Reply to Referee #1

We appreciate the referee for his/her valuable comments to improve the quality of this paper, and respond them as follows.

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.

In this study, we gave priority to taking reliable parts from both observational data and model results as much as possible, considering that present atmospheric N_2O isotope observation network has not yet been well established. Thus we think that we have to try using multiple observation data sets and conventional inversion approach as the next step. With regards to the journal selection, we would like to give more careful consideration when we submit this kind of work next time. We actually struggled to explain the optimization part, but would like to further clarify that as well as presentation style in other parts. Our responses to your individual comments are as follows.

General comments

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 13C(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.

The statement is just based on Eqs (12) and (13). For example, E_i is significantly affected by the trend (dC_i/dt) in Eq (13a). We did not imply anything else, and did not use any scheme for describing online atmosphere-surface interaction of trace gases as you gave as examples. As you have pointed out, we also found that the expression might sound strange for readers, who do not know the contents of the paper. Additionally we have reconsidered the logic. The result does not depend only on the observed trend but also on the lifetime. It is a given parameter in a box model but calculated from simulated results in 3D model. We will rephrase the relevant parts and add lifetime values in Table 3.

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?

Simple mass balance equations (12) and (13) are shown only to explain the base concept of optimization in this study, since the equations are relatively well known. So, Eqs (12) and (13) were not used in our optimization method. We directly fitted the model to the observation data at NMY station. Your understanding regarding the conversion factor (F) is all correct. F always changes with time due to changes in vertical profile, horizontal distribution of the mole fraction.

Secondary, 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.

First, we designed the model framework exclusively for N_2O, which has a very long life time (>100 yrs) and near-linear temporal trend for the last three decades. In this study, we optimized model not only for the troposphere but also for the stratosphere, from around 1990 to 2007, using very limited number of isotopic data (obviously no satellite data of N2O isotopocules in 1990). In order to compare with such data, N2O field in the model needs to be physically well conditioned from the surface to the stratosphere at least, as if it has been so for the past several years. And, profiles in the stratosphere are also affected by surface emissions.

Secondly, we made the model flexible to apply to any isotopic standard-scale and any station's data by adjusting the initial values. As discussed in Sect 5.5, there are still several causes influencing the final isotopic data even if the common standard scale is used. Relatively large spread of the initial values has no impact as long as the spin-up is well done.

Thirdly, we agree that the conventional Bayesian approach using monthly or annual pulse emission simulations better fits observed values and thus estimated emissions are more accurate, compared to our approach. However, computational cost of such runs for 4 isotopic species and for different photolysis cases is quite huge.

Fourthly, N_2O isotopic observation network is still immature in terms of the measurement precision, inter-calibration scale and number of stations, unlike those for only N_2O MF. It is obvious in Fig 10 that discussing year-to-year changes for isotopic values is difficult.

Due to the above reasons, we judged that the conventional approach was slightly early at the present stage. We definitely think that we have to tackle more general inversion approach for the next step when N_2O isotope observation network improves in the next several years.

Our model and optimization method work precisely. The model simulation, in which optimized emission, initial value and photolysis rate are used, shows completely the same result as combination of the first separated simulation results.

These will be inserted in the beginning of Sect 4.2 but in a more concise way.

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.

Thank you very much for pointing out the very important point. First, we found that the description of the spin-up was not exact. We started the spin-up run with a realistic vertical and horizontal distributions. However, to be honest, we were anxious about the spin-up (before your comments came), so had additional decades spin-up, which was repeated in 1983 until middle stratospheric N_2O isotopic MFs became stable. Then, we scaled the initial values to those in Table 2 and reran the model. In consequence, all results showed almost no difference from the first run, but estimations of isotopic values of the hemispheric sources slightly differed as below (but no emission change), so we fairly employed the second run’s results for all tables and figures in the revised version. Description on the spin-up will be modified in the Sect 4.1.4.

Corrections in Table 4 (only top-down estimates by the ACTM for isotope deltas)

	$\delta^{15}N^{bulk}$ / $\delta^{18}O$ / $\delta^{15}N^{sp}$			$\delta^{15}N^{bulk}$ / $\delta^{18}O$ / $\delta^{15}N^{sp}$
GL:	-10.4 / 31.2 / 12.3		GL:	-10.6 / 31.0 / 12.0
NH:	-14.6 / 31.2 / (15.1)	=>	NH:	-14.7 / 31.2 / (15.0)
SH:	-4.7 / 31.1 / (8.6)		SH:	-5.0 / 30.6 / (8.1)

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.

Before answering this comment, we have to apologize that description of the ozone field above 1 hPa in Sect. 4.1.1 was wrong by our misunderstanding. We have used climatological ozone field by UK Universities Global Atmospheric Modelling Programme (UGAMP) (http://browse.ceda.ac.uk/browse/badc/ugamp-o3-climatology/data/~) for above 1 hPa. This correction will be done in the revised version.

We agree that there is a mismatch of dynamics between ERA-Interim O3 and JRA-25 meteorology. We considered to use O3 fields from JRA-25 at first, but unfortunately they were significantly overestimated compared to the observations throughout the stratosphere, so we gave up using them. Then, we found that ERA-Interim O3 was much more realistic. However, we also found that the ERA-Interim O3 (MERRA1&2 also) sometimes shows unrealistic vertical profiles above 1 hPa, so we combined UGAMP O3 field above 1 hPa.

O3 fields of UGAMP, ERA and MERRA show similar large-scale spatiotemporal structure around ozone layer. It is important to reproduce large-scale structure of atmospheric N_2O. Finer scale structure (or shorter time-scale variability) is mainly caused by meteorology. That is the reason why our model's N_2O is plausible in the stratosphere. And, we intrinsically did not need a high precision reproducibility in the stratosphere, because we mainly focused on the troposphere.

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 18O(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 18O(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).

Thank you for this curious discussion. We understand the first part (0.045%), but does the converse calculation becomes 0.66‰ not exceeding 2‰, right ? Similarly, given 0.01‰ uncertainty for $\delta^{15}N^{bulk}$, the uncertainty for 15NNO-MF is 0.45%. Conversely, the uncertainty for $\delta^{15}N^{bulk}$ becomes 0.64‰.

In this study, we made a pseudo observational data set of N_2O-MF and delta values, converted them to the MFs, and fitted the model to the pseudo MFs. At that time, the surface emissions were also automatically determined. By repeating this 100000 times, uncertainty of the emissions were determined. This is like the first case you demonstrated. In our approach, emission estimates for the four N_2O isotopocules were always bounded by the pseudo data set of the N_2O-MF and delta values, which were made at the beginning of the process. Therefore, no uncertainty inflation arises unlike your second case.