**Atmospheric
Chemistry
and Physics**
Discussions

Interactive comment on "Development of an atmospheric N$_2$O isotopocule model and optimization procedure, and application to source estimation" *by* K. Ishijima et al.

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The study of K. Ishijima et al. entitled " Development of an atmospheric N2O isotopocule model and optimization procedure, and application to source estimation" embodies an attempt to better understand the tropospheric isotope-resolved budget of N2O throughout last decades with the use of an atmospheric chemistry transport model and an approximate inversion technique. Whilst the targeted scientific question is complex, interesting and obviously important, I find that that the study itself suffers from inconsistencies in model application and "optimisation" approach used, which unfortunately devalues the findings claimed.

The proportion of sensible discussion and analysis, i.e. those that do not merely end

up concluding that the model uncertainty is smaller than that of the data it is being validated against (or the data uncertainty is too large to make further inferences) is rather small. Contrasting that, the content devoted to model formulation, method description, "optimisation", etc. is tangible, which renders the manuscript suitable for a journal like GMD, but not ACP. The presentation style could certainly be improved, too, through using conventional modelling terminology, avoiding ambiguous expressions (e.g. "blurring trends", "trebling the contributing ratio") and eliminating long sentences with multiple participle clauses, etc.

Below I outline four grave issues that the Authors should clarify in order to ascertain the consistency of their results (I admit that could be a lot of work), before these should be attempted to be offered to the community again.

1. One most perplexing statement I find already in the abstract, it reads "observed atmospheric trend is the dominant factor controlling the source isotopic signature". You likely will not object the statement that the burden/trend of a trace compound residing in the atmosphere is determined by the interplay of the sources and sinks acting on this compound. Such generally holds for the N2O isotope composition simulated in your model (ensues from your Eq. 12a). There are exceptions, e.g. 13C/12C ratio of plant-emitted reactive hydrocarbons has been shown in several cases to correlate with the isotope composition of recently fixed carbon, i.e. that of atmospheric CO2 respired. Reactive C eventually ends up in CO2, hence this (rather weak) feedback mechanism is established. (Caution, here only the local value of δ13C(CO2) is involved, not its global average, or its trend.) Although N2O is known to be cycling between the atmosphere and biosphere, the authors need to present (at least hypothesise) how the trend in atmospheric N2O mole fraction may have a feedback on the isotopic composition of N2O global sources (in other words, please show how the tail's intentions wag the dog), and what model result led to this conclusion.

2. The framework of model "optimisation" is not clear.

Regarding the definitions in Sect. 4.2.1 I am curious about the fate of conversion factors (Fi) during the optimisation (here I reiterate the comment of my reviewing colleague), and even about their actual meaning. From Eqs. 12 & 13, Fi is the ratio of the total atmospheric N2O burden (Mi) to the mole fraction ("MF" hereinafter) observed at particular station (Ci), somehow averaged over a decade. I.e., the Authors proportionate a point measurement/simulated value with the integral atmospheric N2O mass. What physical meaning this has?

In my attempt to elucidate it, Fi embodies the reciprocal fraction of the total N2O mass the station "sees", so to say. This, however, does not fit with the assumption of well-mixed N2O in the troposphere used, as all stations should see about the same fraction (most of N2O resides in the troposphere), should not they? In other words, Ci at NMY does not represent N2O at the South and North Poles equally (although it relates via Fi to the total mass of N2O), otherwise we would not see the latitudinal gradient in the troposphere. Your optimisation relies on the opposite, however.

Irrespective from that, if the distribution of the sources changes throughout the decade, which is likely (e.g., the NH/SH emission ratio changes), the value of Fi will not be actual, so the method will introduce errors in the optimal values obtained. How do you account for that?

Secondly, it is new to me that the initial conditions (Mi0 or Ci0) are being optimised. Why do you fit these having performed the model spin-up (here, however, another problem arises, see below)? The values of Ci0 differ by 12.9 nmol/mol between the small and large "scenarios", i.e. four-fold of about 3 nmol/mol observed in 1984-1986 (cf. your Table 2 and Fig. 10). Varying fE and fI is similar to fitting the N2O trends using both, the slope and shift, parameters (here I use the linear fit model for example). The functional behaviour of the residual being minimised ((Cmodel-Cobservation)^2) in this case is different from that when only emission strengths and their hemispheric ratios are being optimised. Such fitting favours more realistic decadal means of N2O MFs simulated whilst being less sensitive to the slopes. At last, using decadal averages

(p. 19975, ll. 18-21 & Fig. 7) does not validate the similarity of N2O MF dynamics (i.e. trends) observed and simulated in the model. One can show an example of two trends (a strong observed and a weak simulated) which yield the same decadal N2O MF averages with the CIs of the latter being lower than that for the former.

To recap here, having hard times confirming the consistency of the "optimisation" used in this study, I recommend the Authors to review literature on inverse problems (e.g., Bayesian approaches) in atmospheric modelling and implement a proper (mathematically and physically sound) already developed one that will suit the problem being tackled.

3. The spin-up is likely not properly performed, particularly w.r.t. to the isotope ratios.

Despite its recognition, the spin-up problem is often present in modelling studies dealing with compounds whose lifetime is longer than a year in the atmosphere. The Authors have established a "semi-equilibrium" state (which itself is another inverse modelling problem) for N2O throughout 50 consecutive years (despite recalling, however, that the atmospheric lifetime of N2O is about 120 years). What are the grounds for using such a short spin-up period? Can you estimate the error in the atmospheric N2O distribution you introduce by using spin-up times shorter than the compound lifetime? Please, provide the metrics and goodness of the spin-up state you achieved, as "N2O trend was mostly maintained at realistic levels" and "vertical profile in the stratosphere being also realistic" are not appropriate (quantitative) measure here.

A more serious problem is establishing properly equilibrated N2O isotope ratios in the model by the time of spin-up. These, regarding small rare isotope abundances and hemispheric gradients of 15N/14N and 18O/16O ratios, will require a substantially longer period than 50 years for equilibration. A classical illustration to this problem is given by Tans (1997) for CH4 and obviously is valid for N2O. Following this work, one could similarly research an interesting question on what is the equilibration time for δ15N(N2O) and δ18O(N2O) in the atmosphere?

4. Likely inconsistent stratospheric N2O photochemical sink simulated in the model,

is my last concern (here I second my colleague again). The O3 fields derived from any other product are likely inconsistent with the model dynamics driven by the JRA-25. Furthermore, it is not clear how Takigawa et al. (1999) and ERA Interim ozone fields were incorporated? These studies are inconsistent between each other, as Takigawa et al. (1999) use substantially older photochemical kinetics data, model setup, etc. The most consistent solution here is to use same (ERA Interim) dynamics and O3 fields. Simulated stratospheric N2O sink and isotope ratios in the model are a convolution of the photochemistry and transport in the model. Obtained using a blend of O3 and dynamics from three different modelling studies, the results, as well as any discussion on their representativeness in view of stratospheric dynamics, are useless.

5. A bonus on uncertainties (for contemplation).

Isotope measurements provide estimates of the isotope ratios with high certainty. Using these, one derives the MFs of the rare isotopologues with uncertainty comparable to that of the abundant one. That is, when N2O MF is measured with an uncertainty of about 0.14 nmol/mol at NMY in 2000 (assuming average 314 nmol/mol), the uncertainty in simultaneously measured δ18O(N2O) (44.8‰ VSMOW, uncertainty 0.02‰) is that low, so using these two quantities one derives the MF of the NN18O isotopologue with a similar to NN16O uncertainty, or about 0.045%.

The converse does not hold, however. Using the MFs of NN18O and NN16O, both uncertain to within 0.045%, one obtains δ18O(N2O) with the uncertainty exceeding 2‰ (the reference isotope standard ratio is assumed to be known perfectly here), as a consequence of the law of error propagation. You may ascertain that for N isotope ratios the respective uncertainties will be substantially higher than for 18O (see, Natrella, 2003 and http://www.itl.nist.gov/div898/handbook/mpc/section5/mpc55.htm for general formulation).

The Authors emphasise that all isotopocules of N2O are optimised separately, i.e. the

final distributions of 14N15NO, 15N14NO, NN18O and NN16O MFs are obtained independently. Their uncertainties are estimated through the variability analysis in the Monte-Carlo runs, and for N2O MFs are comparable to those of the observed MFs. From this I conclude that the isotopocules' MF relative uncertainties should be not smaller than that of the N2O MF (as they are derived via less uncertain δ-values). Ultimately, these should yield (as in the above example) much higher uncertainties in the optimised δ-values, in contrast to those presented (cf. δ18O(N2O) in panel (c) of Fig. 7). My only explanation here is that the uncertainties of rare isotopologues' MFs were disregarded in the study (i.e., only the MFs of N2O or abundant isotopologues were varied), otherwise the Monte-Carlo runs should properly simulate the uncertainty propagation. If not, please, elucidate this inadequacy.

References

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