

Reply to referee Thomas Rahn comments

Ref. Com. Line 25: *The 1940 atmospheric mole fraction, and hence the growth rate, differs from the determined by Battle et al. (1996) and to a lesser degree with Machida et al. 1995 please discuss (discussion section).*

Author's Resp.: Following the referee's suggestion we have added a discussion (see below) in the discussion section.

"The N₂O mole fraction atmospheric history from our multi-site reconstruction is in agreement with recent work from Meinshausen et al. (2016) who combined all available published N₂O 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 smaller extent with Machida et al. (1995).

Battle et al. (1996) collected firn air data and Machida et al. (1995) used ice data. Both studies 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 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 firn air model and possible differences between sites may contribute. In our case we used measurements from 5 sites to constrain our model while Battle et al. (1996) and Machida et 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 Battle et al. (1996) only used two gases."

Author's changes: Lines 549-563, Lines 738-740, Lines 811-813

Ref. Com. Line 48: *N₂O as a source of stratospheric NO_x was certainly known prior to Ravishankara's 2009 work see McElroy, Khalil, Crutzen, etc.*

Author's Resp.: The following references have been added to the manuscript: McElroy, M. B., and McConnell, J. C.: Nitrous Oxide: A natural source of stratospheric NO, *Journal of Atmospheric Sciences*, 28, 1095-1098, 1971.

Crutzen, P. J.: The role of NO and NO₂ in the chemistry of the troposphere and stratosphere, *Annual review of earth and planetary sciences*, 7, 443-472, 1979.

Author's changes: Line 46, Lines 760-761, Lines 822-823

Ref. Com. Lines 80-81: *Rahn and Wahlen (1997) also contributed here with the first reference that describes a fractionation factor for stratospheric loss.*

Author's Resp.: The suggested reference has been added to the revised manuscript. Rahn, T., and Wahlen, M.: Stable isotope enrichment in stratospheric nitrous oxide, *Science*, 278, 1776-1778, doi: 10.1126/science.278.5344.1776, 1997.

Author's changes: Line 79, Lines 865-866

Ref. Com. Lines 82-84: *Rahn et al. (1998) also contributed here with the first laboratory verification of wavelength dependent kinetic fractionation during photolysis.*

Author's Resp.: The suggested reference has been added to the revised manuscript. Rahn, T., Zhang, H., Wahlen, M., and Blake, G. A.: Stable isotope fractionation during ultraviolet photolysis of N₂O, *Geophys. Res. Lett.*, 25, 4489-4492, 1998.
Author's changes: Line 83, Lines 867-868

Ref. Com. Line 116: *"Carbon composition of"*

Author's Resp.: We corrected this omission and replaced it with "of its carbon composition".

Author's changes: Line 115

Ref. Com. Lines 141-142: *For my own edification, doesn't this require dual bladders so that a specific depth range can be isolated?*

Author's Resp.: When firn samples are collected with this method, a new hole is drilled from the top. The hole is drilled to a certain depth and then the bladder is inserted down close to the bottom of the drill hole, so in practice the bottom of the drill hole plays the role of the second bladder that the referee indicated.

Ref. Com. Lines 270-275: *Mole fraction data from NEEM is substituted for, with CSIRO/IUP/CIC/NOAA data. Does this induce a simple offset or a trending offset? In either case by how much?*

Author's Resp.: NEEM data measured at IMAU was replaced by IUP/CIC/NOAA and CSIRO because IMAU data is less precise. The atmospheric trend reconstruction from IMAU-NEEM data, shown in black, in Fig. 1 has larger uncertainties than the trend scenario based on the more precise IUP/CIC/NOAA/CSIRO data (in red). The IMAU data based scenario is smoother because the model can reconstruct less details from more uncertain data. Thus the replacement of IMAU data with IUP/CIC/NOAA/CSIRO data does not induce an offset but leads to a more accurate and less smoothed output scenario.

Author's changes: Lines 274-276, Lines 468-469, Lines 1018-1019, Lines 1029-1030, Lines 1160-1161, Lines 1183-1184

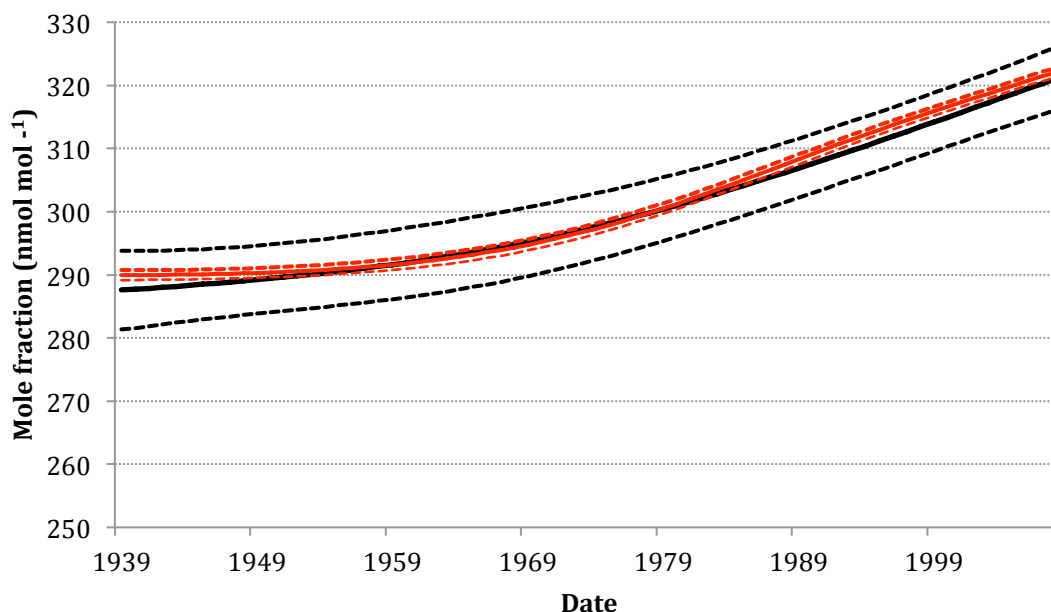


Figure 1: Firm air trend reconstruction using only NEEM measurements from IMAU laboratory (black line) with uncertainty envelopes (dashed black lines) compared to firm air trend reconstruction using NEEM measurements from IUP/CIC/NOAA and CSIRO atmospheric (red line) with corresponding uncertainty envelopes (dashed red lines).

Ref. Com. Lines 289-299: *The natural sources from land and sea have quite different production mechanisms as well as previously observed and predicted different isotopic signatures (Kim and Craig, 1993; Rahn and Wahlen, 2000; and others) yet the isotopic model used here lumps all natural source into a single term. Given the detailed history that the authors are attempting to tease apart, this seems to me detrimental to their efforts. Please justify keeping the natural source as a single term. This should also be elaborated on further in the discussion section.*

Author's Resp.: Yes, the isotope signatures of natural and terrestrial sources are different, and this has indeed been used to reconstruct contributions of marine and terrestrial sources to N_2O variations in the past (Schilt et al., 2014). In the present study we focus on the change since pre-industrial times, where the strong increase in the N_2O mole fraction suggests that this increase is dominated anthropogenic activities. Therefore we apply a model that assumes that the natural source strength has remained constant. This is clearly stated in the paper, but we have added some additional comments in the revised version. We would of course like to be able to differentiate between more processes, but our result indicates that with the present analytical precision, and given the uncertainties in source signatures, it is not really adequate to constrain additional degrees of freedom. In response to the referee comment we have added in the discussion that changes in natural sources that occur in parallel to the anthropogenic emissions cannot be distinguished with our approach, but may as well influence the results.

Author's changes: Lines 333-338, Lines 598-599

Ref. Com. Line 326: *As well as Rahn and Wahlen 2000*

Author's Resp.: The suggested reference has been added to the revised manuscript. Rahn, T., and Wahlen, M.: A reassessment of the global isotopic budget of atmospheric nitrous oxide, *Glob. Biogeochem. Cycl.*, 14, 537-543, 2000.
Author's changes: Line 326, Lines 869-870

Ref. Com. Lines 429-439: *Discussion of interlaboratory variability. The authors state that discrepancies do not exhibit a systematic shift and that Sowers et al. data had good agreement between two different laboratories but then they leave this conundrum hanging. Please elaborate a little on possibilities.*

Author's Resp.: We realize that this is not fully satisfactory, but we have investigated this in quite some detail and cannot resolve the discrepancies. A possible origin of the difference could be based on the reconstruction model. Because the uncertainties on the South Pole data are large, compared to 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 consideration since when pumping firn air and filling the sampling flasks you could encounter uncertainties (contamination, possible leak, fractionation, incomplete flask flushing etc). We have added this as additional discussion to the text.

Author's changes: Lines 438-444

Ref. Com. Line 457: *Regularization term is increased by how much?*

Author's Resp.: The regularization factor was increased by a factor of 10. This was added in the revised manuscript.

Author's changes: Lines 461-463, Line 635, Line 1098

Ref. Com. Lines 469-470: *I find this paragraph confusing. The average annual emission of 3.5 TgN/yr in the last sentence should be the difference between 1940-2008 should it not? But there the difference is 4.4 TgN/yr. I think I am confused because in the one case the natural term is included but in the other they are only considering the anthropogenic. In any case, this entire paragraph could be presented with more clarity.*

Author's Resp.: We have reworded this paragraph to remove the confusion. The average annual emission of 3.5 TgN/yr corresponds to the annual growth rate of 0.7 nmol mol⁻¹ a⁻¹ calculated between years 1995 and 2008. The total change the N₂O mole fraction of (32±1) nmol mol⁻¹ can be explained in the mass balance model by a (4.4±1.7) Tg a⁻¹ N increase in the emissions from in 1940 to 2008. The paragraph has been updated to state the above clearly.

Author's changes: Lines 474-476

Ref. Com. Lines 488-495 and lines 587-595: *Observation of decadal variability in $\delta^{15}\text{N}_{\text{air}}$ and discussion of changes in relative contribution of sources over time. If real, this is possibly the most important observation in the manuscript and needs to be dealt with much more considered manner. Intuitively, one would agree with their statement i.e. that the agricultural source would imprint the record more significantly in the earlier part of the record and decrease, in a relative sense, over time. This would mean that yes, the earliest human influences would be significantly depleted.*

As time goes on, fertilizer use becomes more controlled leading to less overuse and more limited flux of N₂O accompanied by less isotopic discrimination. This along with increased industrial production of N₂O would hypothetically lead the observed increase in $\delta^{15}\text{N}_{\text{ant}}$ over time (both avg and beta). This increase (Fig. 4, right) peaks in the late 1980's however and proceeds to decrease significantly (~10% for $\delta^{15}\text{N}_{\text{av}}$ and ~20% for $\delta^{15}\text{N}_{\text{b}}$). This decrease is much more difficult to explain in a qualitative sense and in truth is difficult to believe.

One possibility is that industries are doing a better job of decreasing and/or capturing fugitive emissions which might increase in the proportion of $\delta^{15}\text{N}$ depleted agriculture relative to industry but:

A. Is there evidence of this?

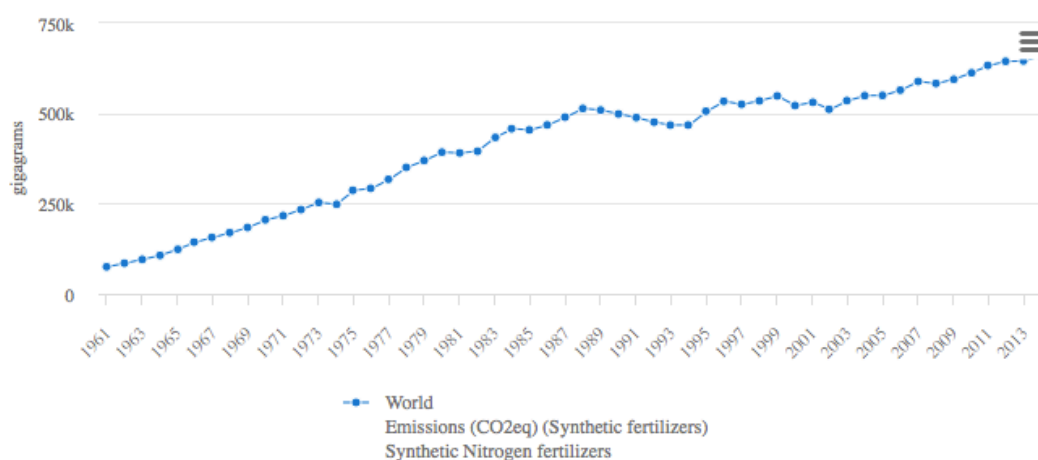
B. Would it yield this large of a result?

A more detailed discussion of this is warranted given the subtly profound implications including discussion of potential artifacts in measuring and modeling that could also lead the observed modeled record.

Author's Resp.: We thank the referee for this a comment. We actually tried to keep a balance between discussing possible scenarios (first part of the referee comment) and examine whether the reconstructed changes are realistic (second part of the referee comment). Independent quantitative evidence for some of the suggested changes is actually available from inventory information, which was not included in the original version of our manuscript. 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 constant or even decreased until 2000, and increased again after 2000. The reasons of the decrease between 1985 and 2000 are a small turn to organic soil cultivation in combination with more efficient agricultural methods and fertilizer use. This qualitatively matches the temporal evolutions of our reconstructed source signatures, but as the referee points out the observed isotopic signature change after 1985 is quite large, especially for $\delta^{15}\text{N}_{\text{av}}$ and $\delta^{15}\text{N}_{\text{b}}$. This is why we did not discuss this in more detail in the original manuscript. In the revised version, we added this information, but also point out that this effect is likely not strong enough to explain the reconstructed isotope signal.

In the manuscript, we do discuss the fact that (part of) decadal variability may originate from small undulations on the reconstructed scenarios, since the emissions are related to the derivative of the trend. It is possible to draw straight lines within the uncertainty envelopes of the scenarios, and therefore the reconstructed decadal variability may not be robust but a product of the reconstruction procedure. Indeed, increasing the regularization term by a factor of 10 leads to much smoother (nearly straight) lines that fit inside the uncertainty envelopes. Therefore the decadal variability may not be realistic, and we do not want to put too much emphasis on the interpretation in terms of underlying processes. We realize that this is a bit unsatisfactory, but given the large uncertainties we think that the level of interpretation that we give is adequate. We do not want to put forward scenarios that are unrealistic and not really backed up by the data.

Author's changes: Lines 621-637



Ref. Com. Line 524: Starting value of *d18O_{anth}*, looks like about 8% to me but I am looking at Fig. 4 because there is no Fig. 5.

Author's Resp.: The mistake has been corrected and substituted with $(7.7 \pm 2.6) \text{ ‰}$.
Author's changes: [Line 529](#)

Ref. Com. Lines 552-562: The authors perform a sensitivity study of changing the lifetime but it seems to me that there should also be a sensitivity study on other terms, in particular *F* (exchange) which is a term that is poorly known. Also given the two box model that is being used it seems that more appropriate lifetime would be stratospheric lifetime in conjunction with *X_{strat}* given that this is the box where all N₂O destruction takes place.

Author's Resp.: Sensitivity tests on the magnitude of *F_{exch}* have been added in the Appendix D. The results show that when the *F_{exch}* value is low, then less N₂O is returned to the troposphere, contrary, when *F_{exch}* is high more N₂O is returned. The study showed that *F_{exch}* has little effect on the isotopic signature results, thus we concluded that only the flux is sensitive to the choice of *F_{exch}* value while the isotopic composition is not.

The use of global mean lifetime is correct because eq. 3 in the manuscript refers to the total atmospheric burden and not the stratospheric burden. The mean stratospheric lifetime would be about 10 times smaller than the global mean lifetime.

Author's changes: [Lines 582-586](#), [Lines 1117-1118](#), [Lines 1124-1126](#), [Lines 1140-1158](#), [Lines 1177-1205](#)

Ref. Com. Lines 563-573: This was also predicted by Rahn and Wahlen (2000), prior to any firn air measurements being made, where they predicted a -0.03 permil/yr trend in $\delta^{15}\text{N}_{\text{av}}$ (identical to that on the line 417) and a -0.03 permil/yr trend in $\delta^{18}\text{O}$ (-0.02 permil/yr on line 418 being within the estimated error).

Author's Resp.: This has been included in the revised manuscript.

Author's changes: Lines 595-596, Lines 869-870

Ref. Com. Lines 576-580: *The 'natural' component of the ocean source is estimated to be on the order of 4Tg N/yr. This new 'anthropogenic' component would then comprise a 25% increase in the ocean source. This gets back to my earlier comment on separating the natural source into land and ocean sources. Would this 'new' oceanic N₂O have an identical isotopic signature to the natural signature or would it be somehow different? In either case, it would certainly be distinct from the land signature. How would this be reflected in the temporal evolution of the firm records?*

Author Resp.: As mentioned above, we cannot really constrain more free parameters, and we have chosen to lump all parts of the “anthropogenic” source together. Here we discuss that variations in different components of the anthropogenic source may leave temporal signals in the source signature. Snider et al. (2015) made a meta-analysis of previously published source signature studies and concluded that freshwater bulk isotope signatures are (-7.78 ± 9.72) ‰ and (40.75 ± 9.63) ‰ for $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{18}\text{O}$ respectively. Similarly for marine waters the results were (5.14 ± 1.93) ‰ for $\delta^{15}\text{N}^{\text{av}}$ and (44.76 ± 3.62) ‰ for $\delta^{18}\text{O}$. We feel that it is not possible at present to make a quantitative statement, given the available information both from bottom-up studies and isotope source signature studies, and therefore discuss these effects qualitatively only.

General comments:

Ref. Com.: *On two occasions reference is made to Fig. 5, but no Fig. 5 exists. I assume they refer to Fig. 4? In the Appendix: Fig. A1 caption, left and right are switched. Figures C1 and C2 appear to be switched, Fig. 3 (page 45) precedes Fig. C2 (page 47) and there is a Fig. 3 and a Fig. C3 (or is it Fig. C3 and C4?). This is all rather sloppy. It is difficult for the reader to tease apart which data sets are new analyses and which were previously published.*

Author's Resp.: We apologize for the mislabeling, and these errors were corrected in the revised version.

Author's changes: Line 485, Line 501, Line 517, Line 530, Line 589, Line 1044, Line 1046, Lines 1088-1092, Lines 1093-1096

Ref. Com.: *The new samples from NEEM are discussed thoroughly and the previously published data sets are referred to but nowhere is there an itemized tabulation of which data is associated with specific publications and which, other than NEEM, if any, are new.*

Author's Resp.: This information has been added in the revised manuscript in the revised Table 1.

Author's changes: Lines 953-960

Ref. Com.: *In addition, there are two different records from NGRIP-01, one which is included in the analysis and one which is not but both are referred to with the same sample name. Please add a subscript or some other differentiating factor so that the reader does not have to try and sort this out for himself.*

Author Resp.: The requested information has been added in the revised manuscript. A subscript indicating the differentiation between the two publications is used (NGRIP-01_{Ishijima}, NGRIP-01_{Bernard}) throughout the manuscript.

Author's changes: Line 211, Line 213, Line 393, Lines 428-429, Line 954, Line 999, Line 1013, Line 1015, Line 1044, Line 1045, Lines 1080-1087, Line 1091

Ref. Com.: Ultimately the authors conclude that 'Based on the changes in the isotopes we conclude that the main contribution to N₂O change in the atmosphere since 1940 is from soils, with agricultural soils being the principal anthropogenic component which is in line with previous studies'. Which is anticlimactic to say the least given the effort that went into sample collection, processing, analysis and modeling.

Author Resp.: We agree that this part of the conclusion should be modified. We set out with this project to detect possible temporal changes in the isotopic composition, but we find that such changes are not clearly quantifiable with the present analytical precision. Therefore the conclusion is a bit negative (as presented in the abstract), but have described our results and the limitations more quantitatively in the revised version.

Reply to Anonymous referee comments

Major comments:

Ref. Com. 1: Box model calculation: The model parameters that kept in varying are not stated clearly. A table that list all time independent parameteres (cross-tropopause exchange fluxes of isotopologues, natural fluxes and their associated isotopic signatures, N₂O lifetime, etc) will be helpful. In addition, a comparison with AR5 fluxes is useful.

Ref. Com. 2: Also box model: the derived time dependent variables. A table that summarizes the derived fluxes and isotopic values (average over a certain period) will be helpful, along with comparisons with other independent work by, for example, Park et al. and AR5.

Author's response to major comments 1 and 2:

We realise that a more detailed presentation of the parameters used is needed therefore we have substituted Table 3 where only natural and anthropogenic isotopic signature results were presented with a more detailed version including stratospheric loss fluxes and isotopic signatures, N₂O lifetime, natural and anthropogenic fluxes as in the two-box model. The values were compared to Park et al. (2012) because they provide results not only for fluxes but also for isotopic signatures. We did not include a comparison with the AR5 for the reason that it provides us only with flux results not isotopic signature ones.

Author's changes: Lines 989-995

Ref. Com. 3: What's the reason(s) behind for the elevated N₂O flux in year 2008?

Author's Resp.: We suspect the referee refers to the very slightly increasing emission strength at the end of the reconstructed record. This apparent upwards trend is likely not significant for our construction and we have not discussed it in more detail. We shortly stated this in the revised manuscript.

Author's changes: Lines 478-480

Ref. Com.4: *What's the reason(s) for the oscillating values in source/anthropogenic delta values in Fig. 4? Moreover, if I understand correctly, natural N₂O_s are kept constant. I then expect to see the same time variability in anthropogenic as in source in Figure 4, but apparently the two are different. This highlights the usefulness of the major comment #1.*

Author's Resp.: The reason why the oscillations of the total and the anthropogenic source are not the same is that in our mass balance model the total source is regarded as the sum of a constant natural source and a changing anthropogenic source, which was small in the beginning of the record and larger at the end of the record. Therefore, changes in the total source signature in the beginning of the record require a substantially stronger isotope signal in the (small) anthropogenic source at that time compared to the (large) anthropogenic source at the end of the record. This was also stated in the manuscript. To make this more comprehensive we have added in Fig. 3 (bottom panel) the assumed constant, natural source, also.

Author's changes: Lines 515-520, Lines 1019-1037

Ref. Com. 5: *In addition to isotopic values, it will be useful and more informative to have isoflux for each process considered. A plot similar Fig. 4 but for the respective flux (better also break into each process considered is recommended).*

Author's Resp.: We have considered adding isofluxes to the manuscript, but since we only distinguish between a natural and an anthropogenic source this does not seem to add very useful information in our opinion. If – as the referee suggested – we were able to distinguish different processes it would indeed be useful, but since we cannot do that, we prefer not to add a discussion on isofluxes.

Minor comments:

Ref. Com. 1 section 2.5: *define all the variables used and no need to define variables not used. For example F_{sink} defined but not used. F_{exch} used but not defined. Also is epsilon_L the same as epsilon_app? Please check carefully the variables in this section.*

Author's Resp.: The section has been updated, F_{sink} is replaced by L, epsilon_L is not the same as epsilon_app. Epsilon_L is constrained by epsilon_app but the numerical values differ depending on F_{exch} and the lifetime. F_{exch} is defined in Table 3.

Author's changes: Lines 295-296, Lines 317-318, Line 320-321, Lines 989-995

Ref. Com. 2: *Line 445: additional decadal variability: raised also above in the major comment #4. What are the underlying mechanisms for the variability? Agricultural activity? Use of fertilizer?*

Author's Resp.: Yes these are the mechanisms we describe and we added some more clarification in the discussion section.

Author's changes: Lines 621-637

Ref. Com. 3: *Line 492: d₁₅N_{av}" is the same notation throughout, in the figure d₁₅N is used.*

Author's Resp.: The notation d15N in the figure was replaced with d15Nav.

Author's changes: Line 26, Line 32, Line 69, Line 70, Line 164, Line 166, Line 167, Line 170, Line 216, Line 224, Line 238, Line 247, Line 315, Line 414, Line 416, Line 430, Line 450, Line 494, Line 498, Line 501, Line 506, Line 520, Line 521, Line 522, Line 527, Line 537, Line 538, Line 544, Line 607, Line 629, Line 640, Line 697, Line 703, Line 708, Line 972-973, Line 991-995, Line 1029, Line 1058, Line 1134, Line 1136, Line 1172, Line 1197

Ref. Com. 4: *Line 495: Fig.5, I believed you meant Fig. 4. Do the corrections for the remaining.*

Author Resp.: Thank you for pointing this out, it has been corrected.

Ref. Com. 5: *Table 3: Is your delta_atm,pi the same as Park et al.? If not, why not compare? If the same then say it.*

Author's Resp.: The delta_atm,pi is the same as Park et al. and it is mention in the footnote denoted with an asterisk located below table 3.

Author's changes: Lines 992-995

Ref. Com. 6: *Same table, the last column double asterisk: what is it for?*

Author's Resp.: Thanks for noting this, the double asterisks was removed.

Ref. Com. 7: *Line 604: d15N_sp: not defined. You mentioned in line 36, but the term not defined.*

Author's Resp.: d15N_sp is now defined in line 37.

Author's changes: Line 37

Ref. Com. 8: *d15N_sp is useful: please also show the time series in Fig. 4*

Author's Resp.: The information has been added in the revised manuscript.

Author's changes: Lines 1029-1034

Constraining N₂O emissions since 1940 using firn air isotope measurements in both hemispheres

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Abstract

N₂O is currently the 3rd most important anthropogenic greenhouse gas in terms of radiative 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 N₂O mole fraction and isotopic composition using new and previously published firn air data collected from Greenland and Antarctica in combination with a firn diffusion and densification model. The multi-site reconstruction showed that while the global mean N₂O mole fraction increased from (290±1) nmol mol⁻¹ in 1940 to (322±1) nmol mol⁻¹ in 2008 the isotopic composition of atmospheric N₂O decreased by (−2.2±0.2) ‰ for $\delta^{15}\text{N}^{\text{av}}$, (−1.0±0.3) ‰ for $\delta^{18}\text{O}$, (−1.3±0.6) ‰ for $\delta^{15}\text{N}^{\alpha}$, and (−2.8±0.6) ‰ for $\delta^{15}\text{N}^{\beta}$ over the same period. The detailed temporal evolution of the mole fraction and isotopic composition derived from the firn air model was then used in a two-box atmospheric model (comprising a stratospheric and

a tropospheric box) to infer changes in the isotopic source signature over time. The precise value of the source strength depends on the choice of the N₂O lifetime, which we choose to be 123⁺²⁹₋₁₉ a. The average isotopic composition over the investigated period is $\delta^{15}\text{N}^{\text{av}} = (-7.6 \pm 0.8) \text{‰}$ (vs. air-N₂) $\delta^{18}\text{O} = (32.2 \pm 0.2) \text{‰}$ (vs. VSMOW) for $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha} = (-3.0 \pm 1.9) \text{‰}$ and $\delta^{15}\text{N}^{\beta} = (-11.7 \pm 2.3) \text{‰}$. $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{15}\text{N}^{\beta}$ show some temporal variability while for 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 site-preference ($= \delta^{15}\text{N}^{\alpha} - \delta^{15}\text{N}^{\beta}$) provides evidence for a shift in emissions from denitrification to nitrification, although the uncertainty envelopes are large.

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).

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 et al., 2011; Galloway et al., 2004; Pérez et al., 2001; Yung and Miller, 1997; Kim and Craig, 1993). The increase of N₂O since pre-industrial times (hereafter referred to as "anthropogenic" increase) has been attributed largely to increased microbial production, resulting from the increased use of nitrogen fertilizers in agriculture. Industry (especially 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 primarily destroyed in the stratosphere via UV photolysis (90 %) and reactions with excited oxygen atoms (10 %) (Minschwaner et al., 1993), with a minor N₂O fraction removed by 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

al., 2011 and references therein). Besides the total source strength, the contributions of individual source processes are also poorly constrained. Due to the long steady-state lifetime of N₂O in the atmosphere (123₋₁₉⁺²⁹ a; SPARC Lifetimes Report 2013), temporal and spatial gradients are small, making it difficult to resolve localised sources.

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 distinguishable as a consequence they tend to attain different isotopic compositions. Beyond oxygen ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$) and average $\delta^{15}\text{N}^{\text{av}}$ ("bulk") signatures, N₂O also displays site specific ¹⁵N isotopic information. Site preference ($\delta^{15}\text{N}^{\text{sp}}$) is defined as the difference in $\delta^{15}\text{N}^{\text{av}}$ between the central (2, μ or α) and terminal position (1, τ or β) of N atoms in N₂O (Kaiser, 2002; Brenninkmeijer and Röckmann, 2000; Yoshida and Toyoda, 1999), i.e. $\delta^{15}\text{N}^{\text{sp}} = \delta^{15}\text{N}^{\alpha} - \delta^{15}\text{N}^{\beta}$. For consistency with many recent publications in the field, we here adopt the nomenclature from Yoshida and Toyoda (1999), α and β , for the two positions.

The different sources and sinks of N₂O are associated with characteristic fractionation 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 stratosphere after partial photochemical removal is enriched in both heavy isotopes (Yoshida 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 observed enrichment is caused by kinetic isotope fractionation in the stratospheric sink reactions (Kaiser et al., 2006; 2002; Park et al., 2004; Röckmann et al., 2001; Yoshida and Toyoda, 2000; Rahn et al., 1998).

The multi-isotope signature of N₂O adds useful constraints on its budget. In particular, when the isotopic composition of tropospheric N₂O 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 N₂O 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

of ice sheets. Within the firn, air exchanges relatively freely in the upper layers and with the 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 densities larger than $\approx 815 \text{ kg m}^{-3}$, air is permanently trapped in closed bubbles in the ice and totally isolated from the atmosphere. The precise age range of air that can be retrieved from polar firn between the surface and bubble close-off depends on site specific characteristics like temperature, accumulation rate and porosity and typically ranges from several decades to 120 years.

For N_2O , a number of studies have reported isotope measurements from different Arctic and Antarctic firn drilling sites showing a steady decrease of the heavy isotope content of N_2O over the past decades (Park et al., 2012; Ishijima et al., 2007; Bernard et al., 2006; Röckmann et al., 2003; Sowers et al., 2002). A more recent study by Park et al. (2012) attempted to reconstruct the long-term trends in N_2O isotopic compositions and its seasonal cycles to further distinguish between the influence of the stratospheric sink and the oceanic source at Cape Grim, Tasmania, demonstrating that isotope measurements can help in the attribution and quantification of surface sources in general.

Taking into account the long atmospheric lifetime of N_2O and the fact that both hemispheres are well mixed on annual timescales, it is reasonable to assume that the results from these 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 signature (Buizert et al., 2012). Interestingly, for atmospheric methane (CH_4), another important greenhouse gas, a recent multi-site analysis of its carbon isotopic composition showed large differences among reconstructions from different sites (Sapart et al., 2013). In particular, firn fractionation effects related to diffusion and gravitational separation and their implementation in models (Buizert et al., 2012) have large effects on the reconstructed signals. Small differences in the diffusivity profiles of the firn column lead to large effects on the isotope signatures. Therefore, more robust results may be obtained by combining isotope information from a number of different sites in a multi-site reconstruction, including a critical 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., 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.

2 Materials and Methods

2.1 Firn air Sampling

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 programme (NEEM) in Greenland (77.45° N 51.06° W). These data are combined with 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 brief description is presented. Essentially a borehole is drilled in the firn to a certain depth and then the firn air sampling device is inserted into the borehole. The device consists of a bladder, a purge line and a sample line. When the sampling device reaches the desired depth the bladder is inflated to seal the firn hole and isolate the air below the bladder from the overlying atmosphere, and air is pumped out from the pore space below the bladder. Continuous online CO₂ concentration measurements are performed to verify that no contamination with contemporary air occurs during the extraction procedure. After the contaminating air has been pumped away, firn air is collected in stainless steel, glass or aluminium containers.

2.2 N₂O isotope analysis

The firn air samples from NEEM are analyzed for N₂O isotopocules at the Institute for Marine and Atmospheric research Utrecht (IMAU). The N₂O 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

remaining traces of CO₂ and other contaminants are removed on a capillary GC column (PoraPlot Q, 0.32 mm i.d., 25 m). The column is separated into a pre-column and an analytical column. This set-up eliminates interferences from other atmospheric compounds that have much longer retention times. Finally the sample is transferred to the IRMS via an open split interface. For the new NEEM samples reported here, each firn air sample has been 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 purposes.

$\delta^{15}\text{N}^{\text{av}}$ values are reported with respect to Air-N₂ while $\delta^{18}\text{O}$ refers to Vienna Standard Mean 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 $\delta^{15}\text{N}^{\text{av}}$ vs. Air-N₂, (44.9±0.4) ‰ for $\delta^{18}\text{O}$ vs. VSMOW. The intramolecular $\delta^{15}\text{N}^{\text{av}}$ values of the air standard are $\delta^{15}\text{N}^{\alpha} = (15.4\pm1.2)$ ‰ and $\delta^{15}\text{N}^{\beta} = (-2.7\pm1.2)$ ‰. The calibration of the intramolecular distribution follows Toyoda and Yoshida (1999). Typically the 1 σ standard deviations of replicate sample measurements are 0.1 ‰ for $\delta^{15}\text{N}^{\text{av}}$, 0.2 ‰ for $\delta^{18}\text{O}$ and 0.3 ‰ for $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$.

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).

In the “forward version” of LGGE-GIPSA, a physical transport model uses a historic evolution of atmospheric N₂O mole fractions to calculate the vertical profiles of mole fractions in firn. For the isotopocules, further simulations are performed separately to calculate their respective vertical profiles. Important parameters needed to constrain the

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 determined as a function of depth for each firn-drilling site by modelling the mole fractions in firn for trace gases with well known atmospheric histories (Buizert et al., 2012; Witrant et al., 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 specific gas. It is noteworthy that diffusivity is not constrained equally well at all sites because different sets of constraints (e.g. number of available reference gases) are used at 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.

Due to the long N_2O residence time in the atmosphere, the global variability of the isotopic composition of N_2O is very small and no significant variations between individual background locations have been detected so far (Kaiser et al., 2003). In particular, the isotope 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 et al. 2006] and isotope ratio difference of -15‰ between average source and average tropospheric isotopic delta value). These differences are within the uncertainties of the firn air measurements used here and therefore the data from the northern and southern hemisphere are 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 $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ were published for those sites. These datasets were used for independent validation of **$\delta^{15}\text{N}^{\text{av}}$** and $\delta^{18}\text{O}$.

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 $\delta^{15}\text{N}^{\text{av}}$, but important for $\delta^{18}\text{O}$ 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 N₂O 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).

2.4 Scaling of different data sets

At present, no international reference materials for the isotopic composition of N₂O exist. Kaiser et al. (2003) and Toyoda et al. (1999) linked the isotopic composition of N₂O in tropospheric air to the international isotopes scales for nitrogen isotopes (Air-N₂) and oxygen isotopes (either VSMOW or Air-O₂). Our measurements are linked to a standard gas cylinder of tropospheric air with known N₂O mole fraction and isotopic composition based on the scale of Kaiser et al. (2003) for $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{18}\text{O}$ values and Yoshida and Toyoda (1999) for position dependent ¹⁵N values. However, the reference air cylinder used for the calibration was exhausted and had to be replaced three times over the years in which the different 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 because long-time isotope standards are not available. In fact, analysis of the data from the convective zone for the different sites, show small but significant differences from the 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 linear trends reported in that paper are $(-0.040 \pm 0.003) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\text{av}}$, $(0.014 \pm 0.016) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\alpha}$, $(-0.064 \pm 0.016) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\beta}$ and $(-0.021 \pm 0.003) \text{‰ a}^{-1}$ for $\delta^{18}\text{O}$. Since they were derived from direct air samples (unaffected by firn fractionation), these trends can be used as

a reference to re-scale the different firn air results from different dates. To do so, data from the diffusive zone ($p < 815 \text{ kg m}^{-3}$) for each individual site were scaled to one reference site, DC-99, taking into account the temporal differences in sampling and the model-assigned mean age of the firn air samples (see below). DC-99 was chosen as reference site because it has most measurements in the diffusive zone. Also, the precision of these measurements was high because high volume cylinders were available from which many measurements could be 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 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 ^{15}N 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.

The mole fraction data were scaled to the most recent international scale, NOAA-2006A from the CSIRO scale or the NOAA-2000 scale. Conversion of the NOAA-2000 data to the NOAA-2006A scale is done using a conversion factor available by National Oceanic and Atmospheric Administration (NOAA) (http://www.esrl.noaa.gov/gmd/cc1/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).

2.5 Global N₂O (isotope) budget calculations

The tropospheric budget is controlled by N₂O 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 N₂O. The model consists of a tropospheric N₂O reservoir (index T) into which N₂O is emitted from natural (E_{nat}) and anthropogenic (E_{anth}) sources. N₂O 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}).

The change in the tropospheric N₂O reservoir is given by the following mass balance equations (Allin et al, 2015):

$$n_T \frac{d\chi_T}{dt} = E_{nat} + E_{anth} - F_{exch}(\chi_T - \chi_S) \quad (1)$$

$$n_S \frac{d\chi_S}{dt} = F_{exch}(\chi_T - \chi_S) - L \quad (2)$$

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:

$$L = \frac{n_T \chi_T + n_S \chi_S}{\tau} \quad (3)$$

where τ is the atmospheric lifetime of 123⁺²⁹₋₁₉ a.

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

$$n_T \frac{d\chi_T \delta_T}{dt} = E_{nat} \delta_{nat} + E_{anth} \delta_{anth} + F_{exch}(\chi_S \delta_S - \chi_T \delta_T) \quad (4)$$

$$n_S \frac{d\chi_S \delta_S}{dt} = F_{\text{exch}}(\chi_T \delta_T - \chi_S \delta_S) - L \delta_L \quad (5)$$

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

$$n_T \frac{d\delta_T}{dt} = \frac{E_{\text{nat}}}{\chi_T} (\delta_{\text{nat}} - \delta_T) + \frac{E_{\text{anth}}}{\chi_T} (\delta_{\text{anth}} - \delta_T) + \frac{F_{\text{exch}} \chi_S}{\chi_T} (\delta_S - \delta_T) \quad (6)$$

$$n_S \frac{d\delta_S}{dt} = \frac{F_{\text{exch}} \chi_T}{\chi_S} (\delta_T - \delta_S) - \frac{L}{\chi_S} \varepsilon_L \quad (7)$$

where δ_T is either $\delta^{15}\text{N}^{\text{av}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ from the multi-site reconstruction as shown below. δ_{nat} and δ_{anth} is the isotopic composition of the natural and anthropogenic N_2O source, respectively (our target quantity). ε_L is the apparent Rayleigh fractionation factor associated with stratospheric destruction.

δ_S is also not known, but can be calculated using the analogue from Röckmann et al. (2003) by employing the observed apparent Rayleigh fractionation in the stratosphere (ε_{app}) (Table 3). Based on this, the relative isotope ratio difference between the stratosphere and the troposphere can be calculated by:

$$\delta_S = \left[(\delta_T + 1) \left(\frac{\chi_S}{\chi_T} \right)^{\varepsilon_{\text{app}}} - 1 \right] \quad (8)$$

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 N_2O 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 $\chi_T = 322 \text{ nmol mol}^{-1}$ to the pre-industrial level of $\chi_{T,\text{pi}} = 270 \text{ nmol mol}^{-1}$ and the relative enrichment of stratospheric N_2O relative to tropospheric N_2O described by Eq. 8 remains constant over time. The effect of changing the N_2O 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 (≈ 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 natural component.

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 firm 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:

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

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

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 N₂O scenarios within the uncertainty envelope of the firm atmospheric N₂O reconstruction constrained by the covariance matrix **B**. For each of these atmospheric N₂O scenarios, we calculated the corresponding N₂O emission time series. The range of emissions from these scenarios then provides a realistic estimate for the uncertainty in N₂O emissions.

We carried out the same analysis for the different N₂O isotopocules: for each isotopocule (δ value), we generated a covariance matrix **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 in the results provides an uncertainty estimate of the isotopic source signatures.

3 Results

3.1 Mean age

The mean age of N_2O in air sampled from different depths in the firn for all datasets that are used in this study is shown in Fig. 1. The strong change in the mean age gradient that is clearly visible in each profile reflects the transition between the diffusive and bubble close-off zones, which occurs at a specific depth and mean age for each site (marked with x on Fig. 1). Fig. 1 also shows that for each site the few samples that are collected within the bubble close-off zone provide the constraints for most of the reconstructed record (for instance, at BKN-03, 50 m depth is the beginning of the bubble close-off zone). In addition to the mean age, the width of the age spectrum also increases with depth. Therefore, the temporal resolution of 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.

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).

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.

The atmospheric history that has been reconstructed from these firn datasets using the multi-site inversion (using the data from NEEM-09, NEEM-EU-08, NGRIP-01^{Bernard}, BKN-03, DC-99, DML-98) as described in section 2.4 is shown in the left column of Fig. 2. The solid line

shows the scenario that leads to the best fit with the firm data as shown in the middle panel, and the dashed lines show the upper and lower range of possible scenarios that would still produce an acceptable fit to the data within the uncertainty bars. Color-coded symbols show data plotted at their respective mean age (as derived from the firm air model). When the best-fit scenario is used as input for the forward firm air model for each individual site, the model produces the vertical profiles that are shown as coloured lines together with the data in the 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, which is expected after a successful inversion procedure and with consistent data sets. The right panels in Fig. 2 show the differences between these model results and the data. For the data that were used in the multi-site inversion the model-data differences are generally very small, although individual firm drilling sites in some cases show small systematic deviations, in particular in the close-off zone. This means that when inversions would have been performed on individual sites, the optimal reconstructions would be slightly different. Hence, 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 left panels show that all data fall within the uncertainty bars of the reconstructed scenario of the inversion.

From 1940 to 2008 the total changes of the δ values of atmospheric N_2O are $(-2.2 \pm 0.2) \text{‰}$ for $\delta^{15}\text{N}^{\text{fav}}$, $(-1.0 \pm 0.3) \text{‰}$ for $\delta^{18}\text{O}$, $(-1.3 \pm 0.6) \text{‰}$ for $\delta^{15}\text{N}^{\alpha}$ and $(-2.8 \pm 0.6) \text{‰}$ for $\delta^{15}\text{N}^{\beta}$ respectively (Fig. 2, left panels). The average linearized trends are $(-0.032 \pm 0.004) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\text{fav}}$, $(-0.014 \pm 0.008) \text{‰ a}^{-1}$ for $\delta^{18}\text{O}$, $(-0.019 \pm 0.015) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\alpha}$ and $(-0.041 \pm 0.020) \text{‰ a}^{-1}$ for $\delta^{15}\text{N}^{\beta}$. These overall trends are slightly lower compared to previous studies that used only the data at individual sites (Ishijima et al., 2007; Bernard et al., 2006; Röckmann et 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 within the combined uncertainties. We note that comparisons of average linear trends can be flawed when the firm air records have different length and the temporal profiles do not change linearly (see below). Trends for $\delta^{15}\text{N}^{\alpha}$ are smaller in magnitude than for $\delta^{15}\text{N}^{\beta}$, while results from Bernard et al. (2006) showed stronger changes for $\delta^{15}\text{N}^{\alpha}$ than for $\delta^{15}\text{N}^{\beta}$. However, in that study the trends were largely determined from measurements on young ice core samples with comparatively higher measurement errors and larger scatter.

Data from two sites were not included in the multi-site inversion and are used as independent 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 thus independently validate our results. The $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{18}\text{O}$ data from Sowers et al. (2002) (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 uncertainty envelopes of the multi-site reconstruction. Inter-laboratory calibration differences might be a possible explanation for the discrepancy, but the differences are not a systematic shift, and they are larger than offsets among laboratories that were established in the past (Sapart et al., 2011; Kaiser et al., 2003). In fact, the data reported by Sowers et al. (2002) were actually measured in two different laboratories with good agreement. So measurement flaws can be excluded. A possible origin of the difference could be based on the reconstruction model. Because the uncertainties on the South Pole data are large, compared to 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 consideration since when pumping firm air and filling the sampling flasks you could encounter uncertainties (contamination, possible leak, fractionation, incomplete flask flushing etc). At 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 N_2O mole fraction and isotopic composition remained the same, but an additional decadal variability was introduced for $\delta^{15}\text{N}^{\text{av}}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$. In addition to that, the uncertainty envelopes doubled because of the scale inconsistencies. All scaling approaches produce results that are consistent with our preferred scaling to DC-99 within the uncertainty envelopes. We conclude that scaling removed the discrepancies that would cause larger uncertainties if the original data were used instead, but the re-scaling does not introduce 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

generalized cross validation criterion, ensuring that the resolution obtained from the inverse 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 the regularization term was increased by a factor 10 led to nearly linear tropospheric histories within the uncertainty envelopes presented in Appendix C (Fig. C2). This combined with the 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 significantly different from straight lines within the current uncertainties.

3.3 Reconstruction of the N₂O emission history

Fig. 3 shows the temporal evolution of the global N₂O 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 can be explained in the mass balance model by a (4.4±1.7) Tg a⁻¹ N increase in the emissions from 1940 to 2008. The emissions increased with an increasing trend until 1975, then the annual increase continued, but at a slower rate up to 1990, and from then on the annual emissions have stayed approximately constant or even decreased slightly. The minor increase in the N₂O mole fraction towards the end of the time series is likely not significant and does influence our reconstructions. The corresponding changes in the mole fraction are difficult to 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 Tg a⁻¹ N.

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 firm 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

in the isotope signatures of the total N₂O source, with their accompanied uncertainties, as calculated from the atmospheric mass balance model (section 2.5). The total source is split into an assumed constant "natural" and an increasing "anthropogenic" component and the right panels show the isotopic evolution of the "anthropogenic" component.

Results show that the average $\delta^{15}\text{N}^{\text{av}}$ of the total N₂O source, over the reconstruction period, is $(-7.6 \pm 0.6) \text{‰}$ where the uncertainty is calculated using the 1σ uncertainty from the scenarios with respect to the mean value (magenta lines). There is no statistically significant long-term trend, but a temporal variability is observed on the decadal scale that might mask this trend. $\delta^{15}\text{N}^{\text{av}}$ first decreased from $(-6.5 \pm 0.6) \text{‰}$ in 1940 to $(-8.5 \pm 0.6) \text{‰}$ in 1965, then slowly increased again to $(-6.6 \pm 0.6) \text{‰}$ in 1985, followed by another decrease to $(-8.5 \pm 0.6) \text{‰}$ in 2008. These oscillations originate from the slightly curved trends in the isotopic reconstructions for $\delta^{15}\text{N}^{\text{av}}$ in Fig. 4 (left panels).

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 $\delta^{15}\text{N}^{\text{av}}$ signature of the anthropogenic source has an average value of $(-18.2 \pm 2.6) \text{‰}$. It initially increases (the small initial decrease is not significant) from $(-21.5 \pm 2.6) \text{‰}$ in 1940 to $(-8.6 \pm 2.6) \text{‰}$ in 1990, when it starts to slowly decrease reaching $(-15.4 \pm 2.6) \text{‰}$ in 2008. During the early part of the reconstruction period before 1970, when the "anthropogenic" 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 calculating the 1σ uncertainties over the entire period from the generated scenarios. This applies to all anthropogenic isotope signatures.

The budget calculations suggest an overall trend towards more enriched anthropogenic emissions, but the uncertainties are large. Mathematically, this trend arises from the fact that the isotope reconstructions yield relatively linear temporal isotope trends, whereas the source strength increases in a strongly non-linear fashion (Fig. 4). In the beginning of the record a 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 shift. This can only be solved mathematically by a lower $\delta^{15}\text{N}^{\text{av}}$ value for the small "anthropogenic" emissions in the early part of the firm record. A constant $\delta^{15}\text{N}^{\text{av}}$ source

signature would result in a small temporal change in $\delta^{15}\text{N}^{\text{av}}$ of atmospheric N_2O in the beginning of the record and increasing isotope trends with increasing emissions, similar to the exponential curves that were fitted to the firn air data in Röckmann et al. (2003).

The $\delta^{18}\text{O}$ of the total source varies within $(27.2 \pm 2.6) \text{‰}$ over the entire period. $\delta^{18}\text{O}$ does not show significant decadal scale oscillations because the reconstructed scenario for $\delta^{18}\text{O}$ is even more linear than the $\delta^{15}\text{N}^{\text{av}}$ scenario. For this reason, as explained above, in the best fit scenario the $\delta^{18}\text{O}$ of the anthropogenic source for the initial 30 years has a more depleted value starting with $(7.7 \pm 2.6) \text{‰}$ in year 1940, reaching $(31.1 \pm 2.6) \text{‰}$ in year 1975 and remaining around this value until 2008 (Fig. 4). However, the relatively larger uncertainty envelopes for the atmospheric history of $\delta^{18}\text{O}$ actually allow scenarios with smaller $\delta^{18}\text{O}$ changes in the beginning of the record and larger changes in the later period, which means that the reconstruction does not exclude a constant value for the anthropogenic $\delta^{18}\text{O}$ source signature. The available dataset thus does not allow quantifying a long-term trend in $\delta^{18}\text{O}$.

For the position dependent ^{15}N signatures of the total source no significant long-term trends were detected. For $\delta^{15}\text{N}^{\alpha}$ no decadal scale variability is observed, whereas for $\delta^{15}\text{N}^{\beta}$ a temporal variability is observed similar to the $\delta^{15}\text{N}^{\text{av}}$. The uncertainty ranges for $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ are about a factor 2 greater than for $\delta^{15}\text{N}^{\text{av}}$, which is due to the larger analytical error that leads to higher uncertainties in the scenario reconstructions. $\delta^{15}\text{N}^{\alpha}$ varies in the range $(-3.0 \pm 1.9) \text{‰}$, $\delta^{15}\text{N}^{\beta}$ in the range $(-11.7 \pm 2.3) \text{‰}$.

The temporal evolution of $\delta^{15}\text{N}^{\alpha}$ of the anthropogenic source looks similar to that of $\delta^{18}\text{O}$, but with even larger variations and uncertainties with a total average of $(-8.1 \pm 1.7) \text{‰}$. $\delta^{15}\text{N}^{\alpha}$ increased from $(-18.2 \pm 1.7) \text{‰}$ in 1940 to an average of $(-5.4 \pm 1.7) \text{‰}$ in 1975 and retained this value until 2008. In contrast, $\delta^{15}\text{N}^{\beta}$ is similar to that of $\delta^{15}\text{N}^{\text{av}}$ with a total anthropogenic source average of $(-26.1 \pm 8.4) \text{‰}$. $\delta^{15}\text{N}^{\beta}$ initially decreases from $(-19.1 \pm 8.4) \text{‰}$ to $(-42.0 \pm 8.4) \text{‰}$ in 1955 only to increase again to $(-10.6 \pm 8.4) \text{‰}$ in year 1990 and then decrease again to $(-26.0 \pm 8.4) \text{‰}$ in 2008.

4 Discussion

The N_2O mole fraction atmospheric history from our multi-site reconstruction is in agreement with recent work from Meinshausen et al. (2016) who combined all available published N_2O 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 smaller extent with Machida et al. (1995).

Battle et al. (1996) collected firn air data and Machida et al. (1995) used ice data. Both studies 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 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 firn air model and possible differences between sites may contribute. In our case we used measurements from 5 sites to constrain our model while Battle et al. (1996) and Machida et 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 Battle et al. (1996) only used two gases."

From the combination of the firn air reconstruction with a simple two-box model we conclude that N₂O emissions increased from (11.9±1.7) Tg a⁻¹ N in 1940 to (16.4±1.7) Tg a⁻¹ N in 2008. This agrees, within uncertainties, with previous firn reconstruction studies from 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 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 agreement with our findings.

To investigate the effect the N₂O lifetime on the N₂O isotopic signatures (Prather et al. (2015)) we performed a sensitivity study where we linearly changed the N₂O lifetime from 123 years pre-industrially (≈1750) to 119 years in modern times (2008). The results are shown in 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 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 lifetime in the model leads to changes in the isotope signatures of the order of (2.0±1.0) ‰. The lifetime effect is most pronounced for the earliest part of the record (<1970) where the reconstruction uncertainties are larger than this systematic uncertainty.

We furthermore investigated the sensitivity to the value of F_{exch} (stratosphere – troposphere 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.

The increase in N_2O emissions over the past decades resulted in an overall decrease of all isotopic signatures of atmospheric N_2O with time. The isotopic signature of the total source of N_2O (Fig. 4, middle panels) is strongly depleted in all heavy isotopes compared to tropospheric N_2O (Table 3), which is due to the strong enrichment associated with the removal in the stratosphere. In Table 3 the isotopic composition for the pre-industrial period (≈ 1750) ($\delta_{\text{nat,pi}}$) is compared with the derived anthropogenic source signature derived from our multi-site reconstruction (δ_{anth} , averaged from 1940 to 2008). The results show that the anthropogenic source is more depleted in heavy isotopes than the natural one for all signatures, confirming results from studies prior to firm air measurements (Rahn and Wahlen, 2000), and from studies that used forward firm air modelling on measurements from individual sites (Park et al., 2012; Ishijima et al., 2007; Röckmann et al., 2003). It is important to remember that we assume the natural sources to be constant, but the method itself does not provide evidence for this.

Anthropogenic N_2O 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 $1 \text{ Tg a}^{-1} \text{ N}$.

N_2O emitted from agricultural soils and biomass burning is more depleted in $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{18}\text{O}$ than the tropospheric background (Park et al., 2011; Goldberg et al., 2010; Ostrom et al., 2010; Tilsner et al., 2003; Perez et al., 2001; 2000) while N_2O emitted from other minor sources, such as automobiles, coal combustion and industry, has values closer to tropospheric N_2O values (Syakila and Kroeze, 2011; Toyoda et al., 2008; Ogawa and Yoshida, 2005a; 2005b). An increase of strongly depleted agricultural emissions in the first part of our reconstruction, followed by a decreasing relative contribution from agriculture and increasing contributions from more enriched sources like industry, automobiles and coal combustion, could qualitatively explain the reconstructed changes of isotope signatures of both the total

source and the anthropogenic component. The global N₂O 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.

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 constant or even decreased until 2000, and increased again after 2000. The reasons of the decrease between 1985 and 2000 are a shift towards organic soil cultivation in combination with more efficient agricultural methods and fertilizer use. This variation in fertilizer use qualitatively matches with the temporal evolutions of our reconstructed source signatures, but the trends in the reconstructions are likely too large to be explained by this source change only.

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

Additional evidence for potential changes in the N₂O source composition between the pre-industrial 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 $\delta^{15}\text{N}^{\text{rav}}$ signature between the pre-industrial and the anthropogenic source derived from our reconstruction is primarily due to a change at position $\delta^{15}\text{N}^{\text{b}}$, whereas $\delta^{15}\text{N}^{\text{a}}$ remains relatively constant. This is reflected by a larger difference in $\delta^{15}\text{N}^{\text{sp}}$ 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 $\delta^{15}\text{N}^{\text{sp}}$. N₂O produced during nitrification and fungal denitrification had a high $\delta^{15}\text{N}^{\text{sp}}$ of (33±5) ‰ and N₂O from denitrification and nitrifier denitrification had a low $\delta^{15}\text{N}^{\text{sp}}$ of

(0±5) ‰. Park et al., (2012) used these two endmembers to calculate a change in the relative fractions of these source classes over time based on their firm air data. Although this approach is strongly simplified and several other sources and factors may contribute (Toyoda et al., 2015), we use the results from our box model calculations (Table 3) in a similar way to estimate the fraction of the two source categories according to the following simple mass balance calculation:

$$F_{\text{high}} = \frac{\delta^{15}\text{N}_{\text{meas}}^{\text{sp}} - \delta^{15}\text{N}_{\text{low}}^{\text{sp}}}{\delta^{15}\text{N}_{\text{high}}^{\text{sp}} - \delta^{15}\text{N}_{\text{low}}^{\text{sp}}} \quad (11)$$

This returns a fractional contribution of the $\delta^{15}\text{N}_{\text{high}}^{\text{sp}}$ component of (19±4) % to the total pre-industrial emissions and (35±11) % to the total present source. The errors were derived by propagating the errors of the $\delta^{15}\text{N}^{\text{sp}}$ endmembers and $\delta^{15}\text{N}_{\text{meas}}^{\text{sp}}$ 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 $\delta^{15}\text{N}^{\text{sp}}$ 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 $\delta^{15}\text{N}_{\text{high}}^{\text{sp}}$ 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 $\delta^{15}\text{N}_{\text{high}}^{\text{sp}}$ component.

The temporal changes of the derived fraction of nitrification are in good qualitative agreement with the results from Park et al. (2012), who reported a change of (13±5) % from 1750 to (23±13) % today. However, the absolute numbers derived from our study are higher than the 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 3; eq. 7,8). In our study we used the averaged lowermost stratospheric apparent isotope 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 isotopic source signatures from the mass balance model. The choice of this value thus adds a

systematic source of uncertainty to the absolute value of the $\delta^{15}\text{N}_{\text{high}}^{\text{sp}}$ fractions reported above (F_{high}).

Nevertheless, this systematic uncertainty should not alter the overall *change* in F_{high} from pre-industrial to modern times and the results from our multi-site reconstruction of the isotopic composition of N_2O 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.

5 Conclusions

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

The reconstruction of mole fraction and isotopic composition was used to investigate temporal changes in the isotopic signature of N_2O emissions over the study period. The average total source for $\delta^{15}\text{N}^{\text{av}}$ and $\delta^{15}\text{N}^{\beta}$ shows no statistically significant long-term trend but possibly significant decadal scale variability. For $\delta^{18}\text{O}$ and $\delta^{15}\text{N}^{\alpha}$ of the total N_2O 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 $\delta^{15}\text{N}^{\text{av}}$ 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 $\delta^{18}\text{O}$ is likely, but not significant given the larger uncertainties for this signature.

Nevertheless, the isotope signal in $\delta^{15}\text{N}^{\text{av}}$ may also be a signal for changing source contributions over time. Bottom-up models suggest that N_2O emitted from agricultural soils was the dominant contributor to the anthropogenic N_2O increase in the first decades. Smaller contributions due to emissions from more enriched sources, like industry, automobiles and 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. 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 scenario is incorrectly constrained.

Results from the mass balance model yield an increase in ^{15}N site preference between the pre-industrial and modern total N_2O source. When this trend is evaluated with a simplified two-endmember mixing model, the results suggest an increase of nitrification sources relative to denitrification-related sources over the industrial period.

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Table 1. Site information on the drilling locations of the North Greenland Ice core Project (NGRIP-01^{Ishijima}, NGRIP-01^{Bernard}), Berkner Island (BKN-03), North Greenland Eemian Ice drilling Project (NEEM-EU-08, NEEM-09), Dome Concordia (DC-99) and Dronning Maud Land (DML-98), where firn air samples were collected, and two key meteorological variables of each site.

Site	Location	Mean annual temperature (°C)	Surface accumulation rate (water equivalent) (cm a ⁻¹)	Sampling year
NGRIP-01 ¹	75° N 42° W	-31	20	2001
BKN-03 ²	79° S 45° W	-26	13	2003
NEEM-EU-08	77.4° N 51.1° W	-29	22	2008
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)

971 Table 2. Detailed information in the mole fraction and the isotopic composition of the
972 laboratory reference gases used for correcting each set of firn air samples.

Site	Sampling year	Mole fraction (nmol mol ⁻¹)	$\delta^{15}\text{N}^{\text{av}}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{15}\text{N}^{\beta}$ (‰)	$\delta^{15}\text{N}^{\alpha}$ (‰)
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- EU-08	2008	324	6.22	44.40	-3.08	15.52
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 3. Emission fluxes and isotopic composition of the natural and anthropogenic source 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).

Natural source (E_{nat} , $\delta_{\text{nat},\text{pi}}$) ¹		
	This study	Park et al. (2012)
E_{nat} (Tg a ⁻¹ N)	11.0±1.7	11.1
$\delta^{15}\text{N}^{\text{av}}$ (‰)	-5.2±0.2	-5.3±0.2
$\delta^{18}\text{O}$ (‰)	33.1±0.2	32.0±0.2
$\delta^{15}\text{N}^{\alpha}$ (‰)	-1.9±1.0	-3.3±1.0
$\delta^{15}\text{N}^{\beta}$ (‰)	-8.3±1.1	-7.5±1.1
$\delta^{15}\text{N}^{\text{sp}}$ (‰)	6.4±1.5	4.2±1.5
Anthropogenic source (E_{anth} , δ_{anth})		
	This study	Park et al. (2012)
E_{anth} (Tg a ⁻¹ N)	5.4±1.7	6.6
$\delta^{15}\text{N}^{\text{av}}$ (‰)	-18.2±2.6	-15.6±1.2
$\delta^{18}\text{O}$ (‰)	27.2±2.6	32.0±1.3
$\delta^{15}\text{N}^{\alpha}$ (‰)	-8.1±1.7	-7.6±6.2
$\delta^{15}\text{N}^{\beta}$ (‰)	-26.1±8.4	-20.5±7.1
$\delta^{15}\text{N}^{\text{sp}}$ (‰)	18.0±8.6	13.1±9.4
Stratospheric Loss ¹		
	This study	Park et al. (2012)
F_{exch} (Tmol s ⁻¹)	0.22	NA
L (Tg a ⁻¹ N)	12.3	NA
$\epsilon_{\text{app}}^{15}\text{N}^{\text{av}}$ (‰)	-16.2	-14.9
$\epsilon_{\text{app}}^{18}\text{O}$ (‰)	-13.4	-13.3
$\epsilon_{\text{app}}^{15}\text{N}^{\alpha}$ (‰)	-23.0	-22.4
$\epsilon_{\text{app}}^{15}\text{N}^{\beta}$ (‰)	-9.4	-7.1

N₂O Lifetime (a)

This study

Park et al. (2012)

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

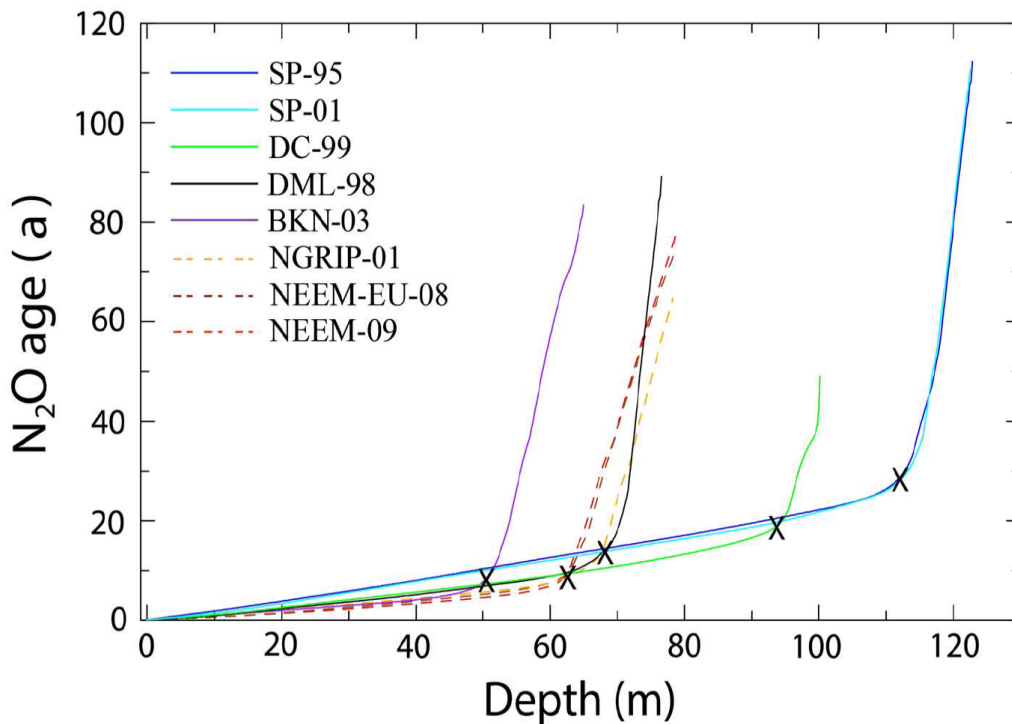
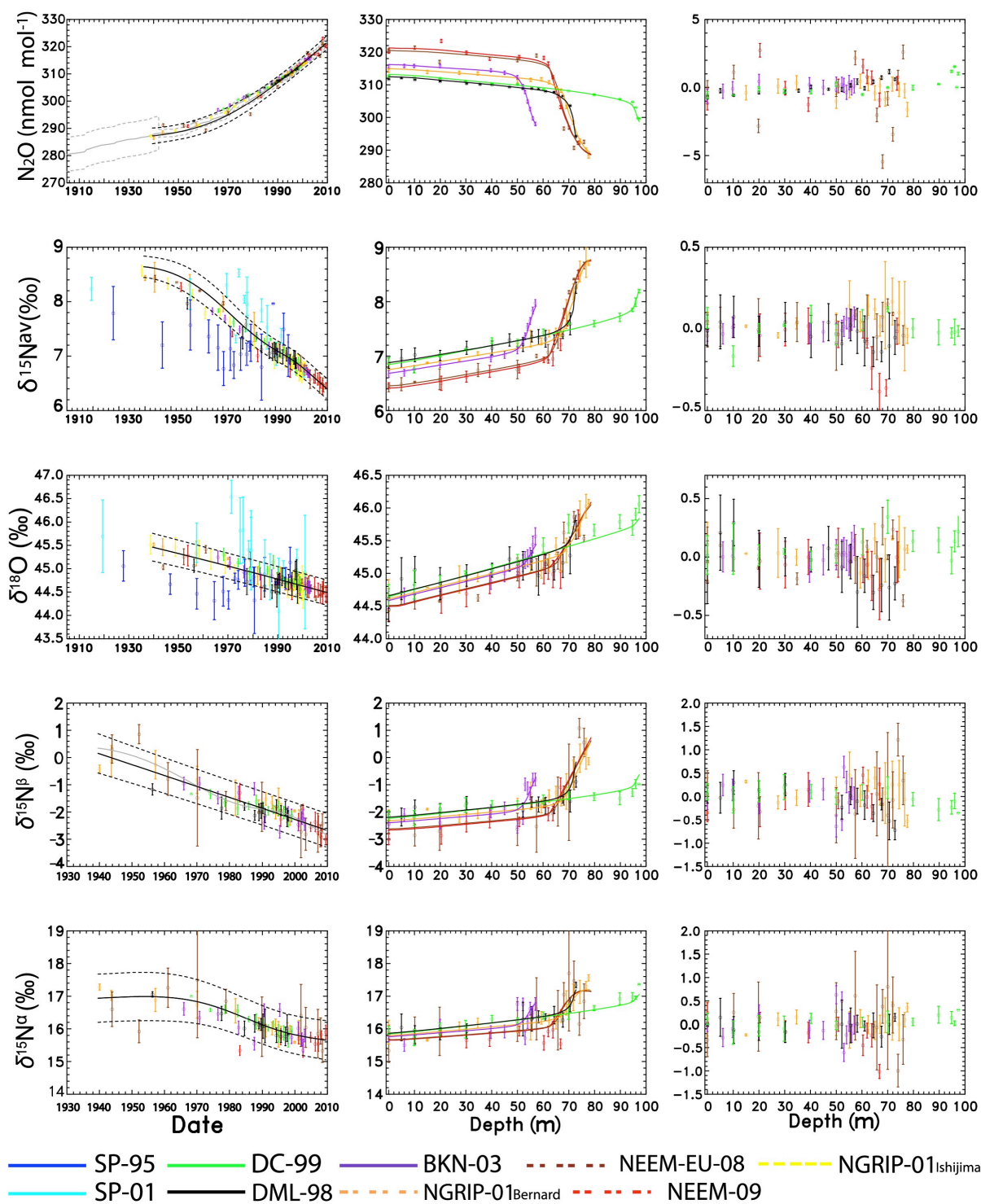


Figure 1. N₂O mean ages in firn versus depth. The dashed lines represent the sites from the NH (North Greenland Ice-core Project [NGRIP-01 Bernard], North Eemian Ice-core Project [NEEM-09, NEEM-EU-08]) and the solid lines the SH sites (South Pole [SP-01, SP-95], Dome C [DC-99], Dronning Maud Land [DML-98] and Berkner Island [BKN-03]). The numbers accompanying the sites are the corresponding drilling years. Marker X indicates the transition between the firn diffusive zone and the bubble close-off zone for each site. Dashed orange line NGRIP-01, dashed brown NEEM-EU-08, dashed red NEEM-09, purple line BKN-03, black DML-98, green DC-99, blue SP-95 and light blue SP-01.



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Figure 2. Left: Reconstructed atmospheric scenarios (black solid line with dashed lines indicating the 2σ uncertainty intervals) and results of the firn air samples (corrected for firn fractionation) plotted at their respective assigned mean age. Middle: corresponding depth profiles, symbols show the measurements and solid lines the results of the forward model 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 NEEM-09, Purple: BKN-03, Black: DML-98, Green: DC-99, Blue: SP-95 and Light Blue: SP-01. Data from NGRIP-01_{Ishijima} SP-95 and SP-01 were not used in the atmospheric reconstruction and are only plotted for comparison purposes here.

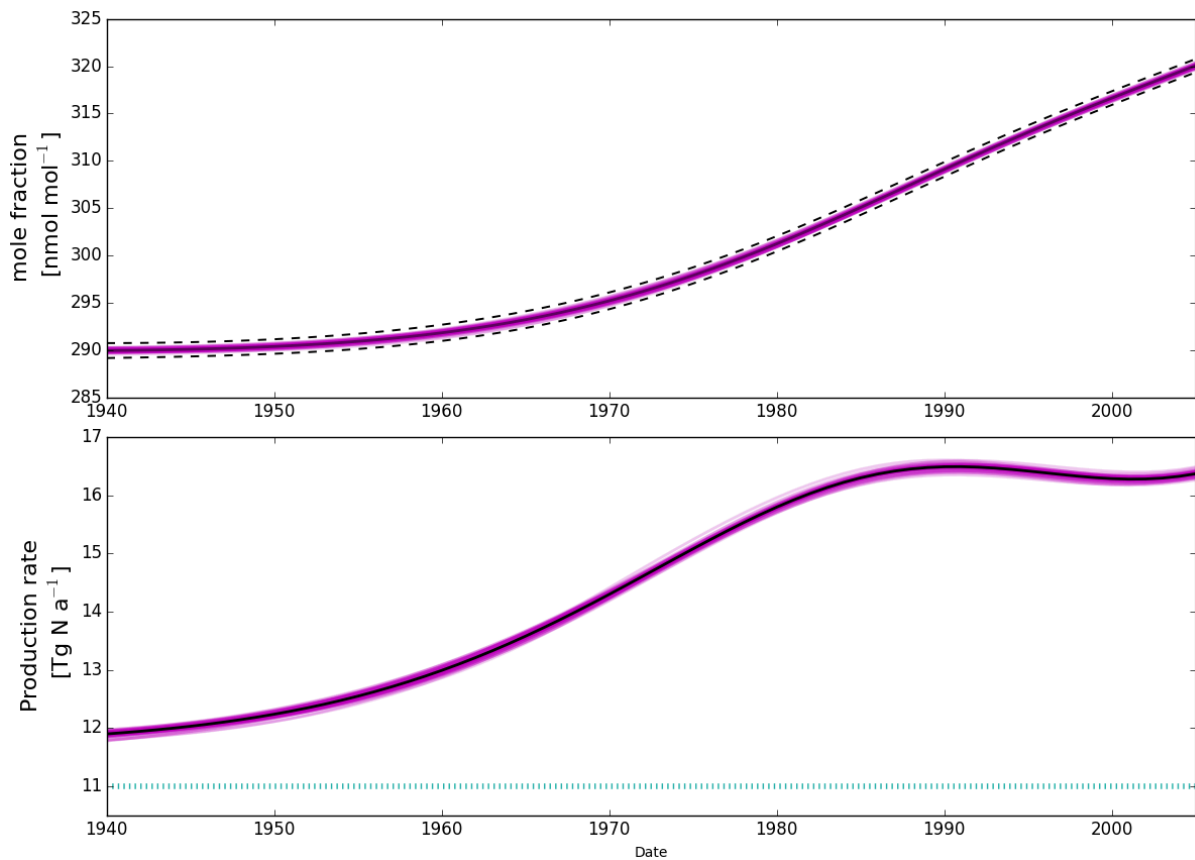


Figure 3: Top panel. N_2O mole fraction history constrained with the most precise data at NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed black lines) and the scenarios within the uncertainty envelopes that were used in the mass balance model (magenta lines)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

Bottom panel. N_2O production rate as calculated from the mass balance model. 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. Dotted light green line denotes the natural source emissions which were kept constant in our model runs.

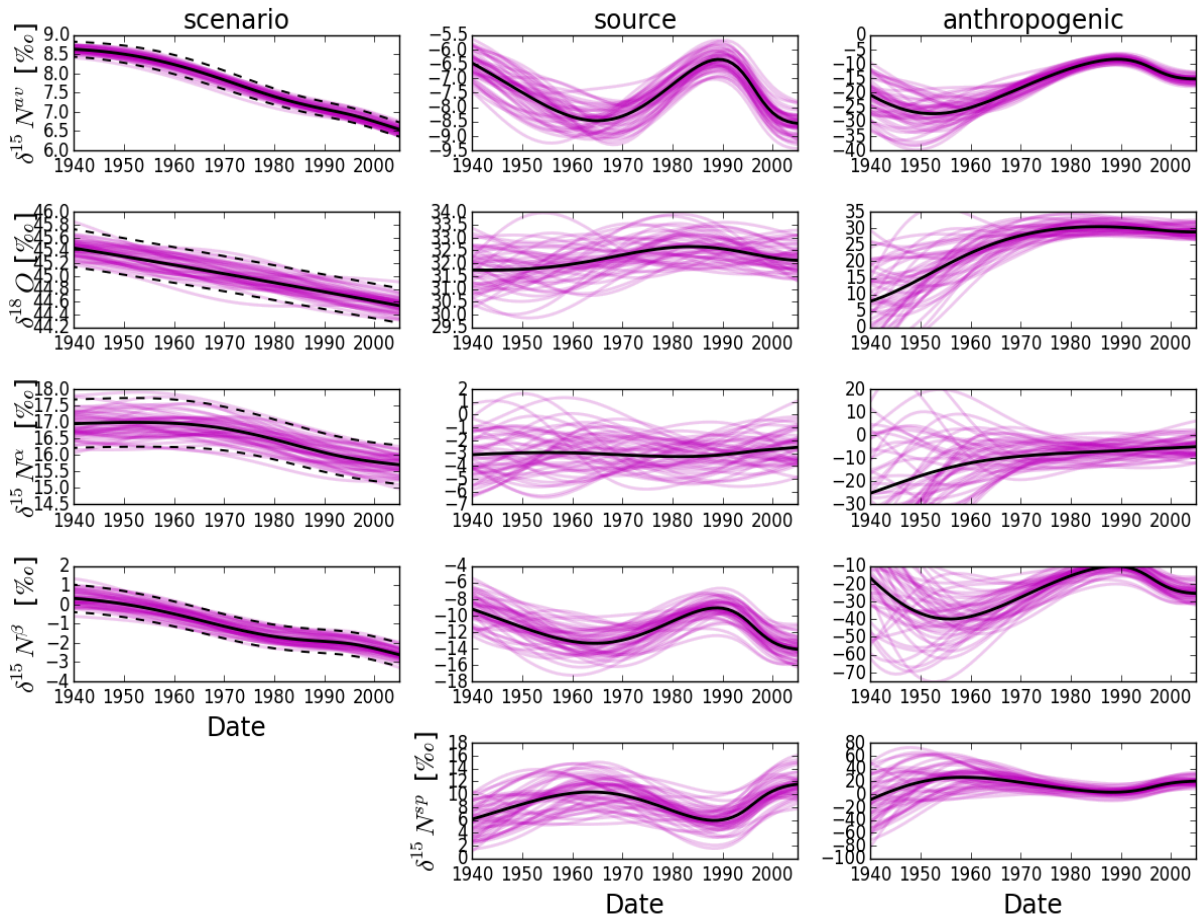


Figure 4: Left panels: Historic evolution of $\delta^{15}\text{N}^{\text{av}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\text{a}}$ and $\delta^{15}\text{N}^{\text{b}}$ in N_2O as derived from the firm air reconstruction. Middle panels: isotope signatures of the total emitted N_2O . Right panels: 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 N_2O histories in the left panels.

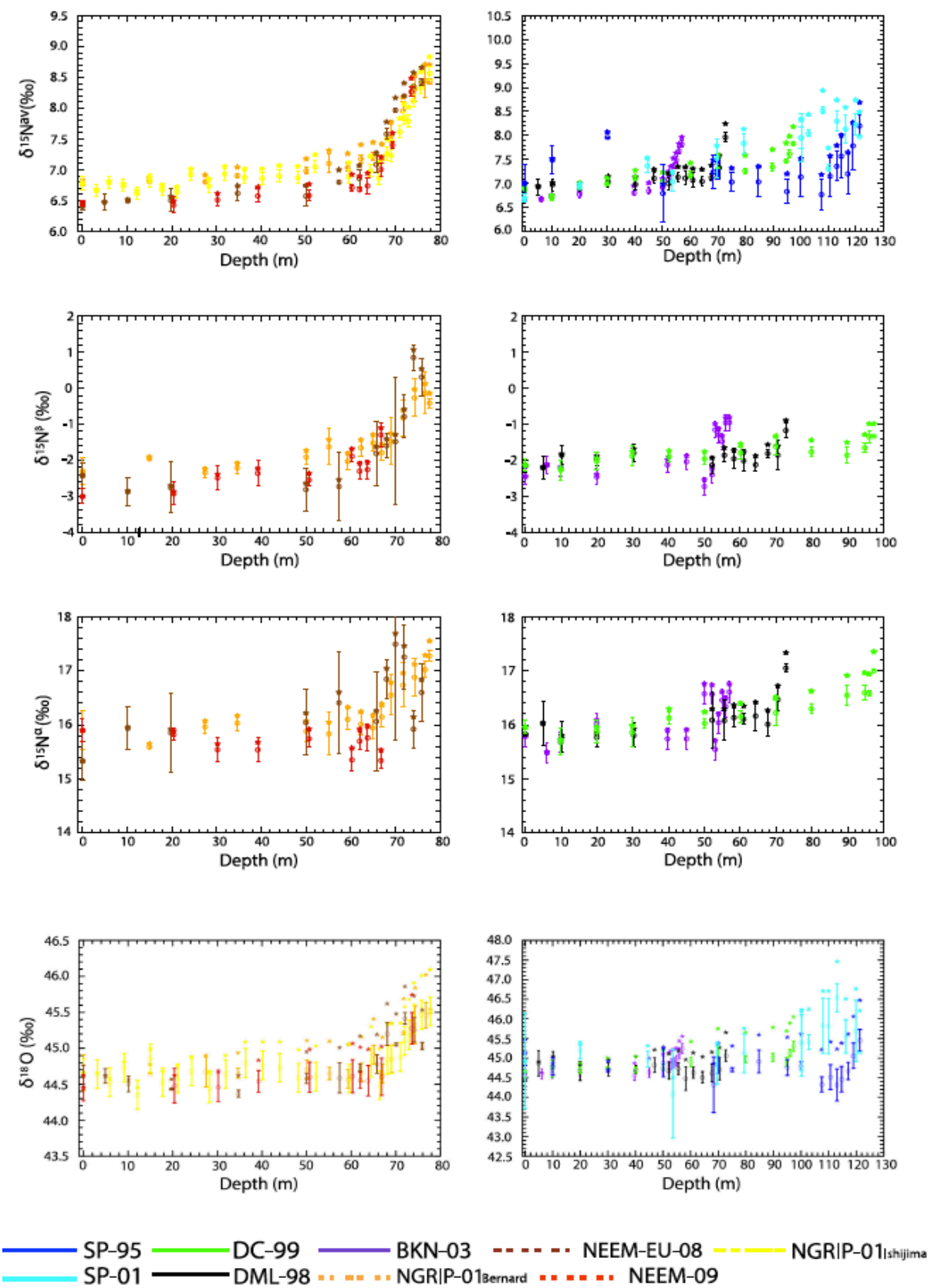


Figure A1: Effect of firn fractionation on N₂O isotopic composition in firn. Original measurements are plotted as stars, data corrected for firn fractionation are plotted as circles with error bars. The left hand side shows Northern hemisphere sites, orange: NGRIP-01_{Bernard}, yellow: NGRIP-01_{Ishijima}, 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

Appendix B: Data processing

In this study isotope deltas (δ) are used to denote the relative $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratio difference of N₂O in firn air with respect to a standard reference,

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

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

There is a disagreement between reported trends of the position dependent $\delta^{15}\text{N}_{\text{av}}$ values reported in the literature from firn air on the one hand and archived air samples on the other 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 directly on archived air samples should be fully consistent with top firn air samples of the various data sets, which were collected over a decade or more, since the air in the diffusive zone is not very old. However, this is not the case. Using the high-precision determination of 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 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 maximum age difference from diffusive zone to surface corresponds to $\Delta\text{age} = \Delta_{\text{DC } t-t_0} = 10$ a. Below you can find the equations used:

$$\delta_{\text{INT}} = \delta_{t-t_0} - \delta_{\text{DC } t-t_0} + m (\Delta_{t-t_0} - \Delta_{\text{DC } t-t_0}) \quad (2)$$

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

Where m is the slope connecting the two points we want to interpolate. The applied scaling (δ_{Final}) is given in the Table B1 below. To bring the data to the most recent international scale, NOAA-2006A, we used an equation extracted from a correlation between a scale ratio of NOAA-2006A to CSIRO versus the mole fraction of N_2O . The correlation showed higher scale ratio for low fraction values and lower scale ratio for higher mole fraction values. The equation extracted is given below:

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

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

Site	$y(\text{N}_2\text{O})(\text{nmol mol}^{-1})$		
	Re-scaled average	Expected trend change	Correction
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

Site	$\delta^{15}\text{N}^{\text{av}}(\text{‰})$		
	Re-scale average	Expected trend change	Correction
SP-95	1.43±0.56	0.16±0.00	-1.27±0.56
DML-98	-0.18±0.12	0.04±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

Site	$\delta^{18}\text{O}$ (‰)		
	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±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

Site	$\delta^{15}\text{N}^{\text{B}}$ (‰)		
	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

Site	$\delta^{15}\text{N}^{\text{A}}$ (‰)		
	Re-scale average	Expected trend	Correction
		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

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

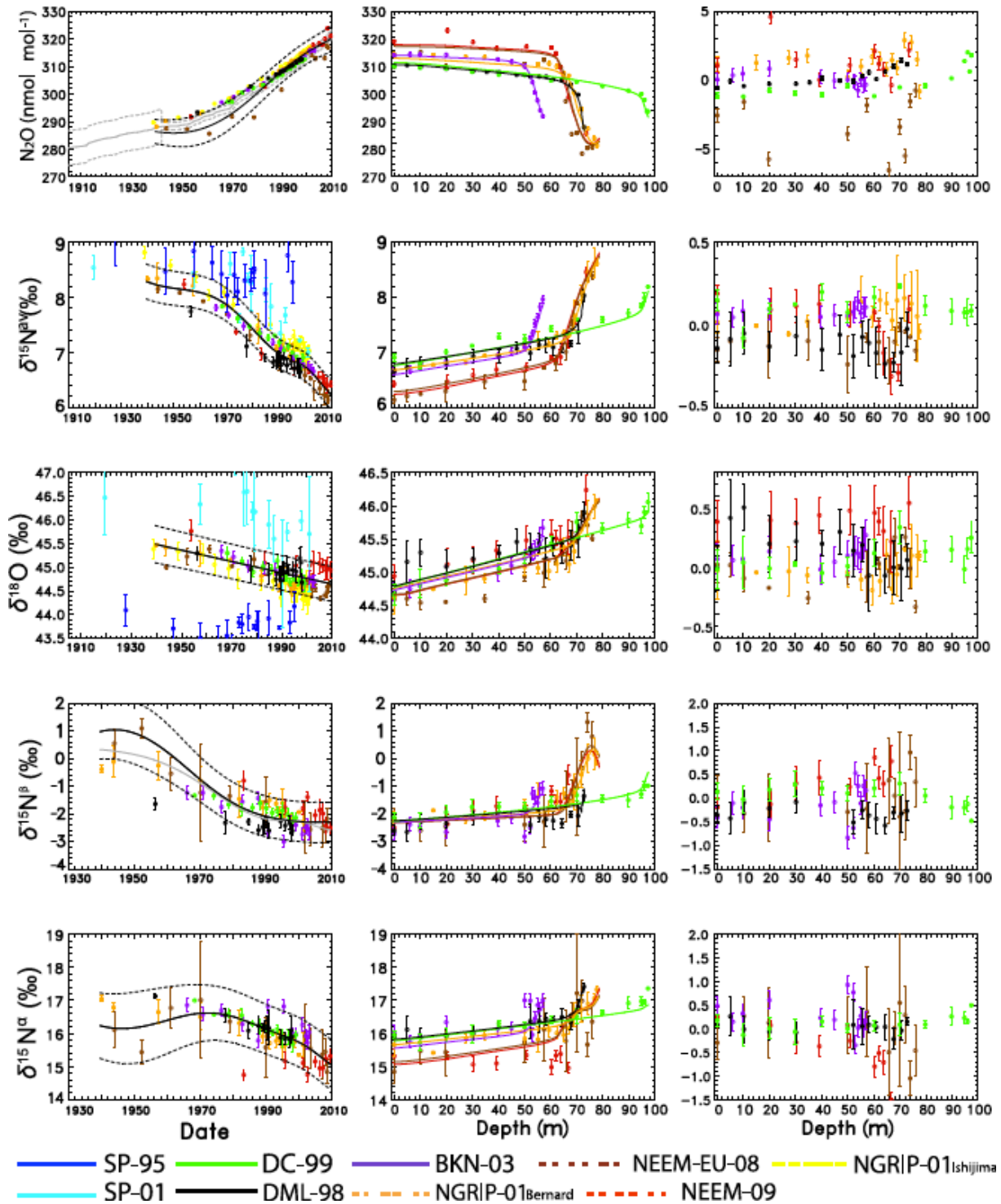


Figure C1. Results of the firn data evaluation (similar to Figure 2) using the data without re-scaling as indicated in the text, Orange: NGRIP-01_{Bernard}, Yellow: NGRIP-01_{Ishijima}, Brown: NEEM-EU-08, Red: NEEM-09, Purple: BKN-03, Black: DML-98, Green: DC-99, Blue: SP-95 and Light Blue: SP-01.

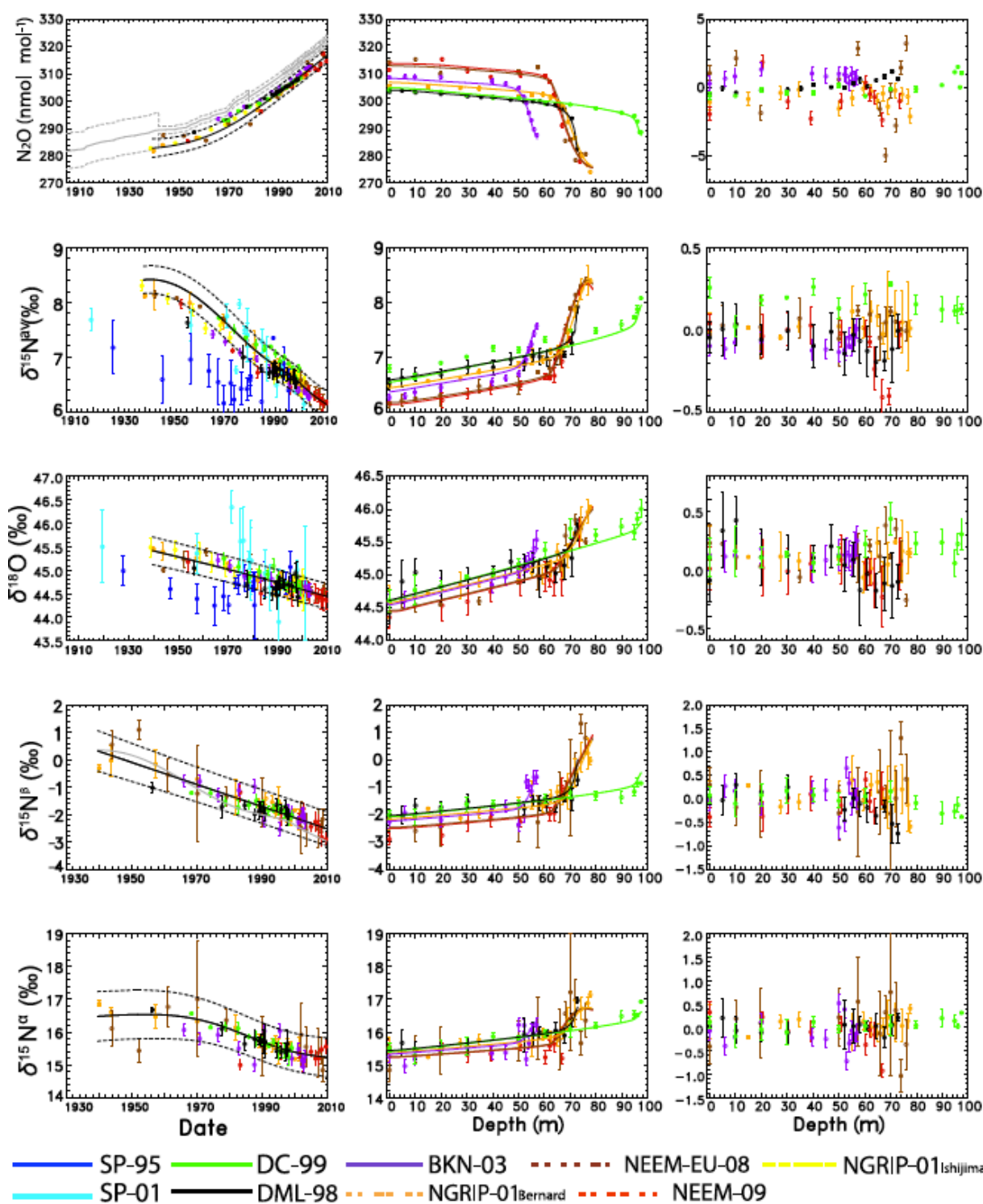


Figure C2. Results of the firn data evaluation (similar to Figure 2) using the data re-scaled to the NEEM-09 site. Colours as in Fig. C1.

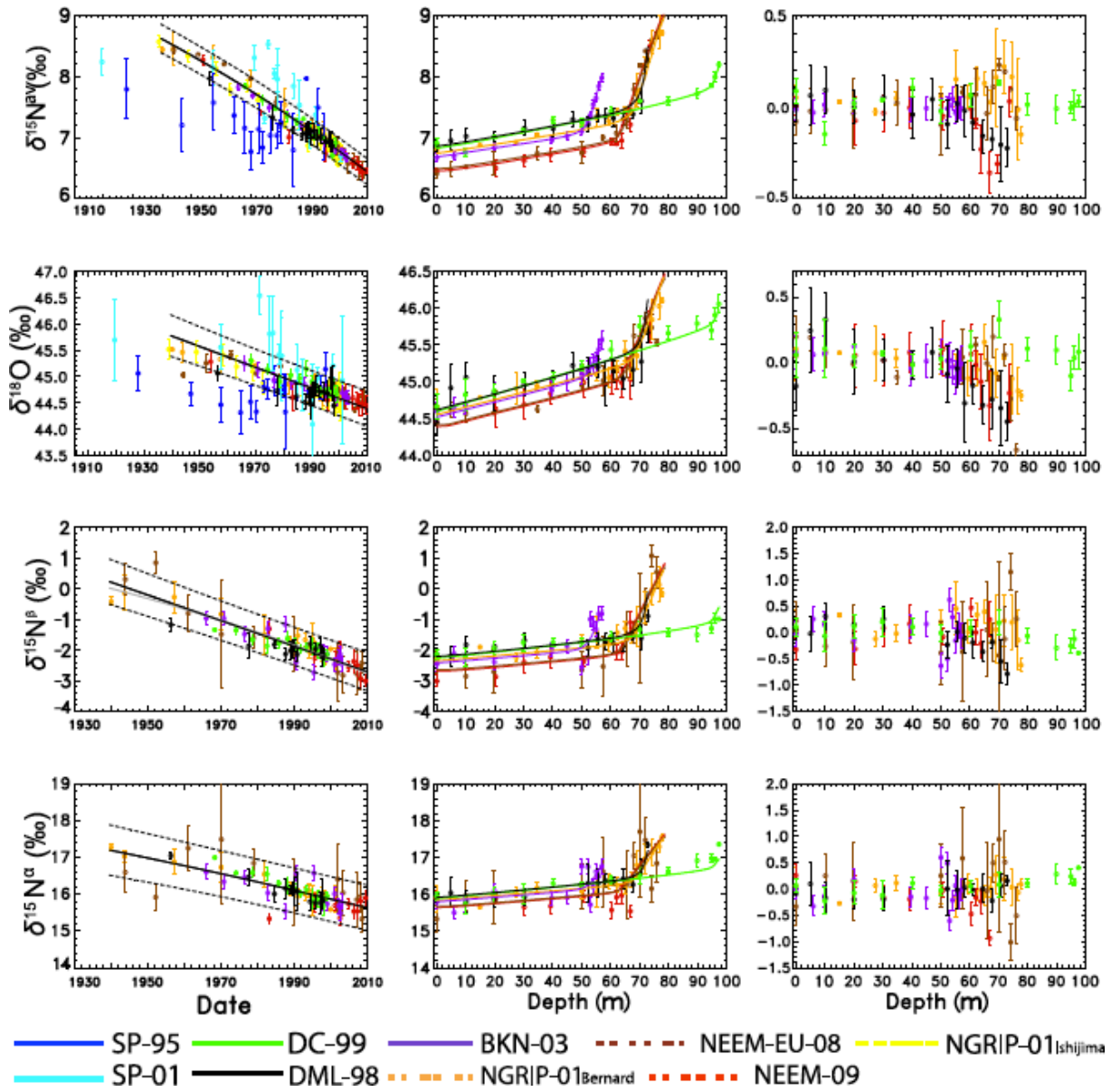


Figure C3. Sensitivity test to the regularization term increased by a factor of 10. Reconstructed atmospheric scenarios (left), corresponding fit of the firn data (centre) and model data discrepancies (right). The best reconstructed scenarios are shown as the black continuous lines, with model derived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

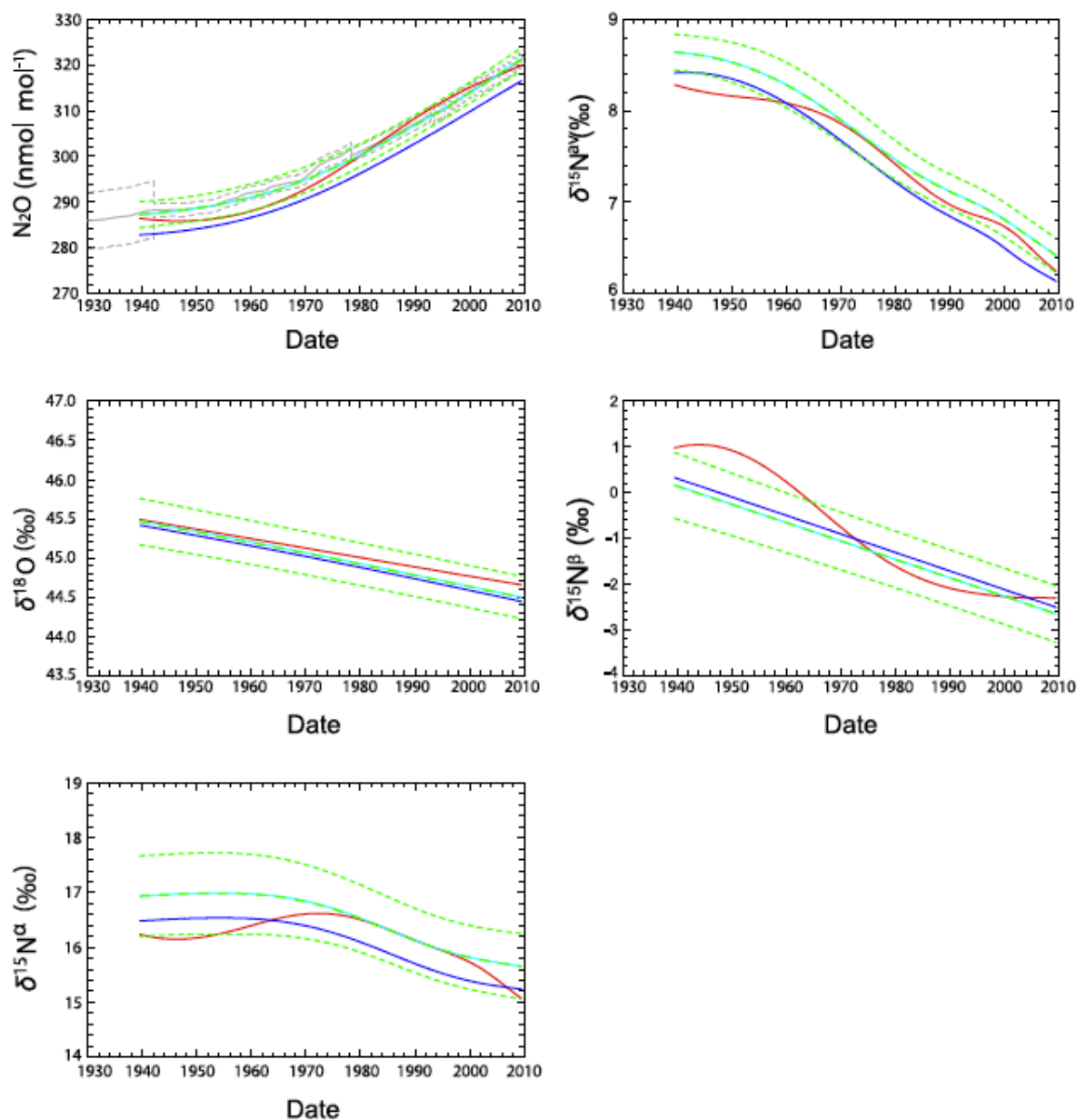


Figure C4. Comparison of the atmospheric reconstructions between different re-scaling methods. Solid and dashed green lines are the scenarios from data re-scaled to DC-99 used in this study. Solid red lines are the best-case scenario for the non re-scaled data and solid blue lines are the best-case scenarios from the data re-scaled to NEEM-09. The latter data series is shifted because of a calibration offset. When this is corrected for the data superimposes the green lines as expected.

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

For the default calculations with the mass balance model a constant lifetime for N₂O was used. A recent study from Prather et al. (2015), though, highlighted that top-down model calculations are sensitive to changes in the N₂O lifetime. To quantify the effect on our results we performed a sensitivity test where we linearly changed the N₂O lifetime from pre-industrial 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 the constant lifetime of 123_{-19}^{+29} a is used. In year 1940 the N₂O emissions are (12.3 ± 2.7) Tg a⁻¹ N and (17.0 ± 1.7) Tg a⁻¹ N in year 2008 with a total increase of (4.7 ± 1.7) Tg a⁻¹ N. When keeping the lifetime constant, the results for the same years are (11.9 ± 1.7) Tg a⁻¹ N and (16.4 ± 1.7) Tg a⁻¹ N with a total increase of (4.5 ± 1.7) Tg a⁻¹ N. In addition, when looking also into the absolute mean value changes in the assumed mean lifetime we only observe a vertical 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 budget as was indicated by Prather et al. (2015).

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

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 (-22.8 ± 8.4) ‰ for $\delta^{15}\text{N}^{\text{av}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ respectively. This agrees within combined errors with the total average values of (-18.2 ± 2.6) ‰, (27.2 ± 2.6) ‰, (-8.1 ± 1.7) ‰ and (-26.1 ± 8.4) ‰ for $\delta^{15}\text{N}^{\text{av}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ respectively when a constant 123_{-19}^{+29} a lifetime is used. On average, the N₂O anthropogenic signature results can differ by 10 % when a different lifetime is chosen, which is equivalent to a (2.0 ± 1.0) ‰ difference in the final anthropogenic values.

Sensitivity tests were also performed on the F_{exch} parameter which gives us the annual fluxes 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 respectively with the one used in the manuscript being 0.22 Tmol s⁻¹. Results are shown in figures D3 and D4 below.

In Figure D3 (middle panel) the atmospheric budget is re-calculated and compared to the optimal scenario values. At the bottom panel the air returned to troposphere from stratosphere is presented (F_{exch}). It is clear that when a low F_{exch} value is chosen, then less N₂O is returned to the troposphere. Contrary when a higher F_{exch} value is used more N₂O is returned.

F_{exch} choice has little effect on the isotopic signature results as shown in Figure D4 and is mainly limited to the earliest part of the record (>1970) where the reconstruction uncertainties are larger. While it is expected when F_{exch} value is low the isotopic results to be more enriched compared to higher F_{exch} , in our case this is not clear from the test. The overall averaged values have a less than 2 % difference compared to the chosen (optimal) scenario and results of total averaged source and anthropogenic isotopic signatures are well within agreement with combined uncertainty errors in both total source and anthropogenic signatures respectively.

Thus, we conclude that while the flux is indeed sensitive on the F_{exch} choice value the isotopic composition is not.

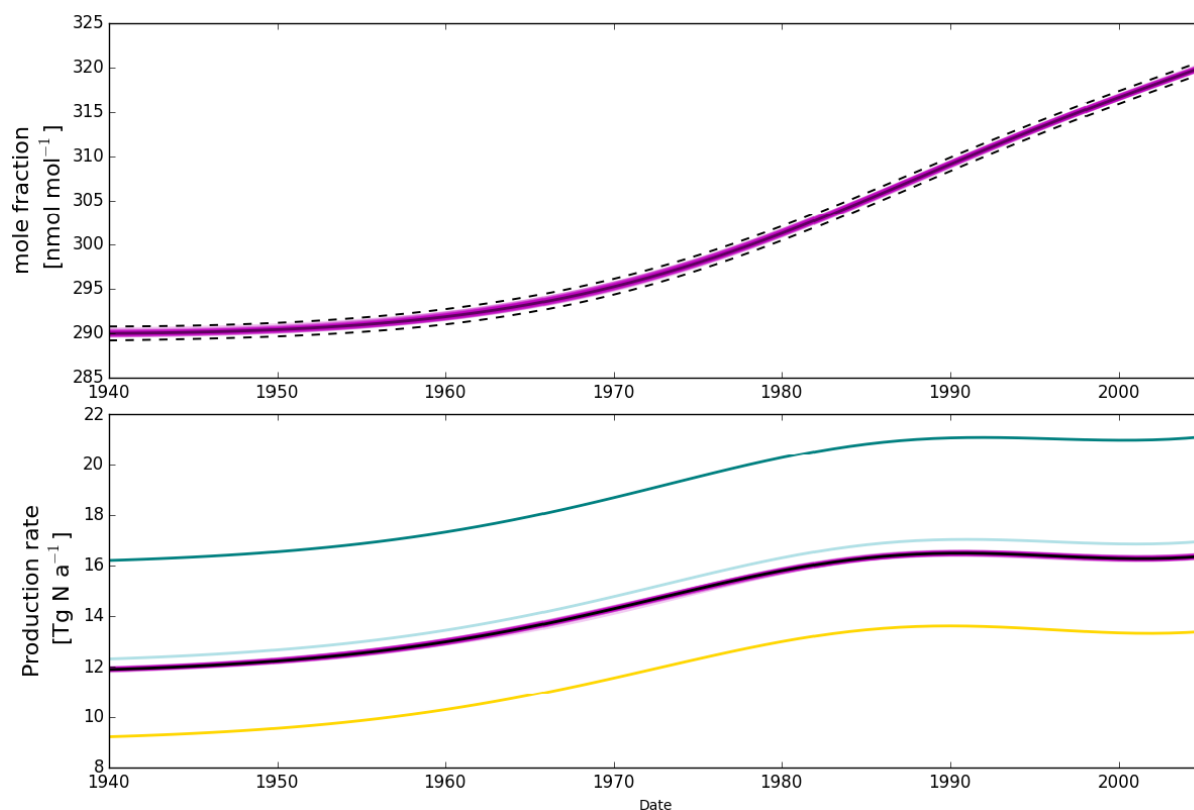


Figure D1: Top panel. N_2O mole fraction history constrained with the most precise data at NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed black lines) and the scenarios within the uncertainty envelopes that were used in the mass balance model (magenta lines)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

Bottom panel. N_2O 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_{-19}^{+29} a) as used in the main paper. Light green and yellow show the results when lifetime is 154 a and 104 a respectively.

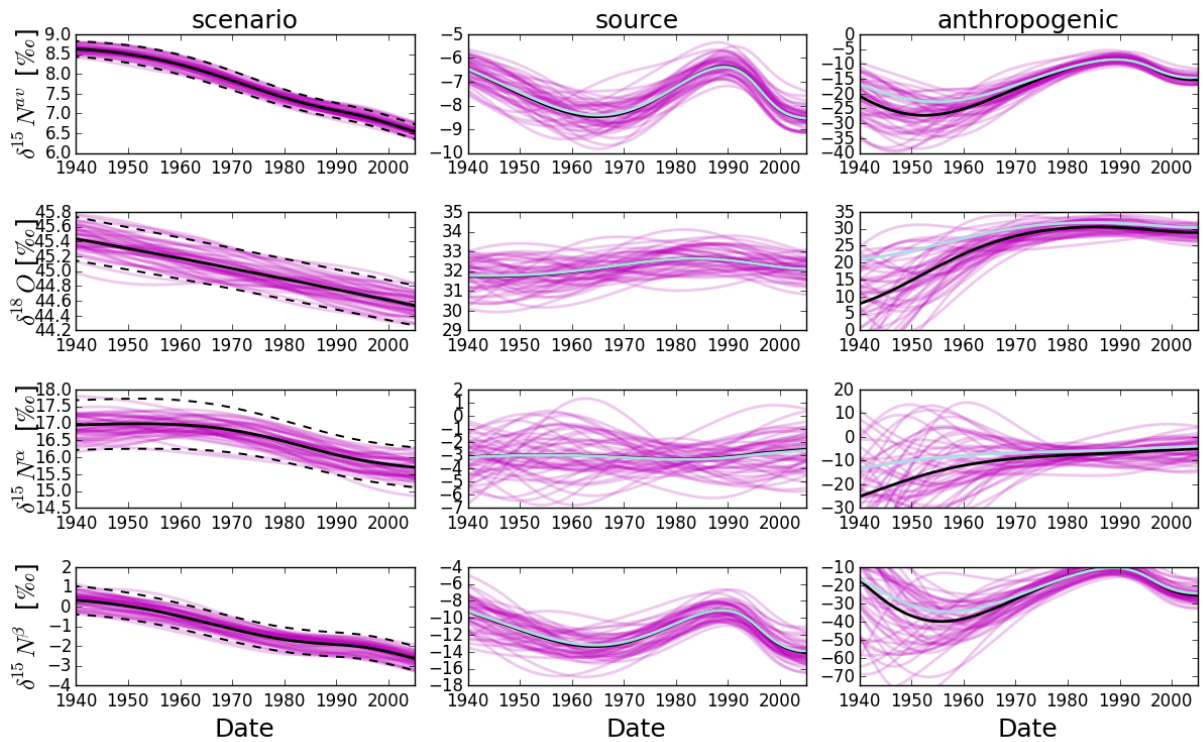
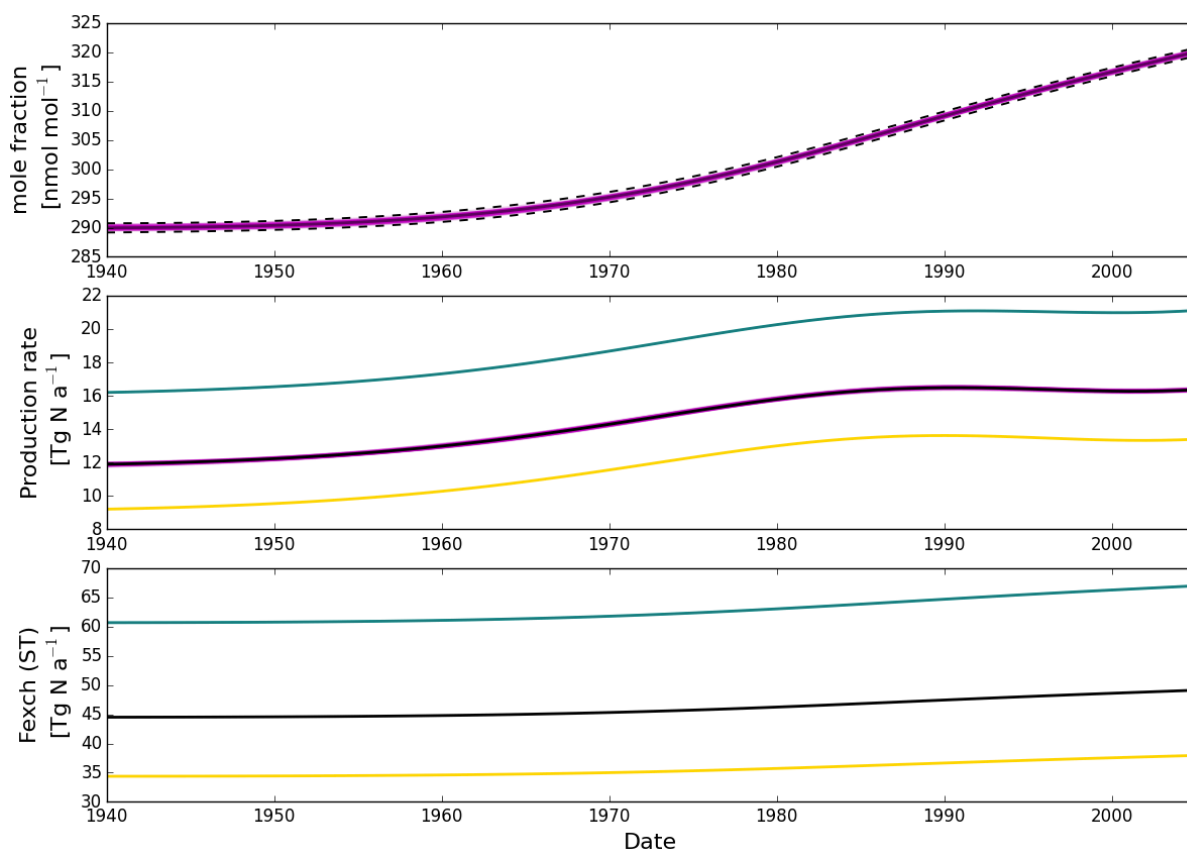


Figure D2: Left panels: Historic evolution of $\delta^{15}\text{N}^{\text{raw}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ in N_2O as derived from the firn air reconstruction. The solid black line represents the best-fit scenario while the dashed ones represent the respective uncertainties as determined by the reconstruction method. Magenta lines represent the emissions that are required to produce the magenta N_2O 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.



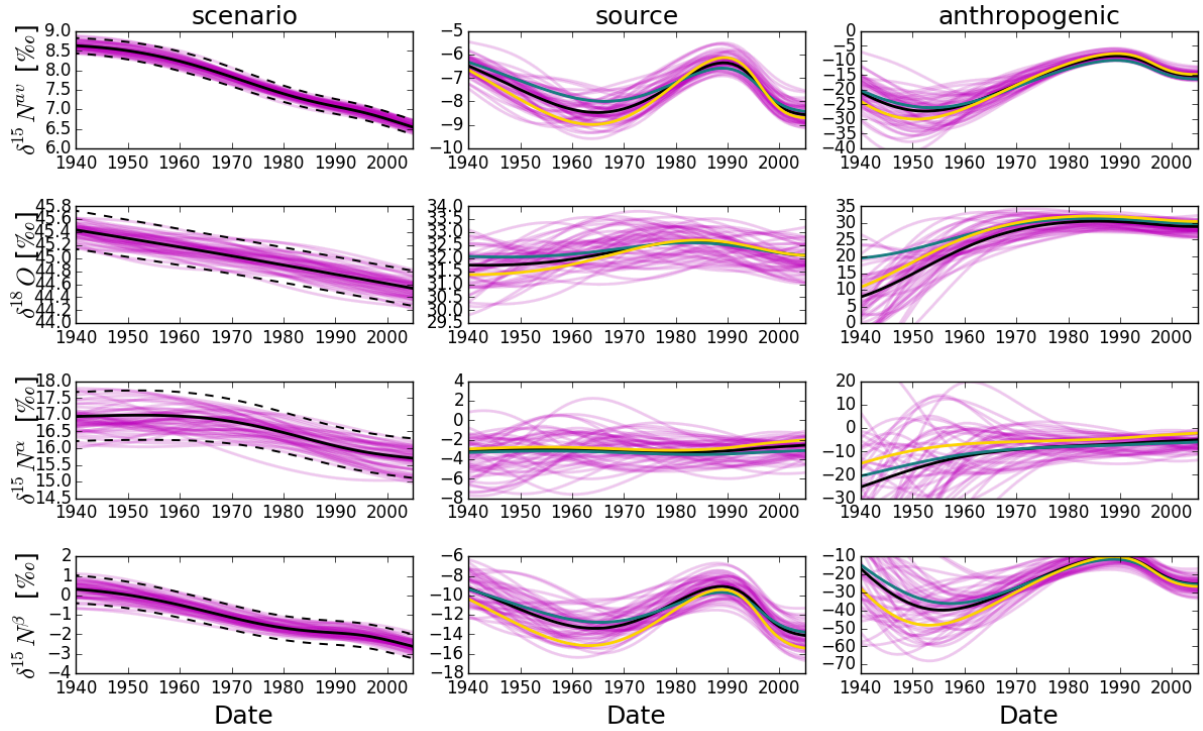
1182

1183 Figure D3: Top panel. N₂O mole fraction history constrained with the most precise data at
 1184 NEEM only to narrow the uncertainties (solid black line with uncertainty envelopes as dashed
 1185 black lines) and the scenarios within the uncertainty envelopes that were used in the mass
 1186 balance model (magenta lines) to evaluate the uncertainties of the atmospheric modelling
 1187 results.

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.

1192 Bottom panel. N₂O flux exchange results between stratosphere and troposphere as calculated
 1193 from the mass balance model assuming a high (0.28 Tmol s^{-1}) F_{exch} in light green and a low

1194 (0.16 Tmol s⁻¹) value in yellow. The solid black line represents the result for the best fit
 1195 reconstruction as used in the main paper.



1196
 1197 Figure D2: Left panels: Historic evolution of $\delta^{15}\text{N}^{\text{av}}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}^{\alpha}$ and $\delta^{15}\text{N}^{\beta}$ in N_2O as derived
 1198 from the firn air reconstruction. The solid black line represents the best-fit scenario while the
 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 N_2O
 1201 histories in the left panels. Middle and right panels: Isotope signatures of the total emitted
 1202 N_2O and anthropogenic source respectively assuming high (0.28 Tmol s⁻¹) F_{exch} in light green
 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.