranges provided by the atmospheric reconstructions and the correlation coefficients defined in Eq.9 and Eq.10 to generate a set of 50 random scenarios within the uncertainty envelopes. For each of these random scenarios, we calculated the corresponding source signature scenario and the range inthe results provides an uncertainty estimate of the isotopic source signatures.

367 3 Results

368 **3.1 Mean age**

369 The mean age of N₂O in air sampled from different depths in the firn for all datasets that are 370 used in this study is shown in Fig. 1. The strong change in the mean age gradient that is 371 clearly visible in each profile reflects the transition between the diffusive and bubble close-off 372 zones, which occurs at a specific depth and mean age for each site (marked with x on Fig. 1). 373 Fig. 1 also shows that for each site the few samples that are collected within the bubble close-374 off zone provide the constraints for most of the reconstructed record (for instance, at BKN-03, 375 50 m depth is the beginning of the bubble close-off zone). In addition to the mean age, the 376 width of the age spectrum also increases with depth. Therefore, the temporal resolution of 377 signals that can be reconstructed from the firn air measurements reduces with depth and approaches the one of ice core samples towards the bottom of the bubble close-off zone. 378

The Greenland sites (NH) have similar meteorological and glaciological conditions (Table 1), thus the differences between the mean age profiles in Fig. 1 are small. The Antarctic sites (SH) show clear differences because the meteorological and glaciological variables differ strongly from site to site. As a result the firn-ice transition is at a different depth for each location (e.g., the firn-ice transition zone for DML-98 is located at about 73.5 m compared to about 99.5 m at DC-99).

385 **3.2 Experimental results and multi-site reconstruction**

Mole fraction and isotopic composition of N_2O in firn air are presented versus depth of the firn air sampling in the middle panels of Fig. 2 for the different sites. The mole fraction decreases with depth in qualitative agreement with the known increase of N_2O in the atmosphere over time. In contrast, all isotope deltas slowly increase with depth in the upper firn and show stronger heavy isotope enrichment in the close-off zone, both indicating heavy isotope depletion in atmospheric N_2O with time.

392 The atmospheric history that has been reconstructed from these firn datasets using the multi-

393 site inversion (using the data from NEEM-09, NEEM-EU-08, NGRIP-01_{Bernard}, BKN-03, DC-

394 99, DML-98) as described in section 2.4 is shown in the left column of Fig. 2. The solid line

395 shows the scenario that leads to the best fit with the firn data as shown in the middle panel, 396 and the dashed lines show the upper and lower range of possible scenarios that would still 397 produce an acceptable fit to the data within the uncertainty bars. Color-coded symbols show 398 data plotted at their respective mean age (as derived from the firn air model). When the best-399 fit scenario is used as input for the forward firn air model for each individual site, the model 400 produces the vertical profiles that are shown as coloured lines together with the data in the 401 middle panels. For the sites that were included in the multi-site reconstruction, the firm profiles based on the best-fit scenarios generally match the experimental data points well, 402 403 which is expected after a successful inversion procedure and with consistent data sets. The 404 right panels in Fig. 2 show the differences between these model results and the data. For the 405 data that were used in the multi-site inversion the model-data differences are generally very 406 small, although individual firn drilling sites in some cases show small systematic deviations, 407 in particular in the close-off zone. This means that when inversions would have been 408 performed on individual sites, the optimal reconstructions would be slightly different. Hence, 409 the advantage of the multi-site reconstruction is that the reconstructed scenario is constrained by all sites and all sampling depths. Despite the small differences between individual sites, the 410 left panels show that all data fall within the uncertainty bars of the reconstructed scenario of 411 412 the inversion.

413 From 1940 to 2008 the total changes of the δ values of atmospheric N₂O are (-2.2±0.2) ‰ for $\delta^{15}N^{av}$, (-1.0±0.3) ‰ for $\delta^{18}O$, (-1.3±0.6) ‰ for $\delta^{15}N^{\alpha}$ and (-2.8±0.6) ‰ for $\delta^{15}N^{\beta}$ 414 respectively (Fig. 2, left panels). The average linearized trends are (-0.032 ± 0.004) ‰ a⁻¹ for 415 $\delta^{15}N^{av}$, (-0.014±0.008) ‰ a⁻¹ for $\delta^{18}O$, (-0.019±0.015) ‰ a⁻¹ for $\delta^{15}N^{\alpha}$ and (-0.041±0.020) 416 $\% a^{-1}$ for $\delta^{15} N^{\beta}$. These overall trends are slightly lower compared to previous studies that 417 418 used only the data at individual sites (Ishijima et al., 2007; Bernard et al., 2006; Röckmann et 419 al., 2003; Sowers et al., 2002) and other studies that used data from the same period, which were not used in the present study (Park et al., 2012). However, the differences are well 420 within the combined uncertainties. We note that comparisons of average linear trends can be 421 flawed when the firn air records have different length and the temporal profiles do not change 422 linearly (see below). Trends for $\delta^{15}N^{\alpha}$ are smaller in magnitude than for $\delta^{15}N^{\beta}$, while results 423 from Bernard et al. (2006) showed stronger changes for $\delta^{15}N^{\alpha}$ than for $\delta^{15}N^{\beta}$. However, in that 424 study the trends were largely determined from measurements on young ice core samples with 425 426 comparatively higher measurement errors and larger scatter.

427 Data from two sites were not included in the multi-site inversion and are used as independent 428 validation of the reconstructed scenarios. The data points from Ishijima et al. (2007) (NGRIP-01_{Ishijima}, yellow) are within the range of scenarios reconstructed by the inverse model and 429 thus independently validate our results. The $\delta^{15} N^{av}$ and $\delta^{18} O$ data from Sowers et al. (2002) 430 431 (SP-01 in light blue and SP-95 in blue) however, agree only for the more recent atmospheric history (Fig. 2, left panels). For mean ages before 1990 most of the points are outside the 432 uncertainty envelopes of the multi-site reconstruction. Inter-laboratory calibration differences 433 434 might be a possible explanation for the discrepancy, but the differences are not a systematic 435 shift, and they are larger than offsets among laboratories that were established in the past 436 (Sapart et al., 2011; Kaiser et al., 2003). In fact, the data reported by Sowers et al. (2002) 437 were actually measured in two different laboratories with good agreement. So measurement 438 flaws can be excluded. A possible origin of the difference could be based on the 439 reconstruction model. Because the uncertainties on the South Pole data are large, compared to 440 the other sites, the multi-site homogenization is more uncertain and less efficient (see Appendix A and C, Fig. A1 and C1-C3). Sampling uncertainty should also be taken into 441 consideration since when pumping firn air and filling the sampling flasks you could encounter 442 uncertainties (contamination, possible leak, fractionation, incomplete flask flushing etc). At 443 444 present though the discrepancy cannot be resolved.

To evaluate our scaling approach we repeated the multi-site reconstruction using the original non re-scaled data and re-scaled them to NEEM-09 instead of DC-99 (see Appendix C). This yielded similar results (within uncertainties) to the original reconstruction, thus results do not depend on the choice of the site used for re-scaling. Without re-scaling, the overall change of N₂O mole fraction and isotopic composition remained the same, but an additional decadal variability was introduced for $\delta^{15}N^{av}$, $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$. In addition to that, the uncertainty

451 envelopes doubled because of the scale inconsistencies. All scaling approaches produce 452 results that are consistent with our preferred scaling to DC-99 within the uncertainty 453 envelopes. We conclude that scaling removed the discrepancies that would cause larger 454 uncertainties if the original data were used instead, but the re-scaling does not introduce 455 artificial signals (see Appendix C).

The regularization of the inversion results using a rugosity factor introduces a free parameter, which is chosen to eliminate overfitting of experimental uncertainties and which controls the smoothness of the reconstruction. The value of this parameter is set based on a robust

459 generalized cross validation criterion, ensuring that the resolution obtained from the inverse 460 model is similar to the experimental data while taking into account the scarcity of the measurements (Witrant and Martinerie, 2013). A sensitivity experiment where the weight of 461 462 the regularization term was increased by a factor 10 led to nearly linear tropospheric histories 463 within the uncertainty envelopes presented in Appendix C (Fig. C2). This combined with the 464 fact that straight lines can be drawn within the uncertainty envelopes of the reconstructed scenarios and the sensitivity tests (see Appendix C) indicates that the isotopic trends are not 465 466 significantly different from straight lines within the current uncertainties.

467 **3.3 Reconstruction of the N₂O emission history**

Fig. 3 shows the temporal evolution of the global N_2O mole fraction as inferred from the atmospheric reconstruction constrained only by the most precise NEEM data in the top panel, and in the bottom panel the emission strength in Tg a⁻¹ N calculated with the mass balance model (Section 2.5). The solid black line denotes the best estimate scenario, which is used as input in the mass balance model. The magenta lines show the ensemble of random scenarios generated to quantify the uncertainty of the emissions (see Section 2.6).

The increase in the N₂O mole fraction of (32 ± 1) nmol mol⁻¹ over the reconstruction period 474 can be explained in the mass balance model by a (4.4 ± 1.7) Tg a⁻¹ N increase in the emissions 475 from 1940 to 2008. The emissions increased with an increasing trend until 1975, then the 476 477 annual increase continued, but at a slower rate up to 1990, and from then on the annual 478 emissions have stayed approximately constant or even decreased slightly. The minor increase 479 in the N₂O mole fraction towards the end of the time series is likely not significant and does 480 influence our reconstructions. The corresponding changes in the mole fraction are difficult to 481 discern due to the long atmospheric lifetime of N₂O. On average, the annual growth rate from 1995 to 2008 period is 0.7 nmol $mol^{-1} a^{-1}$, corresponding to average annual emissions of 3.5 482 $Tg a^{-1} N.$ 483

484 **3.4** The temporal evolution of the N₂O isotope signatures

The results from the isotope budget calculations are presented in Fig. 4. The left panels show the atmospheric trends. The solid black lines represent the best-fit scenarios while the dashed black lines represent the upper and lower uncertainty envelope of the firn air reconstructions. The magenta lines represent 50 scenarios generated randomly within the reconstructed uncertainty range, as described in section 2.6. The middle panels show the temporal changes

- 490 in the isotope signatures of the total N_2O source, with their accompanied uncertainties, as 491 calculated from the atmospheric mass balance model (section 2.5). The total source is split 492 into an assumed constant "natural" and an increasing "anthropogenic" component and the 493 right panels show the isotopic evolution of the "anthropogenic" component.
- Results show that the average δ^{15} N^{av} of the total N₂O source, over the reconstruction period, is 494 495 (-7.6 ± 0.6) % where the uncertainty is calculated using the 1 σ uncertainty from the scenarios 496 with respect to the mean value (magenta lines). There is no statistically significant long-term 497 trend, but a temporal variability is observed on the decadal scale that might mask this trend. δ^{15} N^{av} first decreased from (-6.5±0.6) ‰ in 1940 to (-8.5±0.6) ‰ in 1965, then slowly 498 499 increased again to (-6.6 ± 0.6) ‰ in 1985, followed by another decrease to (-8.5 ± 0.6) ‰ in 500 2008. These oscillations originate from the slightly curved trends in the isotopic reconstructions for δ^{15} N^{av} in Fig. 4 (left panels). 501
- When the source is split into a constant natural and a varying anthropogenic component, the variability is projected on the anthropogenic part and the temporal variations increase accordingly. However, also the uncertainties increase substantially, because the differences between the individual scenarios are attributed to only a small fraction of the total source.
- The δ^{15} N^{av} signature of the anthropogenic source has an average value of (-18.2±2.6) ‰. It 506 507 initially increases (the small initial decrease is not significant) from (-21.5 ± 2.6) ‰ in 1940 to 508 (-8.6 ± 2.6) ‰ in 1990, when it starts to slowly decrease reaching (-15.4 ± 2.6) ‰ in 2008. 509 During the early part of the reconstruction period before 1970, when the "anthropogenic" 510 contribution was only a small fraction of the total source, the uncertainty ranges of the source signatures are larger. Therefore, the uncertainties for the early part were excluded when 511 512 calculating the 1σ uncertainties over the entire period from the generated scenarios. This 513 applies to all anthropogenic isotope signatures.
- 514 The budget calculations suggest an overall trend towards more enriched anthropogenic 515 emissions, but the uncertainties are large. Mathematically, this trend arises from the fact that 516 the isotope reconstructions yield relatively linear temporal isotope trends, whereas the source 517 strength increases in a strongly non-linear fashion (Fig. 4). In the beginning of the record a 518 small increase in the source strength needs to produce a certain absolute isotope shift, whereas a smaller increase in the source strength is needed during later years to cause a similar isotope 519 shift. This can only be solved mathematically by a lower $\delta^{15}N^{av}$ value for the small 520 "anthropogenic" emissions in the early part of the firn record. A constant $\delta^{15} N^{av}$ source 521

- signature would result in a small temporal change in $\delta^{15}N^{av}$ of atmospheric N₂O in the beginning of the record and increasing isotope trends with increasing emissions, similar to the exponential curves that were fitted to the firm air data in Röckmann et al. (2003).
- The δ^{18} O of the total source varies within (27.2±2.6) % over the entire period. δ^{18} O does not 525 show significant decadal scale oscillations because the reconstructed scenario for δ^{18} O is even 526 more linear than the $\delta^{15}N^{av}$ scenario. For this reason, as explained above, in the best fit 527 scenario the δ^{18} O of the anthropogenic source for the initial 30 years has a more depleted 528 529 value starting with (7.7±2.6) ‰ in year 1940, reaching (31.1±2.6) ‰ in year 1975 and 530 remaining around this value until 2008 (Fig. 4). However, the relatively larger uncertainty envelopes for the atmospheric history of δ^{18} O actually allow scenarios with smaller δ^{18} O 531 changes in the beginning of the record and larger changes in the later period, which means 532 that the reconstruction does not exclude a constant value for the anthropogenic δ^{18} O source 533 signature. The available dataset thus does not allow quantifying a long-term trend in δ^{18} O. 534
- For the position dependent ¹⁵N signatures of the total source no significant long-term trends were detected. For $\delta^{15}N^{\alpha}$ no decadal scale variability is observed, whereas for $\delta^{15}N^{\beta}$ a temporal variability is observed similar to the $\delta^{15}N^{av}$. The uncertainty ranges for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ are about a factor 2 greater than for $\delta^{15}N^{av}$, which is due to the larger analytical error that leads to higher uncertainties in the scenario reconstructions. $\delta^{15}N^{\alpha}$ varies in the range (- 3.0 ± 1.9) ‰, $\delta^{15}N^{\beta}$ in the range (-11.7±2.3) ‰.
- The temporal evolution of $\delta^{15}N^{\alpha}$ of the anthropogenic source looks similar to that of $\delta^{18}O$, but with even larger variations and uncertainties with a total average of (-8.1 ± 1.7) ‰. $\delta^{15}N^{\alpha}$ increased from (-18.2 ± 1.7) ‰ in 1940 to an average of (-5.4 ± 1.7) ‰ in 1975 and retained this value until 2008. In contrast, $\delta^{15}N^{\beta}$ is similar to that of $\delta^{15}N^{av}$ with a total anthropogenic source average of (-26.1 ± 8.4) . $\delta^{15}N^{\beta}$ initially decreases from (-19.1 ± 8.4) ‰ to (-42.0 ± 8.4) ‰ in 1955 only to increase again to (-10.6 ± 8.4) ‰ in year 1990 and then decrease again to (-26.0 ± 8.4) ‰ in 2008.

548 **4** Discussion

549 The N_2O mole fraction atmospheric history from our multi-site reconstruction is in agreement 550 with recent work from Meinshausen et al. (2016) who combined all available published N_2O 551 data (atmospheric, firn, ice) in order to reconstruct a historical atmospheric record of the past 2000 years. It differs slightly from the one determined by Battle et al. (1996) and to smallerextent with Machida et al. (1995).

Battle et al. (1996) collected firn air data and Machida et al. (1995) used ice data. Both studies 554 555 used samples from a single Antarctic site. One could argue that the difference is due to an interhemispheric difference, but it is too large to be explained by this alone. In the past, N₂O 556 557 mole fraction measurements have been reported on different calibration scales, which is likely to explain part of the differences between individual studies. Furthermore, differences in the 558 559 firn air model and possible differences between sites may contribute. In our case we used 560 measurements from 5 sites to constrain our model while Battle et al. (1996) and Machida et 561 al. (1995) used only one site. In addition, the atmospheric histories of up to 9 known gases (depending on site, Witrant et al. 2012) were used to constrain diffusivity in our model while 562 Battle et al. (1996) only used two gases." 563

564 From the combination of the firn air reconstruction with a simple two-box model we conclude that N₂O emissions increased from (11.9 \pm 1.7) Tg a⁻¹ N in 1940 to (16.4 \pm 1.7) Tg a⁻¹ N in 565 566 2008. This agrees, within uncertainties, with previous firn reconstruction studies from 567 Ishijima et al. (2007) and Park et al. (2012) and bottom-up approaches using emission databases (Syakila and Kroeze, 2013; Kroeze et al., 1999). A more recent study by Thompson 568 569 et al. (2014b) performed inversions of atmospheric measurements for 2006 to 2008 with multiple models and reported emissions of 16.1-18.7 Tg a⁻¹ N for 2008, which is also in 570 571 agreement with our findings.

To investigate the effect the N₂O lifetime on the N₂O isotopic signatures (Prather et al. (2015) 572 we performed a sensitivity study where we linearly changed the N₂O lifetime from 123 years 573 574 pre-industrially (\approx 1750) to 119 years in modern times (2008). The results are shown in 575 Appendix D, where the effect on the emission strength and isotopic composition is discussed in detail. Results from this sensitivity study showed that the effect of a decreasing lifetime 576 577 gives higher N₂O emissions for year 2008 while keeping the same pre-industrial value, confirming the sensitivity to the lifetime in line with Prather et al. (2015). This change in 578 579 lifetime in the model leads to changes in the isotope signatures of the order of (2.0 ± 1.0) %. 580 The lifetime effect is most pronounced for the earliest part of the record (<1970) where the 581 reconstruction uncertainties are larger than this systematic uncertainty.

582 We furthermore investigated the sensitivity to the value of F_{exch} (stratosphere – troposphere 583 flux) between a low and high value of 0.16 and 0.28 Tmol s⁻¹, respectively following Appenzeller et al. (1996) and Holton et al. (1990) with the default value being 0.22 Tmol s⁻¹. As shown in Appendix D, the isotope values are not very sensitive to the changes in F_{exch} , the results are well within the uncertainty envelopes.

587 The increase in N₂O emissions over the past decades resulted in an overall decrease of all 588 isotopic signatures of atmospheric N₂O with time. The isotopic signature of the total source of 589 N₂O (Fig. 4, middle panels) is strongly depleted in all heavy isotopes compared to 590 tropospheric N₂O (Table 3), which is due to the strong enrichment associated with the 591 removal in the stratosphere. In Table 3 the isotopic composition for the pre-industrial period (≈ 1750) ($\delta_{nat ni}$) is compared with the derived anthropogenic source signature derived from 592 593 our multi-site reconstruction (δ_{anth} , averaged from 1940 to 2008). The results show that the 594 anthropogenic source is more depleted in heavy isotopes than the natural one for all 595 signatures, confirming results from studies prior to firn air measurements (Rahn and Wahlen, 596 2000), and from studies that used forward firn air modelling on measurements from individual 597 sites (Park et al., 2012; Ishijima et al., 2007; Röckmann et al., 2003). It is important to 598 remember that we assume the natural sources to be constant, but the method itself does not 599 provide evidence for this.

Anthropogenic N₂O emissions are dominated by agricultural soil (70 %) with smaller contributions from automobiles, coal combustion, biomass burning and industry. Oceanic emissions were previously assumed to be only natural. However, the latest IPCC Assessment Report (Ciais et al., 2013) for the first time separated oceanic emissions into a natural and an anthropogenic component, e.g. due to atmospheric N deposition to rivers (Syakila and Kroeze, 2011; Duce et al., 2008; Kroeze et al., 2005). The oceanic fraction of the anthropogenic source was estimated as 1 Tg a⁻¹ N.

N₂O emitted from agricultural soils and biomass burning is more depleted in δ^{15} N^{av} and δ^{18} O 607 608 than the tropospheric background (Park et al., 2011; Goldberg et al., 2010; Ostrom et al., 609 2010; Tilsner et al., 2003; Perez et al., 2001; 2000) while N₂O emitted from other minor 610 sources, such as automobiles, coal combustion and industry, has values closer to tropospheric 611 N₂O values (Syakila and Kroeze, 2011; Toyoda et al., 2008; Ogawa and Yoshida, 2005a; 612 2005b). An increase of strongly depleted agricultural emissions in the first part of our 613 reconstruction, followed by a decreasing relative contribution from agriculture and increasing 614 contributions from more enriched sources like industry, automobiles and coal combustion, 615 could qualitatively explain the reconstructed changes of isotope signatures of both the total

source and the anthropogenic component. The global N_2O budget study from Syakila and Kroeze (2011) indicates that agricultural emissions were 78 % of the total during the 1940-1980 period with little input from industry, vehicle exhaust and coal combustion. After 1980 the relative share of agricultural emissions dropped to 64 %, while the other sources increased, supporting our suggestion.

621 According to FAO statistics (http://www.fao.org/faostat/en/#data/GY/visualize), emissions from synthetic nitrogenous fertilizers increased between 1961 and 1985, then stayed relatively 622 623 constant or even decreased until 2000, and increased again after 2000. The reasons of the 624 decrease between 1985 and 2000 are a shift towards organic soil cultivation in combination 625 with more efficient agricultural methods and fertilizer use. This variation in fertilizer use 626 qualitatively matches with the temporal evolutions of our reconstructed source signatures, but 627 the trends in the reconstructions are likely too large to be explained by this source change 628 only.

Although the decadal variability for $\delta^{15}N^{av}$ and $\delta^{15}N^{\beta}$ appears statistically significant with 629 630 respect to the choice of scenarios constructed within the error bars of the firn air 631 reconstruction, additional systematic uncertainties in this reconstruction could potentially produce such trends artificially from small undulations on the scenarios, since the emissions 632 633 are related to the derivative of the trend. As it is possible to draw straight lines within 634 uncertainty envelopes of the scenarios, the decadal variability may not be robust. An increase 635 of the regularization term by 10 confirms that the generated scenarios are straight lines well 636 withing the uncertainty envelopes, thus the decadal variability could be a artifact of the model 637 (see Appendix C).

Additional evidence for potential changes in the N₂O source composition between the preindustrial and present atmosphere may be derived from the position-dependent ¹⁵N signatures, quantified by the ¹⁵N site preference. Table 3 shows that the difference in the $\delta^{15}N^{av}$ signature between the pre-industrial and the anthropogenic source derived from our reconstruction is primarily due to a change at position $\delta^{15}N^{\beta}$, whereas $\delta^{15}N^{\alpha}$ remains relatively constant. This is reflected by a larger difference in $\delta^{15}N^{sp}$ between natural and anthropogenic emissions, which could indicate a temporal change in production processes.

Sutka et al. (2006) suggested that there may be two distinct classes of N₂O sources with different $\delta^{15}N^{sp}$. N₂O produced during nitrification and fungal denitrification had a high $\delta^{15}N^{sp}$ of (33±5) ‰ and N₂O from denitrification and nitrifier denitrification had a low $\delta^{15}N^{sp}$ of 648 (0±5) ‰. Park et al., (2012) used these two endmembers to calculate a change in the relative 649 fractions of these source classes over time based on their firn air data. Although this approach 650 is strongly simplified and several other sources and factors may contribute (Toyoda et al., 651 2015), we use the results from our box model calculations (Table 3) in a similar way to 652 estimate the fraction of the two source categories according to the following simple mass 653 balance calculation:

654
$$F_{\text{high}} = \frac{\delta_{15}^{15} N_{\text{meas}}^{\text{sp}} - \delta_{15}^{15} N_{\text{low}}^{\text{sp}}}{\delta_{5}^{15} N_{\text{high}}^{\text{sp}} - \delta_{5}^{15} N_{\text{low}}^{\text{sp}}}$$
 (11)

This returns a fractional contribution of the $\delta^{15} N_{high}^{sp}$ component of (19±4) % to the total preindustrial emissions and (35±11) % to the total present source. The errors were derived by propagating the errors of the $\delta^{15} N^{sp}$ endmembers and $\delta^{15} N_{meas}^{sp}$ within the ranges stated above. We note that the errors associated with the precise isotopic composition of the endmembers are correlated if the values of $\delta^{15} N^{sp}$ for the two endmembers remain relatively constant in time. Therefore, the change in the relative fraction of the two categories is likely better constrained than the absolute values.

Splitting the total present emission strength into a natural (pre-industrial, 11.0 Tg a⁻¹ N) and anthropogenic (5.4 Tg a⁻¹ N) component, we derive a fraction of the δ^{15} N^{sp}_{high} component (which includes nitrification) of (54±26) % for the "anthropogenic" emissions. This is another piece of evidence for agricultural sources being the main contributor to the N₂O increase, because nitrification-dominated agricultural emissions can be associated with the δ^{15} N^{sp}_{high} component.

668 The temporal changes of the derived fraction of nitrification are in good qualitative agreement 669 with the results from Park et al. (2012), who reported a change of (13 ± 5) % from 1750 to 670 (23±13) % today. However, the absolute numbers derived from our study are higher than the 671 results from Park et al. (2012). The difference is due to the fact that different apparent isotope fractionations during stratospheric removal (ε_{app}) are used in the mass balance model (Table 672 3; eq. 7,8). In our study we used the averaged lowermost stratospheric apparent isotope 673 674 fractionations from Kaiser et al. (2006), which we consider more representative than the numbers used by Park et al. (2012). Using different values for ε_{app} causes a shift in the 675 isotopic source signatures from the mass balance model. The choice of this value thus adds a 676

677 systematic source of uncertainty to the absolute value of the δ^{15} N^{sp}_{high} fractions reported above 678 (*F*_{high}).

Nevertheless, this systematic uncertainty should not alter the overall *change* in F_{high} from preindustrial to modern times and the results from our multi-site reconstruction of the isotopic composition of N₂O thus confirm the suggestion by Park et al. (2012) that the relative importance of the high-SP component (presumably nitrification) has increased with increasing mole fraction since pre-industrial times.

684 **5** Conclusions

685 The temporal evolution of the total N₂O emission fluxes and the source isotopic composition 686 have been estimated in a top-down approach using a multi-site reconstruction of N_2O mole 687 fraction and isotopic composition from 6 firn air samplings at 5 different Arctic and Antarctic 688 locations in a two-box model. The results from a mass balance model constrain the source strength and suggest a total increase in N₂O emissions of (4.5 \pm 1.7) Tg a⁻¹ N between the 1940 689 and 2008 due to anthropogenic processes. This agrees with previous top-down estimates, but 690 691 deviates from bottom-up model estimates, which suggest higher N₂O emission increases. A 692 significant source of the uncertainty in top-down estimates is a possible change in the N₂O 693 lifetime over the reconstruction period, which we have quantified following the recent results 694 from Prather et al. (2015).

The reconstruction of mole fraction and isotopic composition was used to investigate temporal changes in the isotopic signature of N₂O emissions over the study period. The average total source for $\delta^{15}N^{av}$ and $\delta^{15}N^{\beta}$ shows no statistically significant long-term trend but possibly significant decadal scale variability. For $\delta^{18}O$ and $\delta^{15}N^{\alpha}$ of the total N₂O source, no significant temporal changes can be detected with the present dataset because the uncertainties are large, especially in the beginning of the reconstruction period.

When the total source is split into a constant natural and a varying anthropogenic component, the reconstruction of the δ values of the anthropogenic source indicates a significant increase of $\delta^{15}N^{av}$ from the early to the modern part of the record. This originates from the near-linear isotope histories of the best guess scenario, which would imply that small emissions in the early part had a similar absolute effect on the δ values as stronger emissions in the latter part. A similar effect for $\delta^{18}O$ is likely, but not significant given the larger uncertainties for this signature.

Nevertheless, the isotope signal in $\delta^{15} N^{av}$ may also be a signal for changing source 708 709 contributions over time. Bottom-up models suggest that N₂O emitted from agricultural soils 710 was the dominant contributor to the anthropogenic N₂O increase in the first decades. Smaller 711 contributions due to emissions from more enriched sources, like industry, automobiles and 712 coal combustion increased. This may have contributed to an isotope enrichment of the emissions, which is not detectable within the error bars for the other isotope signatures. 713 714 However, one has to be cautious with a firm interpretation of these trends since the reconstruction method itself may also induce decadal variability if the smoothness of the 715 716 scenario is incorrectly constrained.

Results from the mass balance model yield an increase in 15 N site preference between the preindustrial and modern total N₂O source. When this trend is evaluated with a simplified twoendmember mixing model, the results suggest an increase of nitrification sources relative to denitrification-related sources over the industrial period.

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953 Table 1. Site information on the drilling locations of the North Greenland Ice core Project

954 (NGRIP-01_{Ishijima}, NGRIP-01_{Bernard}), Berkner Island (BKN-03), North Greenland Eemian Ice

955 drilling Project (NEEM-EU-08, NEEM-09), Dome Concordia (DC-99) and Dronning Maud

956 Land (DML-98), where firn air samples were collected, and two key meteorological variables

957 of each site.

Site	Location	Mean annual temperature	Surface accumulation rate (water equivalent)	Sampling year
		(°C)	$(cm a^{-1})$	
NGRIP-01 ¹	75° N 42° W	-31	20	2001
BKN-03 ²	79° S 45° W	-26	13	2003
NEEM-	77.4° N 51.1° W	-29	22	2008
EU-08				
NEEM-09	77.4° N 51.1° W	-29	22	2009
DC-99 ³	75° S 123° E	-53	3	1999
DML-98 ³	75° S 65° E	-38	6	1998

¹ Data retrieved from Bernard et al. (2006), Ishijima et al. (2007) ² Data retrieved from Bernard et al. (2006) ³ Data retrieved from Röckmann et al. (2003)

	Site	Sampling	Mole	$\delta^{15} \mathrm{N}^{\mathrm{av}}$	$\delta^{18} \mathrm{O}$	$\delta^{15} N^{eta}$	$\delta^{15} N^{lpha}$
		year	fraction $(nmol mol^{-1})$	(‰)	(‰)	(‰)	(‰)
	NGRIP-01	2001	318	6.64	44.61	-2.79	16.07
	BKN-03	2003	318	6.64	44.61	-2.79	16.07
	NEEM-	2008	324	6.22	44.40	-3.08	15.52
	EU-08						
	NEEM-09	2009	318	6.38	44.92	-2.66	15.41
	DC-99	1999	318	6.64	44.61	-2.79	16.07
	DML-98	1998	318	6.64	44.61	-2.79	16.07
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Table 2. Detailed information in the mole fraction and the isotopic composition of thelaboratory reference gases used for correcting each set of firn air samples.

- 989 Table 3. Emission fluxes and isotopic composition of the natural and anthropogenic source
- 990 results from the mass balance model. Stratospheric isotope fractionation (ε_L) used in the mass
- balance model, and the respective results from Park et al. (2012).

<u>Autural source (Enat, Onat,pi)</u>				
	This study	Park et al. (2012)		
E _{nat} (Tg a ⁻¹ N)	11.0±1.7	11.1		
$\delta^{15} \mathrm{N}^{\mathrm{av}}$ (%)	-5.2±0.2	-5.3±0.2		
δ^{18} O (‰)	33.1±0.2	32.0±0.2		
$\delta^{15} \mathrm{N}^{lpha}$ (‰)	-1.9±1.0	-3.3±1.0		
$\delta^{15} \mathrm{N}^{\mathrm{eta}}$ (‰)	-8.3±1.1	-7.5±1.1		
$\delta^{15} \mathrm{N}^{\mathrm{sp}}$ (‰)	6.4±1.5	4.2±1.5		

Natural source $(E_{nat}, \delta_{nat, pi})^{1}$

Anthropogenic source (E_{anth}, δ_{anth})

	This study	Park et al. (2012)
E _{anth} (Tg a ⁻¹ N)	5.4±1.7	6.6
$\delta^{15} \mathrm{N}^{\mathrm{av}}$ (%)	-18.2±2.6	-15.6±1.2
δ^{18} O (‰)	27.2±2.6	32.0±1.3
$\delta^{15} \mathrm{N}^{lpha}$ (‰)	-8.1±1.7	-7.6±6.2
$\delta^{15} \mathrm{N}^{\mathrm{eta}}$ (‰)	-26.1±8.4	-20.5±7.1
$\delta^{15}\mathrm{N}^{\mathrm{sp}}$ (‰)	18.0±8.6	13.1±9.4

Stratospheric Loss¹

	This study	Park et al. (2012)
F _{exch} (Tmol s ⁻¹)	0.22	NA
L (Tg a^{-1} N)	12.3	NA
$\varepsilon_{\mathrm{app}} ~^{15}\mathrm{N}^{\mathrm{av}}$ (‰)	-16.2	-14.9
ε _{app} ¹⁸ Ο (‰)	-13.4	-13.3
$\varepsilon_{\rm app} {}^{15} { m N}^{lpha}$ (‰)	-23.0	-22.4
$\varepsilon_{app} \ ^{15} N^{\beta}$ (‰)	-9.4	-7.1

<u>N₂O Lifetime (a)</u>		
	This study	Park et al. (2012)
	123_{-19}^{+29}	120

992 ${}^{1}\delta_{atm,pi}$ values are from Park et al. (2012) who also calculated $\delta_{nat,pi}$ and δ_{anth} in a two-box model. The values are (9.3±0.2) (993 ‰) for $\delta^{15}N^{av}$, (45.5±0.2) (‰) for $\delta^{18}O$, (18.8±1.0) (‰) and (-0.6±1.1) (‰) for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ respectively. In this study, 994 the δ_{anth} values are the averaged values over the whole investigated period. ε_{L} values used in this study are averaged values 995 from the lower stratosphere from Kaiser et al. (2006) and ε_{L} values from Park et al. (2012) were used from Park et al. (2004).

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1008 Figure 2. Left: Reconstructed atmospheric scenarios (black solid line with dashed lines 1009 indicating the 2 σ uncertainty intervals) and results of the firm air samples (corrected for firm 1010 fractionation) plotted at their respective assigned mean age. Middle: corresponding depth 1011 profiles, symbols show the measurements and solid lines the results of the forward model 1012 using the best estimate scenario as input. Right: model data discrepancies as a function of depth. Orange: NGRIP-01_{Bernard}, Yellow: NGRIP-01_{Ishijima}, Brown: NEEM-EU-08, Red 1013 NEEM-09, Purple: BKN-03, Black: DML-98, Green: DC-99, Blue: SP-95 and Light Blue: 1014 SP-01. Data from NGRIP-01_{Ishijima} SP-95 and SP-01 were not used in the atmospheric 1015 1016 reconstruction and are only plotted for comparison purposes here.



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Figure 3: Top panel. N_2O mole fraction history constrained with the most precise data at NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed black lines) and the scenarios within the uncertainty envelopes that were used in the mass balance model (magenta lines) to evaluate the uncertainties of the atmospheric modelling results.

1023 Bottom panel. N₂O production rate as calculated from the mass balance model. The solid 1024 black line represents the result for the best fit reconstruction while magenta lines represent the results for the individual scenarios from the top panel. Dotted light green line denotes the natural source emissions which were kept constant in our model runs.



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Figure 4: Left panels: Historic evolution of $\delta^{15}N^{av}$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ in N₂O as derived from the firn air reconstruction. Middle panels: isotope signatures of the total emitted N₂O. Right panels: isotope signatures of the anthropogenic source, respectively. The solid black line represents the best-fit scenario while the dashed ones represent the respective uncertainties as determined by the reconstruction method. Magenta lines represent the emissions that are required to produce the magenta N₂O histories in the left panels.

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Figure A1: Effect of firn fractionation on N_2O isotopic composition in firn. Original measurements are plotted as stars, data corrected for firn fractionation are plotted as circles with error bars. The left hand side shows Northern hemisphere sites, orange: NGRIP-01_{Bernard}, yellow: NGRIP-01_{Ishijima},brown: NEEM-EU-08, red NEEM-09 and the right hand side shows Southern hemisphere sites, purple: BKN-03, black DML-98, green DC-99, blue SP-95 and light blue SP-01

1048 Appendix B: Data processing

1049 In this study isotope deltas (δ) are used to denote the relative ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratio 1050 difference of N₂O in firm air with respect to a standard reference,

1051
$$\delta^{15} N = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1$$
 (1)

1052 where R represents the ¹⁵N/¹⁴N or ¹⁸O/¹⁶O abundance ratio of a standard or a sample. δ^{15} N 1053 values are reported relative to ¹⁵R of atmospheric N₂, δ^{18} O values relative to ¹⁸R of Vienna 1054 Mean Standard Ocean Water (VSMOW). The ¹⁵N/¹⁴N, ¹⁸O/¹⁶O and position dependent 1055 ¹⁵N/¹⁴N isotope ratios were derived from measurement of the *m/z* 45 / *m/z* 44, *m/z* 46 / *m/z* 44 1056 and *m/z* 31 / *m/z* 30 ion current ratios according to Kaiser et al., (2008), assuming a constant 1057 ¹⁷O excess of 0.9 ‰.

There is a disagreement between reported trends of the position dependent $\delta^{15}N^{av}$ values 1058 reported in the literature from firn air on the one hand and archived air samples on the other 1059 1060 hand (Park et al., 2012; Ishijima et al., 2007; Bernard et al., 2006; Röckmann and Levin, 2005; Röckmann et al., 2003; Sowers et al., 2002). In principle the temporal trend measured 1061 1062 directly on archived air samples should be fully consistent with top firn air samples of the 1063 various data sets, which were collected over a decade or more, since the air in the diffusive 1064 zone is not very old. However, this is not the case. Using the high-precision determination of 1065 the temporal trend of the N₂O isotope signatures on archived air samples from Röckmann and Levin (2005) as reported in section 2.4 we rescale the different firn profiles to match this 1066 1067 trend in the diffusive zone by interpolating the measurements from the diffusive zone of all sites to DC-99 (δ_{INT}). By using the firn model – assigned mean age of each sample. The 1068 maximum age difference from diffusive zone to surface corresponds to $\Delta age = \Delta_{DC t-t_0} = 10 a$. 1069 1070 Below you can find the equations used:

1071
$$\delta_{\text{INT}} = \delta_{\text{t-t}_0} - \delta_{\text{DC t-t}_0} + m \left(\Delta_{\text{t-t}_0} - \Delta_{\text{DC t-t}_0} \right)$$
 (2)

1072
$$\delta_{\text{Final}} = \delta_{\text{meas}} - (\delta_{\text{exp}} - \delta_{\text{INT}})$$
 (3)

1073 Where *m* is the slope connecting the two points we want to interpolate. The applied scaling 1074 (δ_{Final}) is given in the Table B1 below. To bring the data to the most recent international scale, 1075 NOAA-2006A, we used an equation extracted from a correlation between a scale ratio of 1076 NOAA-2006A to CSIRO versus the mole fraction of N₂O. The correlation showed higher 1077 scale ratio for low fraction values and lower scale ratio for higher mole fraction values. The

1078 equation extracted is given below:

1079
$$y(NOAA-2006) = -1.535 \times 10^{-4} y^2(CSIRO) + 1.045 y(CSIRO)$$
 (4)

1080 Table B1. Implemented scaling for N₂O mole fraction and isotopic composition. The re-1081 scaled average was extracted from the diffusivity zone for each site, which corresponds to the 1082 50 The top m. expected trends are averaged values from CSIRO 1083 (http://www.csiro.au/greenhouse-gases) for the last 30 years for the mole fraction and 1084 measured trends from Röckmann and Levin (2005) for the isotopic composition. The rather 1085 large corrections to the isotope data from the SP-01 and SP-95 drillings are likely due to inter-1086 laboratory scale differences.

	$y(N_2O)(nmol mol^{-1})$			
Site	Re-scaled average	Expected trend	Correction	
		change		
DML-98	0.09±0.29	-0.80±0.06	-0.89±0.32	
NGRIP-01 _{Bernard}	3.39±0.54	1.60 ± 0.06	-1.79±0.54	
NGRIP-01 _{Ishijima}	4.12±0.32	1.60 ± 0.06	-2.52±0.32	
BKN-03	3.47±0.22	3.20±0.06	-0.27±0.23	
NEEM-EU-08	3.57±1.81	7.20±0.06	3.63±1.81	
NEEM-09	8.84±1.82	8.00±0.06	-0.84±1.82	

	<u>δ¹⁵N^{av} (‰)</u>			
Site	Re-scale average	Expected trend	Correction	
		change		
SP-95	1.43±0.56	0.16±0.00	-1.27±0.56	
DML-98	-0.18±0.12	$0.04{\pm}0.00$	0.22±0.12	
SP-01	0.22±0.22	-0.08±0.00	-0.30±0.22	
NGRIP -01 _{Bernard}	-0.18±0.07	-0.08±0.00	0.10±0.07	
NGRIP -01 _{Ishijima}	0.17±0.13	-0.08±0.00	-0.25±0.13	
BKN-03	-0.17±0.12	-0.16±0.00	0.01±0.12	
NEEM-EU-08	-0.63±0.15	-0.36±0.00	0.27±0.15	
NEEM-09	-0.43±0.05	-0.40±0.00	-0.03±0.05	

	δ ¹⁸ Ο (‰)			
Site	Re-scale average	Expected trend	Correction	
		change		
SP-95	-0.88±0.27	0.08 ± 0.00	0.96±0.27	
DML-98	0.26±0.15	0.02 ± 0.00	-0.24±0.15	
SP -01	0.74±0.62	-0.04±0.00	-0.78±0.62	
$NGRIP-01_{Bernard}$	-0.08±0.05	-0.04±0.00	$0.04{\pm}0.05$	
NGRIP-01 _{Ishijima}	-0.17±0.12	-0.04±0.00	0.13±0.12	
BKN-03	0.02±0.06	-0.08±0.00	-0.10±0.06	
NEEM-EU-08	-0.21±0.15	-0.19±0.00	0.02±0.15	
NEEM-09	0.28±0.04	-0.21±0.00	-0.49±0.04	

	$\delta^{15} \mathrm{N}^{\beta}$ (‰)			
Site	Re-scale average	Expected trend	Correction	
		change		
DML-98	-0.41±0.20	0.06±0.02	0.47±0.20	
NGRIP-01 _{Bernard}	-0.10±0.25	-0.13±0.02	-0.02±0.25	
BKN-03	-0.53±0.30	-0.26±0.02	0.27±0.30	
NEEM-EU-08	-0.33±0.27	-0.58±0.02	-0.25±0.27	
NEEM-09	-0.14±0.17	-0.64±0.02	-0.50±0.17	

	δ ¹⁵ N ^a (‰)			
S:40	Re-scale average	Expected trend	Correction	
Site		change		
DML-98	0.09±0.11	0.01±0.02	-0.08±0.11	
$NGRIP-01_{Bernard}$	-0.26±0.19	-0.03±0.02	0.23±0.19	
BKN-03	0.19±0.32	-0.06±0.02	-0.25±0.32	
NEEM-EU-08	-0.61±0.35	-0.13±0.02	0.48±0.35	
NEEM-09	-0.72±0.16	-0.14±0.02	0.58±0.16	

- 1087 Appendix C: Atmospheric reconstruction re-scaled to NEEM-09 and without
- 1088 data re-scaling



Figure C1. Results of the firn data evaluation (similar to Figure 2) using the data without rescaling as indicated in the text, Orange: NGRIP-01_{Bernard}, Yellow: NGRIP-01_{Ishijima}, Brown:
NEEM-EU-08, Red: NEEM-09, Purple: BKN-03, Black: DML-98, Green: DC-99, Blue: SP95 and Light Blue: SP-01.



Figure C2. Results of the firn data evaluation (similar to Figure 2) using the data re-scaled tothe NEEM-09 site. Colours as in Fig. C1.



1098 Figure C3. Sensitivity test to the regularization term increased by a factor of 10. 1099 Reconstructed atmospheric scenarios (left), corresponding fit of the firn data (centre) and 1100 model data discrepancies (right). The best reconstructed scenarios are shown as the black 1101 continuous lines, with model derived uncertainties (2σ) in dashed lines. Colours as in Fig. C1.



 $\begin{array}{c} 1103\\1104 \end{array}$ Figure C4. Comparison of the atmospheric reconstructions between different re-scaling 1105 methods. Solid and dashed green lines are the scenarios from data re-scaled to DC-99 used in 1106 this study. Solid red lines are the best-case scenario for the non re-scaled data and solid blue 1107 lines are the best-case scenarios from the data re-scaled to NEEM-09. The latter data series is 1108 shifted because of a calibration offset. When this is corrected for the data superimposes the 1109 green lines as expected.

1111 Appendix D: Sensitivity of the reconstructed N₂O emissions and isotopic 1112 signatures on N₂O lifetime.

For the default calculations with the mass balance model a constant lifetime for N_2O was used. A recent study from Prather et al. (2015), though, highlighted that top-down model calculations are sensitive to changes in the N_2O lifetime. To quantify the effect on our results we performed a sensitivity test where we linearly changed the N_2O lifetime from preindustrial to modern times from 123 a in 1700 to 119 a in 2008. We also included runs with the absolute mean value changes in the assumed mean lifetime. The results are shown in Figures D1 and D2 below.

In Figure D1 the N₂O atmospheric budget is re-calculated and compared with the results when 1120 the constant lifetime of 123_{-19}^{+29} a is used. In year 1940 the N₂O emissions are (12.3±2.7) Tg a⁻¹ 1121 N and (17.0 \pm 1.7) Tg a⁻¹ N in year 2008 with a total increase of (4.7 \pm 1.7) Tg a⁻¹ N. When 1122 keeping the lifetime constant, the results for the same years are (11.9 \pm 1.7) Tg a⁻¹ N and 1123 (16.4 \pm 1.7) Tg a⁻¹ N with a total increase of (4.5 \pm 1.7) Tg a⁻¹ N. In addition, when looking also 1124 1125 into the absolute mean value changes in the assumed mean lifetime we only observe a vertical 1126 shift of the scenarios that do not affect the temporal change. This shows that there is a sensitivity on the choice of lifetime for our mass balance model on the N₂O atmospheric 1127 budget as was indicated by Prather et al. (2015). 1128

1129 The N₂O source isotopic signature shows no significant change with the choice of lifetime 1130 giving similar average source values for all source signatures as for when using a constant 1131 lifetime of 123_{-19}^{+29} a.

- 1132 On the other hand, the N₂O average anthropogenic source signature displays a sensitivity in the choice of lifetime returning values (-15.9 ± 2.6) ‰, (28.5 ± 2.6) ‰, (-7.2 ± 1.7) ‰ and (-7.2 ± 1.7) ‰ 1133 22.8±8.4) % for $\delta^{15}N^{av}$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ respectively. This agrees within combined 1134 errors with the total average values of (-18.2±2.6) ‰, (27.2±2.6) ‰, (-8.1±1.7) ‰ and (-1135 26.1±8.4) ‰ for δ^{15} N^{av}, δ^{18} O, δ^{15} N^{α} and δ^{15} N^{β} respectively when a constant 123⁺²⁹₋₁₉ a lifetime 1136 is used. On average, the N₂O anthropogenic signature results can differ by 10 % when a 1137 1138 different lifetime is chosen, which is equivalent to a (2.0 ± 1.0) % difference in the final 1139 anthropogenic values.
- 1140 Sensitivity tests were also performed on the F_{exch} parameter which gives us the annual fluxes 1141 between the two reservoirs (stratosphere - troposphere). Following Appenzeller et al. (1996)

- and Holton et al. (1990) the value was tested at a low and high value of 0.16 and 0.28 Tmol s⁻¹
 ¹ respectively with the one used in the manuscript being 0.22 Tmol s⁻¹. Results are shown in
 figures D3 and D4 below.
- 1145 In Figure D3 (middle panel) the atmospheric budget is re-calculated and compared to the
- 1146 optimal scenario values. At the bottom panel the air returned to troposphere from stratosphere
- 1147 is presented (F_{exch}). It is clear that when a low F_{exch} value is chosen, then less N₂O is returned
- 1148 to the troposphere. Contrary when a higher F_{exch} value is used more N_2O is returned.
- 1149 F_{exch} choise has little effect on the isotopic signature results as shown in Figure D4 and is 1150 mainly limited to the earliest part of the record (>1970) where the reconstruction uncertainties 1151 are larger. While it is expected when F_{exch} value is low the isotopic results to be more 1152 enriched compared to higher F_{exch}, in our case this is not clear from the test. The overal 1153 averaged values have a less than 2 % difference compared to the chosen (optimal) scenario 1154 and results of total averaged source and anthropogenic isotopic signatures are well within 1155 agreement with combined uncertainty errors in both total source and anthropogenic signatures 1156 respectively.
- 1157 Thus, we conclude that while the flux is indeed sensitive on the F_{exch} choice value the isotopic 1158 composition is not.



Figure D1: Top panel. N_2O mole fraction history constrained with the most precise data at NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed black lines) and the scenarios within the uncertainty envelopes that were used in the mass balance model (magenta lines) to evaluate the uncertainties of the atmospheric modelling results.

Bottom panel. N₂O production rate as calculated from the mass balance model assuming a change in the lifetime from 123 a in 1700 to 119 a in 2008 (relative change similar to Prather et al., 2015) in light blue. The solid black line represents the result for the best fit reconstruction while magenta lines represent the results for the individual scenarios from the top panel (lifetime kept constant at 123^{+29}_{-19} a) as used in the main paper. Light green and yellow show the results when lifetime is 154 a and 104 a respectively.

Figure D2: Left panels: Historic evolution of $\delta^{15}N^{av}$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ in N₂O as derived from the firn air reconstruction. The solid black line represents the best-fit scenario while the dashed ones represent the respective uncertainties as determined by the reconstruction method. Magenta lines represent the emissions that are required to produce the magenta N₂O histories in the left panels. Middle and right panels: Isotope signatures of the total emitted

- 1177 N₂O and anthropogenic source respectively assuming a change in the lifetime from 123 a in
- 1178 1700 to 119 a in 2008 (relative change similar to Prather et al., 2015) in light blue. The solid
- 1179 black line represents the result for the best fit reconstruction while magenta lines represent the
- 1180 results for the individual scenarios from the top panel (lifetime kept constant at 123_{19}^{+29} a) as
- 1181 used in the main paper.

Figure D3: Top panel. N_2O mole fraction history constrained with the most precise data at NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed black lines) and the scenarios within the uncertainty envelopes that were used in the mass balance model (magenta lines) to evaluate the uncertainties of the atmospheric modelling results.

Bottom panel. N₂O flux exchange results between stratosphere and troposphere as calculated from the mass balance model assuming a high (0.28 Tmol s⁻¹) F_{exch} in light green and a low

¹¹⁸⁸ Middle panel. N₂O production rate as calculated from the mass balance model assuming a 1189 high (0.28 Tmol s⁻¹) F_{exch} in light green and a low (0.16 Tmol s⁻¹) value in yellow. The solid 1190 black line represents the result for the best fit reconstruction while magenta lines represent the 1191 results for the individual scenarios from the top panel as used in the main paper.

1194 $(0.16 \text{ Tmol s}^{-1})$ value in yellow. The solid black line represents the result for the best fit

Figure D2: Left panels: Historic evolution of $\delta^{15}N^{av}$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ in N₂O as derived 1197 from the firn air reconstruction. The solid black line represents the best-fit scenario while the 1198 1199 dashed ones represent the respective uncertainties as determined by the reconstruction 1200 method. Magenta lines represent the emissions that are required to produce the magenta N₂O 1201 histories in the left panels. Middle and right panels: Isotope signatures of the total emitted N₂O and anthropogenic source respectively assuming high (0.28 Tmol s⁻¹) F_{exch} in light green 1202 1203 and a low (0.16 Tmol s⁻¹) value in yellow. The solid black line represents the result for the 1204 best fit reconstruction while magenta lines represent the results for the individual scenarios 1205 from the top as used in the main paper.