

## ***Interactive comment on “Constraining N<sub>2</sub>O emissions since 1940 using firn air isotope measurements in both hemispheres” by M. Prokopiou et al.***

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The authors provide a synthesis of firn air N<sub>2</sub>O isotopic data sets in an attempt to better constrain our understanding of the natural and anthropogenic components of N<sub>2</sub>O emissions. The synthesis of these geographically diverse records is acceptable since the long atmospheric lifetime of N<sub>2</sub>O allows the assumption that all sites experience an N<sub>2</sub>O history that is identical within the precision of the measurement capabilities and indeed the authors have done a fine job in the firn air modeling and in the scaling of the different data sets. I do however have issues with some of the follow on modeling and discussion which I itemize in the line by line comments below. I recommend publication following revision. Line 25. The 1940 atmospheric mole fraction, and hence

C1

the growth rate, differs from that determined by Battle et al., 1996 and to a lesser degree with Machida et al., 1995, please discuss (in the discussion section). Line 48. N<sub>2</sub>O as a source of stratospheric NO<sub>x</sub> was certainly known prior to Ravishankara's 2009 work, see McElroy, Khalil, Crutzen, etc. Lines 80-81. Rahn and Wahlen (1997) also contributed here with the first reference that describes a fractionation factor for stratospheric loss. Lines 82-84. Rahn et al. (1998) also contributed here with the first laboratory verification of wavelength dependent kinetic fractionation during photolysis. Line 116. “carbon isotopic composition of”??? Lines 141-142. For my own edification, doesn't this require dual bladders so that a specific depth range can be isolated? 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? 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, 93; 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 to be detrimental to their efforts. Please justify lumping the natural source into a single term. This should also be elaborated on further in the discussion section. Line 326. As well as Rahn and Wahlen 2000. Lines 429-439, discussion of inter-laboratory variability. The authors state that discrepancies do not exhibit a systematic shift and that the Sowers et al data had good agreement between two different laboratories but then they leave this conundrum hanging. Please elaborate a little on possibilities. Line 457. Regularization term is increased by how much? 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 and 2008 should it not? But this 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. Lines 488-495 and lines 587-595. Observation of decadal variability in d<sub>15</sub>N<sub>avg</sub> and discussion of changes in relative contribution of sources

C2

over time. If real, this is possibly the most important observation in the manuscript and needs to be dealt with in a much more considered manner. Intuitively, one would agree with their first 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 N<sub>2</sub>O accompanied by less isotopic discrimination. This, along with increased industrial production of N<sub>2</sub>O could hypothetically lead to the observed increase in d<sup>15</sup>N<sub>anth</sub> over time (both avg and beta). This increase (seen in Fig. 4 right) peaks in the late 1980s however and proceeds to decrease significantly (~10 per mil for d<sup>15</sup>N<sub>avg</sub> and 20 per mil for d<sup>15</sup>N<sub>beta</sub>). 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 the proportion of d<sup>15</sup>N depleted agriculture relative to industry but A) is there any evidence for this and 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/modeling that could also lead to the observed/modeled record. Line 524. Starting value of d<sup>18</sup>O<sub>anth</sub> looks more like about 8 per mil to me but I'm looking at Fig. 4 because there is no Fig. 5. Lines 552-562. The authors perform a sensitivity study of changing the life time but it seems to me that there should also be sensitivity study of 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 a more appropriate lifetime would be stratospheric lifetime in conjunction with X<sub>strat</sub> given that this is the box where all of the N<sub>2</sub>O destruction takes place. Lines 563-573. This was also predicted by Rahn and Wahlen (2000), prior to any firm air measurements being made, where they predicted a -0.03 per mil/yr trend in <sup>15</sup>N<sub>avg</sub> (identical to that on line 417) and a -0.03 per mil/yr trend in <sup>18</sup>O (-0.02 per mil/yr on line 418 being within their estimated error). Lines 576-580. The "natural" component of the ocean source is estimated to be on the order of 4Tg N/yr. This new

C3

"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 N<sub>2</sub>O 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? General comments. 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. 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. 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. Ultimately the authors conclude that "Based on the changes in the isotopes we conclude that the main contribution to N<sub>2</sub>O 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.

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C4