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Discussions

Interactive comment on "Constraining N_2O emissions since 1940 using firn air isotope measurements in both hemispheres" *by* M. Prokopiou et al.

M. Prokopiou et al.

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RC 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).

AR: 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." Lines 549-563, Lines 738-740, Lines 811-813

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

AR: 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. Line 46, Lines 759-760, Lines 822-823

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

AR: 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. Line 79, Lines 865-866

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

AR: 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. Line 83, Lines 867-868

RC Line 116: "Carbon composition of"?

AR: We corrected this omission and replaced it with "of its carbon composition". Line 115

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

AR: 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.

RC 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?

AR: 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, show in 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. Lines 274-276, Lines 468-469, Lines 1029-1030, Lines 1169-1170, Lines 1191-1192
RC 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.

AR: 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 N2O 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 N2O 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. Lines 333-338, Lines 595-597

RC Line 326: As well as Rahn and Wahlen 2000

AR: 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. Line 326, Lines 869-870

RC 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.

AR: 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. Lines 438-444

RC Line 457: Regularization term is increased by how much?

AR: The regularization factor was increased by a factor of 10. This was added in the revised manuscript. Lines 461-463, Line 633, Line 1109

RC 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.

AR: 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. Lines 474-476

RC Lines 488-495 and lines 587-595: Observation of decadal variability in d15Nav 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 d15Nanth over time (both avg and beta). This increase (Fig. 4, right) peaks in the late 1980's however and proceeds to decrease significantly ($\sim$10% for d15Nav and $\sim$20% for d15Nb). 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 a doing a better job of decreasing and/or capturing fugitive emissions which might increase in the proportion of d15N 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.

AR: 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 δ15Nav and δ15Nβ. 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. Lines 621-637

RC Line 524: Starting value of d18Oanth, looks like about 8% to me but I am looking at Fig. 4 because there is no Fig. 5.

AR: The mistake has been corrected and substituted with (7.7±2.6) ‰ Line 529

RC 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 Xstrat given that this is the box where all N2O destruction takes place.

AR: Sensitivity tests on the magnitude of Fexch have been added in the Appendix D. The results show that when the Fexch value is low, then less N2O is returned to the troposphere, contrary, when Fexch is high more N2O is returned. The study showed that Fexch has little effect on the isotopic signature results, thus we concluded that only the flux is sensitive to the choice of Fexch 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

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lifetime would be about 10 times smaller than the global mean lifetime. Lines 582-586, Lines 1148-1166, Lines 1190-1213

RC 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 15Nav (identical to that on the line 417) and a -0.03 prmil/yr trend in 18O (-0.02 permil/yr on line 418 being within the estimated error).

AR: This has been included in the revised manuscript. Lines 593-594, Lines 869-870

RC 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 firn records?

AR: 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 δ15Nav and δ18O respectively. Similarly for marine waters the results were (5.14±1.93) for δ15Nav and (44.76±3.62) for δ18O. 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: RC: 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 CI and C2 appear to be switched, Fig. 3 (page 45) precedes

C8

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.

AR: We apologize for the mislabeling, and these errors were corrected in the revised version.

RC: 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 which with specific publications and which, other than NEEM, if any, are new.

AR: This information has been added in the revised manuscript in the revised Table 1. Lines 953-960

RC: 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.

AR: The requested information has been added in the revised manuscript. A subscript indicating the differentiation between the two publications is used (NGRIP-01Ishijima, NGRIP-01Bernard) throughout the manuscript. Line 211, Line 213, Line 393, Lines 428-429, Line 954, Line 1010, Lines 1055-1056, Line 1102

RC: 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.

AR: 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.
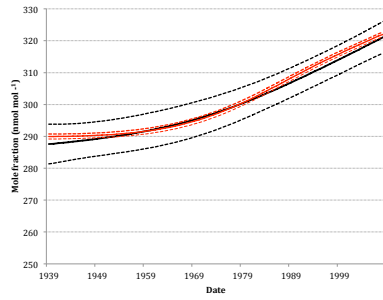
Fig. 1. Figure 1: Firn air trend reconstruction using only NEEM measurements from IMAU laboratory (black line) with uncertainty envelopes (dashed black lines) compared to firn air trend reconstruction using N
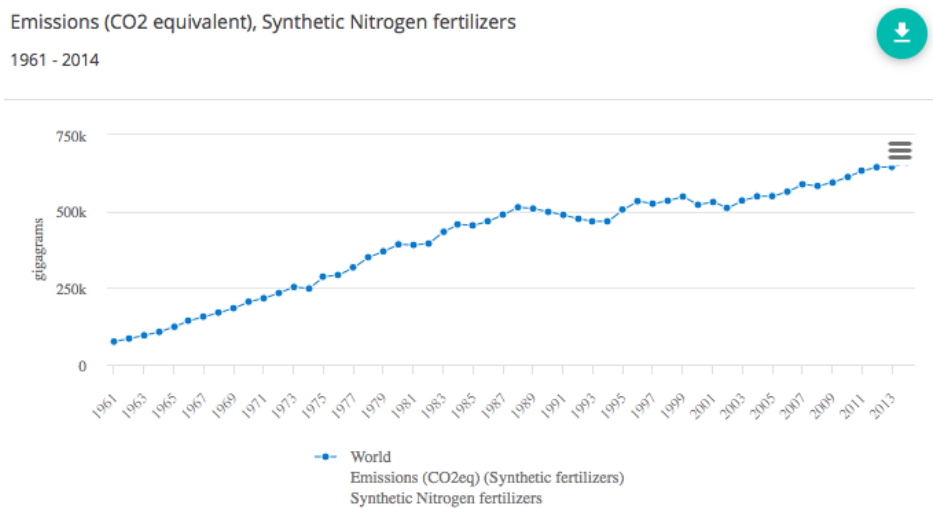
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Fig. 2. Figure 2: Global synthetic fertiliser emissions from 1961-2014 in CO2eq. Figure retrieved from FAO statistics (http://www.fao.org/faostat/en/#data/GY/visualize)

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