Reply to Referee #2

We are grateful to the referee for his/her helpful comments to significantly improve this paper, and respond them as follows.

Review for the following manuscript Journal: ACP Title: Development of an atmospheric
N2O isotopocule model and optimization procedure, and application to source
estimation Author(s): K. I. Ishijima et al. MS No.: acpd-15-19947-2015 MS Type: Research
Article
I have major criticisms on technical justifications. The model sections were written in a way that I
cannot tell whether the approaches they adopted are reasonable or not. Interpretation was not well
presented and what the new things the current modeling is delivering are not clear. Details are listed
below.

We actually struggled to explain the optimization part, but will further clarify that as well as the presentation style in other parts. Our responses to your individual comments are as follows.

General comments

1. Section 4.1.2 Given that the photolysis in the stratospheric is critical for N2O fractionation. One has to examine carefully the constants used in the simulation. Without correct realization, the results derived and conclusions drawn are weak. It is known that the degree of fractionation is a strong function irradiation wavelength. Indeed wavelength dependent photodissociation is account for for normal species (though at limited resolution) but not for isotopic species, if my understanding is correct. Single epsilon is obtained for each isotopocule. Mixing/transport and photon attenuation affect the distributions of the N2O isotopocules. Simply fitting the isotopocules observed in the stratosphere to get epsilon's is not acceptable. Though optimization is done (though not clear to me how this is done, given that the data are limited and variable), the correction is applied uniformly to all latitudes/altitudes. I'd suggest examine wavelength dependence carefully in the model before optimization starts.
Lower stratospheric N2O concentrations are critical for cross-tropopause exchange, i.e., >200 nm photolysis where you have 3 bins only. An attempt to estimate the error due to poor simulation with 3 bins is required. To make the model more applicable, finer spectral resolution is preferred.

We agree that the wavelength resolution is not enough for precisely describing photolysis for isotopocules. However, our main focus is to simulate tropospheric N_2O isotopic species and to estimate spatiotemporal variations of their surface emissions. Definitely, we cannot ignore the stratospheric N_2O because isotopic fractionation due to photochemistry and its cross-tropopause propagation into the troposphere affect the tropospheric N_2O. In this sense, it is acceptable for us that the model can apparently well simulate the vertical profiles and apparent fractionations in the low to middle stratosphere as shown in Figs 6, S2 and S3, even if the photolysis is roughly adjusted by the single factor.

We recognize that our ACTM model is competent for cross-tropopause transport (or stratosphere-troposphere exchange; STE), compared to other models, from our past studies (Ishijima et al., 2010; Thompson et al., 2014b; 2014c, also see Patra et al., 2011 but only 32 layers version; references are shown at the end of responses).

2. Next critical parameter is transport Two transports are crucial for N2O modeling. One is the transport in the stratosphere and the other is cross-tropopause exchange. The former can be done by trying to model the so-called age of air in the stratosphere. ECMWF-Interim does a good job but other new reanalyses (NCEP R1/R2 and ERA40 are bad) are unknown to me. The authors have to show and demonstrate the robustness of the transport they used. I'm not convinced with the authors saying in section 5.1 that ~2 year underestimation is not important.

The latter can be checked against, for example, data made in the mid-troposphere, if not upper-troposphere. To my knowledge, CARIBIC project (see, e.g., Assonov et al. 2013) provides a good dataset for the verification.

The above three are critical before any solid conclusion can be given.

The ACTM tends to underestimate the age of the air roughly by up to one year at middle to high latitudes around 20km altitude. The age in the polar vortex is worse, but the effect is thought to be not so serious as discussed in Sect 5.2. Such age underestimation is partly shown in Ostler et al. (ACPD, 2015). At the current setting of the model, which is nudged to reanalysis meteorological data, it is difficult to improve the age underestimation shortly, as is the case with many other climate models. Therefore, based on the fact that the reproducibility for isotopic fractionation in the lower stratosphere and for STE is reasonable, we judged that our model transport is enough to simulate mainly for the troposphere.

3. 50-yr spun-up. Given that the lifetime of N2O is >100 yr in the atmosphere. The model spun-up

should be longer than that. Please explain.

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 re-ran 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. Despite being with such a more complicated 3D model framework, I don't see what new things learned from the exercise. The authors conclude that 3D model agrees with updated box-model estimation.

In this study, we explicitly gave surface emission in the N_2O isotopocule model for the first time, and estimated N_2O isotopic emissions by a top-down approach with 3D model. These are very new. And, hemispheric estimations by our model are different from those by another top-down 2 box model. In this study we performed hemispheric bottom-up estimation with updated various source measurement data, and they agreed with our 3D model results within half of the uncertainty.

5. For trends in each hemisphere, given the long lifetime in the troposphere I expect the trends are similar. Moreover given the facts of long N2O lifetime and short cross-hemisphere mixing/transport, why there's noticeable difference in trend between stations?

Thank you for giving us a chance to revisit the issue. For example, if a large emission change occurs lasting for a year or so, it could cause regional mole fraction biases, considering about one year interhemispheric exchange time. We mentioned such emission change due to El Nino in section 5.5.

However, some changes in large-scale transport such as tropical convection and stratosphere-troposphere transport are also possible to significantly overlap such emission signals in model, as indicated by Nevison et al. (GBC, 2007) with observational evidences. It is thought that the ACTM is capable of simulating the underlying process but it is another science topic.

These sentences will be added in the section.

Other comments:

6. Section 4.2.1 is not clearly written I was lost initially. After reading through it once more more carefully, I can follow. I don't have good suggestions how to reorganize it at the moment. The authors should do some work polish/rephrase.

Actually we also much struggled for explaining the section as simply as possible. We will make further effort to clarify that in the revised version.

7. The validity of linear assumption for Equations 10-11. Typical photolytic fractionation can be described by Rayleigh distillation, which is not linear. How the resulting parameters become linear, with respect to variations in input variables, like E. Linear assumption may be a good approximation for small varying variables, but this has to be shown, though in the first sentence of section 4.2.1 it's written that this is confirmed. Given the number of N2O dissociative photons is limited, the total destruction rate is not constant, due to additional UV absorption from other molecules. To what extent the linear approximation is valid has to be shown.

This can be calculated by Excel. We put an example on the final page, since it is difficult to explain by words or equation here. We hope that you understand that.

8. Seasonal cycles It would be good if the authors also present a comparison of the model seasonal cycles with the observed ones, in a table.

We thought about this, and concluded that at the present stage isotopic observation data do not have enough precision for the seasonality analysis as mentioned in the paper. Comparisons of mole fraction have been already shown in several publications (Ishijima et al, 2010; Thompson et al., 2014b; 2014c).

9. Please show spatial homogeneity of N2O in figures for each hemisphere.

We have already shown meridional distributions in Figs 7 and 8, so will show them in the Supplement.

10. Age of air to verify the transport Stratospheric transport is crucial for N2O modeling. Please verify your transport against the determined age of air. I know ECMWF-interim reanalysis is good but am not sure JMA reanalysis.

Please see our response to your similar comment above. The age in the ACTM does not so much depend on the reanalysis data, but comes from the model structure itself.

11. Too busy fig 4 If possible, please separate 3 variables into 3 figures. Same for fig 10, difficult to compare model with data.

Fig 4 is already separated into three Figs. In Fig 10, we have changed the daily mean model data to the monthly mean, and moved Figs of $\delta^{18}O$, and $\delta^{15}N^{sp}$ into the Supplement.

12. Section 4.1.3 that a single scaling factor was used, inconsistent with Fig S1 that latitudinal profiles between the 2 cases in each hemisphere are not off by a single factor. Please check. I may misunderstand the plot.

All of Sect 4.1.3 and Fig S1 are correct. In order to make an $E_{NH}:E_{SH}$ ratio (low or high), different scaling factor was applied to each hemisphere in the base emission. We will modify this description in the section.

13. Section 5.1, to scale the fractionation to reproduce stratospheric observations requires a modification beyond the uncertainly of von Hessberg et al. Please compare explicitly the values of the two.

Do you mean "Section 5.1" ? The ratio of the tuned photolysis to the original photolysis based on von Hessberg et al. (2004) is shown in Table S1.
As we have replied above, we guess the underestimation of the photolytic fractionation is mainly due to deficient wavelength resolution in model. Therefore, we largely modified the photolysis so that the

fractionation apparently agreed with the observation, considering the main target of this study is the troposphere.

14. Why not include Toyoda et al. (2013) data? Please also state clearly why not include the new data for model optimization. Anthropogenic is a component of the model.

As mentioned in Sect 3.1 and 3.2, we gave first priority to the data precision in this study. As the first step of top-down estimation based on the 3D model, we wanted to discuss the hemispheric differences. Since the isotopic scale differences are not yet unified with better precision than natural atmospheric contrast at the present, we regarded data by Röckmann et al. (2005) and Ishijima et al. (2007) as the best data sets. Also their data periods are enough overlapped. If other data sets are included, we would have to make further effort to consider several uncertainty sources (scale, local source effect etc). We avoided that.

To include the data by Toyoda et al. (2013), we would need conventional inversion approach to optimize regional emissions, because the data seems to have high continental emission influences. For example, recent several inversion studies are advocating that the anthropogenic inventory much overestimate methane emission from China in the 2000s. This could happen for N_2O, but N_2O isotopic observation network is still immature in terms of the measurement precision, inter-calibration scale and number of stations. We definitely think that the next step is the conventional inversion with multiple station's data.

15. Latitudinal gradient in section 5.3 should be in unit of nmol mol^-1 per deg latitude.
Or you meant hemispheric difference?

Do you mean this sentence "showing the maximum gradients, between the surface and 8 km altitude, of about 1.3 nmol mol^{-1}, …." ? If so, yes, you are right. We will correct it.

References
P. K. Patra, Y. Niwa, T. J. Schuck, C. A. M. Brenninkmeijer, T. Machida, H. Matsueda, and Y. Sawa, Carbon balance of South Asia constrained by passenger aircraft CO2 measurement, Atmos. Chem. Phys., 11, 4163-4175, 2011.
A. Ostler et al., The imprint of stratospheric transport on column-averaged methane, Atmos. Chem. Phys. Discuss., 15, 20395-20447, 2015.

Nevison et al., Interannual and seasonal variability in atmospheric N2O, Global Biogeochem. Cycles, 21, GB3017, 2007.

Response to comment 7 (for photolytic fractionation tuing)

Original photolysis case (A)

A1

Alt (km)	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{14}N^{14}N^{18}O$
NMY	3.02789e+2	1.11169e+0	1.13183e+0	6.34724e−1
16.1	2.93970e+2	1.07931e+0	1.09886e+0	6.16237e−1
18.1	2.86140e+2	1.05083e+0	1.07020e+0	6.00037e−1
20.8	2.41218e+2	8.87319e−1	9.05503e−1	5.07029e−1
24.6	1.89765e+2	7.00608e−1	7.18098e−1	4.00935e−1
26.6	1.62381e+2	6.00584e−1	6.16984e−1	3.43893e−1
29.1	1.21090e+2	4.49496e−1	4.64127e−1	2.57906e−1
31.1	7.95229e+1	2.97282e−1	3.09693e−1	1.71046e−1
33.5	6.27872e+1	2.35387e−1	2.46259e−1	1.35628e−1
34.7	4.39810e+1	1.65531e−1	1.74173e−1	9.55659e−2

A2

Alt (km)	N_2O	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
NMY	3.05667e+2	−1.35221e+0	1.67388e+1	4.54105e+1
16.1	2.96764e+2	−1.35221e+0	1.67388e+1	4.54105e+1
18.1	2.88861e+2	−1.09431e+0	1.73188e+1	4.57851e+1
20.8	2.43518e+2	5.50981e−1	2.10561e+1	4.82505e+1
24.6	1.91585e+2	4.21728e+0	2.92861e+1	5.36566e+1
26.6	1.63942e+2	6.02314e+0	3.34937e+1	5.61608e+1
29.1	1.22262e+2	9.68549e+0	4.25488e+1	6.21716e+1
31.1	8.03009e+1	1.68241e+1	5.92734e+1	7.26601e+1
33.5	6.34044e+1	1.97193e+1	6.68179e+1	7.72567e+1
34.7	4.44163e+1	2.37268e+1	7.71684e+1	8.36268e+1

A3

Alt (km)	$-\ln([N_2O]/[N_2O]_b)$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$
16.1	2.95588e−2	0.00000e+0	0.00000e+0	0.00000e+0
18.1	5.65522e−2	2.58214e−4	5.70225e−4	3.58273e−4
20.8	2.27307e−1	1.90395e−3	4.23722e−3	2.71297e−3
24.6	4.67166e−1	5.56153e−3	1.22651e−2	7.85703e−3
26.6	6.22982e−1	7.35820e−3	1.63447e−2	1.02308e−2
29.1	9.16332e−1	1.09920e−2	2.50682e−2	1.59059e−2
31.1	1.33672e+0	1.80372e−2	4.09830e−2	2.57321e−2
33.5	1.57296e+0	2.08805e−2	4.80800e−2	3.00081e−2
34.7	1.92889e+0	2.48028e−2	5.77355e−2	3.59040e−2

	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
ε (A4)	1.34781e−2	3.12363e−2	1.94571e−2

Reduced photolysis case (B)

B1

Alt (km)	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{14}N^{14}N^{18}O$
NMY	3.02789e+2	1.11169e+0	1.13183e+0	6.34724e−1
16.1	2.93970e+2	1.07946e+0	1.09901e+0	6.16319e−1
18.1	2.86140e+2	1.05111e+0	1.07047e+0	6.00185e−1
20.8	2.41218e+2	8.88197e−1	9.06365e−1	5.07490e−1
24.6	1.89765e+2	7.02370e−1	7.19813e−1	4.01823e−1
26.6	1.62381e+2	6.02526e−1	6.19153e−1	3.44963e−1
29.1	1.21090e+2	4.51903e−1	4.66643e−1	2.59204e−1
31.1	7.95229e+1	2.99826e−1	3.12267e−1	1.72437e−1
33.5	6.27872e+1	2.37698e−1	2.48608e−1	1.36958e−1
34.7	4.39810e+1	1.67463e−1	1.76154e−1	9.66950e−2

B2

Alt (km)	N_2O	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
NMY	3.05667e+2	−1.35221e+0	1.67388e+1	4.54105e+1
16.1	2.96765e+2	−1.21036e+0	1.68794e+1	4.55507e+1
18.1	2.88861e+2	−8.32381e−1	1.75724e+1	4.60421e+1
20.8	2.43520e+2	1.54106e+0	2.00278e+1	4.92051e+1
24.6	1.91589e+2	6.74296e+0	3.17438e+1	5.59904e+1
26.6	1.63947e+2	9.27556e+0	3.71281e+1	5.94497e+1
29.1	1.22268e+2	1.50908e+1	4.82020e+1	6.75181e+1
31.1	8.03074e+1	2.55245e+1	6.80792e+1	8.13825e+1
33.5	6.34104e+1	2.97303e+1	7.69927e+1	8.78206e+1
34.7	4.44213e+1	3.56737e+1	8.94252e+1	9.64306e+1

B3

Alt (km)	$-\ln([N_2O]/[N_2O]_b)$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$
16.1	2.95575e−2	1.42029e−4	1.38241e−4	1.34109e−4
18.1	5.65498e−2	5.20395e−4	8.19469e−4	6.04028e−4
20.8	2.27298e−1	2.89300e−3	5.18844e−3	3.62320e−3
24.6	4.67143e−1	8.07345e−3	1.46501e−2	1.00695e−2
26.6	6.22951e−1	1.05859e−2	1.98551e−2	1.33401e−2
29.1	9.16282e−1	1.63312e−2	3.04760e−2	2.00269e−2
31.1	1.33663e+0	2.65573e−2	4.92616e−2	3.38307e−2
33.5	1.57287e+0	3.06501e−2	5.75723e−2	3.97666e−2
34.7	1.92878e+0	3.64053e−2	6.90499e−2	4.76504e−2

	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
ε (B4)	1.97492e−2	3.73402e−2	2.57470e−2

Tuned photolysis case (C)

C1

Alt (km)	$^{14}N^{14}N^{16}O$	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{14}N^{14}N^{18}O$
NMY	3.02789e+2	1.11169e+0	1.13183e+0	6.34724e−1
16.1	2.93970e+2	1.07936e+0	1.09898e+0	6.16270e−1
18.1	2.86140e+2	1.05092e+0	1.07042e+0	6.00096e−1
20.8	2.41218e+2	8.87582e−1	9.06193e−1	5.07213e−1
24.6	1.89765e+2	7.01137e−1	7.19470e−1	4.01290e−1
26.6	1.62381e+2	6.01166e−1	6.18719e−1	3.44321e−1
29.1	1.21090e+2	4.50218e−1	4.66140e−1	2.58425e−1
31.1	7.95229e+1	2.98045e−1	3.11752e−1	1.71602e−1
33.5	6.27872e+1	2.36080e−1	2.48138e−1	1.36160e−1
34.7	4.39810e+1	1.66111e−1	1.75758e−1	9.60175e−2

C2

Alt (km)	N_2O	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
NMY	3.05667e+2	−1.35221e+0	1.67388e+1	4.54105e+1
16.1	2.96764e+2	−1.30965e+0	1.68513e+1	4.54666e+1
18.1	2.88861e+2	−1.01573e+0	1.75216e+1	4.58879e+1
20.8	2.43519e+2	8.48005e−1	2.18335e+1	4.86323e+1
24.6	1.91587e+2	4.97498e+0	3.12523e+1	5.45901e+1
26.6	1.63945e+2	6.99887e+0	3.64012e+1	5.74764e+1
29.1	1.22265e+2	1.13071e+1	4.70713e+1	6.43102e+1
31.1	8.03043e+1	1.94342e+1	6.63180e+1	7.61491e+1
33.5	6.34075e+1	2.27226e+1	7.49577e+1	8.14822e+1
34.7	4.44189e+1	2.73109e+1	8.69738e+1	8.87483e+1

C3

Alt (km)	$-\ln([N_2O]/[N_2O]_b)$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$	$\ln((\delta+1000)/(\delta_0+1000))$
16.1	2.95581e−2	4.26108e−5	1.10594e−4	5.36457e−5
18.1	5.65510e−2	3.36876e−4	7.69625e−4	4.56582e−4
20.8	2.27303e−1	2.20077e−3	4.99827e−3	3.07716e−3
24.6	4.67154e−1	6.31577e−3	1.41736e−2	8.74260e−3
26.6	6.22966e−1	8.32761e−3	1.91540e−2	1.14757e−2
29.1	9.16306e−1	1.25968e−2	2.39868e−2	1.79173e−2
31.1	1.33667e+0	2.06009e−2	4.76114e−2	2.89794e−2
33.5	1.57291e+0	2.38214e−2	5.56811e−2	3.39229e−2
34.7	1.92883e+0	2.82977e−2	6.67973e−2	4.06191e−2

	$\delta^{15}N^{\beta}$	$\delta^{15}N^{\alpha}$	$\delta^{18}O$
ε (C4)	1.53670e−2	3.61240e−2	2.19615e−2

	$^{15}N^{14}N^{16}O$	$^{14}N^{15}N^{16}O$	$^{14}N^{14}N^{18}O$
Scaling factor (f)	0.7	0.2	0.6
(O4)	1.53595e−2	3.61194e−2	2.19730e−2

In this table, model results of $^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, and $^{14}N^{14}N^{18}O$ for a balloon observation over Japan in 1990 are used, as an example.

Original, reduced photolysis cases are represented by case (A) and (B). They are converted to the N2O-MF and delta values (A2, B2), and their Rayleigh plots are made (A3, B3). By linear fitting to them, apparent fractionation constants (ε) are calculated (A4, B4).

In order to make pseudo ε for the observation, scaling factors (f) are assumed to be 0.7, 0.2 and 0.6. Here, observed ε is O4 (= f*A4+(1-f)*B4).

Going back to mole fractions and applying the scaling factors to A1 and B1, optimized data set C1 (=f*A1+(1-f)*B1) is produced. At the same time, J_C=f*J_A+(1-f)*J_B is also valid following Eq (10) in the main text. Similarly to A1 and B1, ε for optimized model is calculated (C4). The C4 agrees with O4 within 0.1 %. Their agreement is not perfect, but it is obvious that this approach well works for tuning the photolysis.

For conversion between mole fraction and delta value, Eqs (1)~(9) in the main text are needed.