Reply to the referee #1

Referee's comment is typed in blue, and authors' response is typed in black.

This paper extends previous measurements and analysis of the vertical distribution of N2O isotopocules into the tropical stratosphere. It introduces a new sampling system with a much weight-reduced cryogenic sampler. The measurements are impressively accurate and precise and show systematic differences to previously published mid latitude profiles, with implications for the balance between photolysis and photooxidation of N2O, and transport, in determining the vertical distributions. The paper is clearly written and presented. It is well suited to ACP and I recommend publication as is except for a few technical edits as listed below.

We appreciate the referee for his/her constructive comments. We have revised the manuscript according to his/her suggestions.

Technical comments:

P3 L11: …but it has not been FULLY examined because of…

Revised as suggested. (P3 L22 in the revised text)

P8 L13 and elsewhere – please replace all instances of “transportation” with “transport”.

Revised as suggested.

P8 L14 & 15: I suggest using “photochemistry” rather than “photolysis” here because the first reference on L14 is to both photolysis and phot-oxidation.

This paragraph has been deleted according to the comments by referee #2.

P8 L19: “faster” would be more unambiguous than “larger” in this context

This paragraph has been deleted according to the comments by referee #2.

Caption figure 2 – it would be helpful here to list the site names and three letter abbreviations so the reader is not obliged to go to the supplementary material to find out. Defined once is enough to cover all later figures.

Revised as suggested.

Reply to the referee #2

Referee's comment is typed in blue, authors' response is typed in black, and the change in the revised text is highlighted with red.

In this manuscript, Toyoda et al present the first vertical profiles of the isotopic composition of N2O in the deep tropical stratosphere (i.e., quite literally over the equator) that extend above 21 km. They use a new, unique very small cryogenic whole air sampler that can be launched from ships using small balloons and retrieved from the ocean surface after a water landing; this is critical since more traditional cryogenic whole air samplers are extremely heavy and therefore must be launched with very large balloons, greatly limiting their deployment in the deep tropics, especially if they must also be designed to survive ocean landings in addition to the difficulty of finding suitable launch sites near the equator. The magnitudes of the isotopic fractionation of N2O in the deep tropics and the character of the relationships between the N2O isotopic compositions with N2O mixing ratios have been a topic of speculation for over a decade, especially given the promise that deep tropical data up to 30 to 35 km could hold for further elucidation of the patterns and rates of transport between the tropics and extratropics and for the competition between transport and photochemistry in determining the isotopic composition of N2O. This first new deep tropical dataset with measurements up to 30 km is therefore exciting and interesting. These data, their comparison with previous measurements and model results from a number of research groups, and their analysis will therefore be of great interest to the stratospheric and isotope communities of researchers. That said, there are a number of improvements to the analysis, discussion, and presentation of the data that I think should be considered before publication.

We appreciate the referee for his/her many critical and constructive comments. We have revised the manuscript according to his/her suggestions.

Major points to consider:

1. A more clear motivation for the need for and applications of N2O isotope observations in the tropics could be given in the introduction as well as in the discussion and conclusions. The context and questions that remain unanswered or are controversial (or at least that some of us think are controversial and not proven) are not clearly outlined or discussed in the manuscript as currently laid out. In addition, many other tracer measurements have been used to study transport and mixing – what might be unique about N2O isotopocules? This could be mentioned, especially in the concluding section.

In the introduction, we revised or added following sentences describing the motivation, context, remaining questions, and uniqueness of N_2O isotopocules.

P2, L18–20

> Mixing ratios of trace gases such as N_2O and their interrelationships are regarded as useful tools to establish a detailed picture of stratospheric circulation (Plumb, 2007), and previous observations showed compact tracer relationships that depend on latitude (e.g, Michelsen et al., 1998).

P2, L25–28

In the context of stratospheric distribution, isotopocule ratios are unique in their ability to provide the degree of photochemical decomposition and the relative importance of the above-mentioned two decomposition pathways (Toyoda et al., 2001; Röckmann et al., 2001).

P3, L23–27

As noted above, tropical stratosphere is the starting point of meridional transportation of N_2O injected from the troposphere and the rates of photochemical reactions are faster than those in the extratropics because of stronger actinic flux. Although there are a few reports on vertical profiles of N_2O isotopocules over India (18°N) (Röckmann et al., 2001; Kaiser et al., 2006), isotopic composition of N_2O in upwelling tropical air has not been characterized.

P3, L29–P4, L4

Another controversial problem about the stratospheric N_2O is whether the photooxidation sink (Eq. 2) has larger contribution than 10% in the lower stratosphere. Kaiser and coworkers found that the ratios of enrichment factors of isotopocule during photolysis and photooxidation are distinct (Kiaser et al., 2002a) and they estimated that a much larger fraction than 10% is removed by photooxidation at least in the lower stratosphere (N_2O mixing raitos > 300 nmol mol^{-1}) (Kaiser et al., 2006). However, similar but a little simplified analyses by Park et al. (2004) and Toyoda et al. (2004) could not detect significant differences in the enrichment factor ratios between the lower and middle stratospheres, and Park et al. (2004) speculated that the enrichment factor ratios could be affected not only by the relative share of the two sink pathways but also by other factors such as transport.

In the concluding section, we revised the sentences to clarify the points revealed by our new observations as follows.

P11, L24–P12, L5

Vertical profiles of isotopocule ratios of N_2O in the equatorial stratosphere are found using balloon-borne compact cryogenic samplers and mass spectrometry in the laboratory. This report of the relevant literature is the first describing observations of them over the equator. Unlike other region of the stratosphere, enrichment factors for isotopocules in the middle equatorial stratosphere (25–30 km, or $[N_2O] < 260$ nmol mol^{-1}) agreed with those obtained with laboratory photolysis experiments, suggesting that the isotopocule ratios are determined mainly by photolysis because of weak vertical or horizontal mixing in the tropical upwelling. In the lower equatorial stratosphere (< 25 km or $[N_2O] >$ 260 nmol mol^{-1}), isotopocule ratios suggest that differently aged air masses are mixed because of the meridional transport and that decomposition by photooxidation might also plays a significant role. Vertical and latitudinal distributions of N_2O and its isotopocules are found to be a unique tool to diagnose the relationship between photochemistry and transport in the stratosphere. Further observations of temporal variations and comparison with ACTM simulation will be needed to examine the change in the meridional circulation and obtain the quantitative estimate of the importance of photooxidation pathway.

2. A lot of detail is given to 'normalize' the N2O isotope and mixing ratio data since there is quite a large time span of datasets with which the new tropical observations are compared. There are also ratios of epsilon values, which in some cases may be referred to as 'normalized' (i.e., relative to the tropopause). It is unclear to me what 'age corrected' and 'normalized' mean in various places. And it is also unclear which data are plotted in the main text and in the supplementary material. All this information should be made more explicit and clear in both the main text and the figure captions. I think it is also important to plot up and/or give in tables both the 'raw' data as well as the age-corrected/normalized data for comparison. I have further specific comments on this topic below.

The 'normalized' means that mixing ratio or delta values are expressed as relative values against those at the time when the measured air mass existed in the troposphere. We note that neither 'age corrected' nor "normalized epsilon" appear in our manuscript. The main text and the figure captions have been revised as follows, avoiding the ambiguous expression like "normalized δ". Also we added Table S3 to present raw data as well as converted data.

P8, L2–3

In Fig. 3, the $\delta^{15}N^{bulk}$ is shown against the N_2O mixing ratio after the normalization described in Eq. 6 (Rayleigh plot).

P9, L5–9

The ratio of ε values for independent isotopocules (e.g., $\varepsilon(^{15}N^{bulk})/\varepsilon(^{18}O)$), however, has been identified as a useful parameter to distinguish photolysis and photooxidation (Kaiser et al., 2002a) because its sensitivity to wavelength and temperature is small and it is not affected by mixing process. Figure 5 shows the data obtained in this study and some previous ones in δ–δ space after the normalization described in Eq. 6.

P11, L2–10

Kaiser et al. (2006) used the ratio of ε values for $^{15}N^{bulk}$ and ^{18}O (ψ) and the ratio of ε values for $^{15}N^{\alpha}$ and $^{15}N^{\beta}$ (η) to estimate the relative share of photolysis and photooxidation based on the fact that ψ and η are almost independent of transport processes and are significantly different between the two decomposition processes. They computed ψ and η values directly for each individual sample in order to avoid statistical errors associated with linear regression to the δ–δ plot which was adopted by Toyoda et al. (2004) and Park et al. (2004). In Fig. 10, we show ψ and η values calculated using the data presented in Fig. 2 in the manner similar to that of Kaiser et al. (2006) except that we used individual date of stratospheric entry for each data to normalize the δ values instead of using a single tropopause date. Although it is noteworthy that errors in ψ and η values increase concomitantly with decreasing altitude because of the decrease in the δ values, ….

Caption of Figure 3

… Both parameters are normalized to their values at the time when the corresponding air mass entered the stratosphere (see Eq. 6 in the text).

Caption of Figure 10

Vertical profiles of ratio of ε values for $^{15}N^{bulk}$ and ^{18}O (ψ) and the ratio of ε values for $^{15}N^{\alpha}$ and $^{15}N^{\beta}$ (η) calculated in the manner similar to that of Kaiser et al. (2006).

3. My own opinion is that analyzing the isotope data in subsets of altitude bins (which depend on latitude) is a lot less illuminating than with respect to grouping by N2O mixing ratio, which is in some ways less complicated than altitude given the Brewer-Dobson circulation bringing much older air down from higher altitudes in the extratropics and the polar vortices. Indeed, by binning by N2O mixing ratio, aircraft data from other researchers and I'm sure from the authors' own aircraft datasets can be more easily compared, rather than being limited here by vertical profiles obtained by balloons. This might also be why the Esrange flight from Sweden in early February was not split into a 'lower' and a 'middle' because figuring out where to put the altitude bin might have been difficult for this flight since N2O is so low at a given altitude relative to the other balloon profiles. For example, the data plotted in Figure 3 for the Swedish vortex flight beg to be plotted into 2 groups "M" and "L" (for 'middle' and 'lower' respectively), and yet they are given as one group. It would be interesting to see how small the apparent epsilon value would be for the vortex data, as well as to compare that with remnant vortex data on samples collected by aircraft from Park et al. [2004]. The more complicated the transport and mixing history of air masses in different regions of the stratosphere and/or at different times, the lower the apparent epsilon value is, and the Esrange data and some aircraft data could be very convincing in showing this, and contrasting it with these first deep tropical data at altitudes >23 km and N2O mixing ratios <250 ppb, for which transport and mixing have the least influence compared with the rest of the stratosphere. This is the point the authors are trying to make but I think it could be made much more clear.

We thank the referee for the constructive comment. We analyzed the data in subset of altitude bins simply because all of our data were obtained as vertical profiles. We agree that it would be better to use N_2O mixing ratio for the grouping to compare with data obtained by aircrafts. Even so, we consider the normalization is necessary to account for the increasing trend of tropospheric N_2O and the time lag from the entrance into the stratosphere, instead of simply using mixing ratio. In the revised manuscript, we use $-\ln\{[N_2O]/[N_2O]_0\} = 0.2$ and 0.6 as a boundary for tropics and extratropics, respectively, because at these points slope of Rayleigh plots change significantly and the highest R^2 values are obtained in most cases. Based on the new binning, ε values in the middle and lower stratosphere of the winter arctic polar vortex are now also shown. Abstract, a few sentences in section 3.2, conclusion and Figure 4 have been revised accordingly.

4. The exciting thing about the new deep tropical dataset is that it clearly shows what we all expected: that in the deep tropics where the stratosphere is effectively the most “isolated” relative to all other regions, the fractionation for all the N2O isotopocules is as “Rayleigh” as it gets, and that the apparent epsilon values are close to that for photolysis in the lab. However, rather than discuss this qualitatively from a “Rayleigh” perspective, and using other stratospheric data/observations to show that this is consistent with what we know about relative transport and chemical time scales in different regions (and seasons) in the stratosphere, the authors instead jump right to an equation from Kaiser et al [2006] (which also appears in Kaiser et al. 2002a, an observation and lab study, and Morgan et al. 2004, a modeling study) that is an approximation to an approximation for a 1D model of the stratosphere. This would, I suppose, be all right except that – given what we know about transport time scales and the photochemical lifetime of N2O in the tropics and the extratropics as a function of altitude from models and from other stratospheric observations (such as N2O, CO2, H2O, CH4 and other long-lived tracers and their correlations) – this 1D model analogy I think actually gives us the wrong answer! Thus, I find this section misleading and not especially useful or illustrative at best and incorrect at worst.

Here is my point as to why I think simple departures from a Rayleigh model based on how much transport and mixing there has been relative to other regions of the stratosphere are more enlightening than this pseudo 1D model treatment: First, below 22 km, transport time scales are fast (and the pseudo 1D treatment convolves both vertical and horizontal/quasi-isentropic transport as ‘eddy diffusion’) and the photochemical decomposition of N2O is very slow (by both photolysis and reaction with O(1D)). At 20 km, the transport time scale may be months while the e-folding time for N2O destruction is 70 years, for example. If you plug t(trans)«t(chem) into Equation 7, however, the result is epsilon effective = epsilon sink. In contrast, higher up in the tropical stratosphere, t(trans)»t(chem) [where the photochemical destruction really starts picking up speed], so now Equation 7 simplifies to epsilon effective = 1/2 epsilon sink. But that’s exactly where one would expect Rayleigh fractionation to hold – where the change in N2O isotopic composition is going to follow the change in N2O mixing ratio according to epsilon for the sink without transport messing things up. So these two limits from Equation 7 are the opposite of what the new deep tropical observations show! At midlatitudes below 30 km where t(trans)«t(chem) for N2O [again, from many other stratospheric ‘non-isotope’ studies], Equation 7 would give epsilon effective = epsilon sink and yet the observations show it is more like the other limit, epsilon effective = 1/2 epsilon sink. So also the opposite of the Equation 7 limits. Indeed, even Kaiser et al. [2006] say the following: “even though the apparent fraction constants could possibly be reconciled with certain diffusion coefficients and [N2O] destruction rates, the [observed] increase of the magnitude of the apparent fractionation constant with altitude is actually the opposite to what one would expect from a simple vertical reactiondiffiusion-advection model. . . Despite the conceptual usefulness of this 1D description, it has to be stressed that stratospheric transport cannot be characterized as a function of altitude alone and that vertical diffusion is actually not an important process, even though it can be helpful to describe stratospheric transport to some extent. Meridional transport schemes have to be included to explain the variation of epsilon apparent.” Thus, Equation 7 gives the opposite answer to all the N2O isotope observations I am aware of, including these new ones in the deep tropics, and even Kaiser et al [2006] had to invoke what we know about meridional patterns of transport and mixing to explain all the stratospheric observations available in 2006. Thus, it is not true, as stated by the authors in this manuscript on Lines 15-20 on Page 8 in this section, that Kaiser et al “used this simplified scheme in Equation to describe qualitatively the vertical and meridional trends in epsilon [values] obtained over latitudes ranging from 18 to 80 (N or S).” Hence I do not find Equation 7 nor the discussion around it to be useful and I think it is actually wrong to use it here. The 2D nature of the Brewer-Dobson circulation and the concomitant chemical and transport timescales associated with the transport and mixing in 2D is required to understand the distribution of N2O isotopes and their relationship with N2O mixing ratios everywhere; Equation 7 does not work.

That said, the 2D mixing scheme the authors use does qualitatively work for me. While I’m not sure where their ‘10%’ number comes from (it’s arbitrary), qualitatively it can explain the 2D mixing patterns relative to the photochemical time scales for N2O destruction and why (a) at higher altitudes in the tropics, epsilon apparent = epsilon sink (again a very exciting set of observations) and (b) at lower altitudes in both the tropics and the extratropics, epsilon apparent is more like 1/2 epsilon sink). Thus, I recommend simply removing the 1D model equation and discussion entirely. It leads the reader to the opposite conclusion, as has been pointed out previously, while the qualitative mix-ing model is actually more realistic (or at least illustrative), despite it perhaps seeming somewhat arbitrary to some readers.

And the 3D model comparison is a nice follow-on to the 2D results and discussion, and shows quite a nice quantitative agreement with the observations in Figures 8 and 9. In fact, the authors conclude that “Because in situ epsilon photolysis used in the model calculation is nearly the same between low and high latitudes (Fig. S3a), this agreement supports the inference that the major causes of the difference [in epsilon values] are transport and mixing.” I agree, and Morgan et al. [2004] have similar results from their 2D CTM results.

The 1D Equation 7 conclusions being the opposite of what these and all past data (I think) show, if the authors modify their approach on this, then these ideas also need to modified in the abstract and conclusions as well, where in some cases the opposite of ‘transport’ vs ‘chemical time scales’ and what that means for epsilon values are reversed.

We thank the referee for the critical comments and detailed explanation. We realize that the 1D model is inappropriate to explain the difference in ε values between the lower and middle stratosphere. We have revised section 3.3.2 as follows, removing the discussion with 1D model.

P9, L15–24

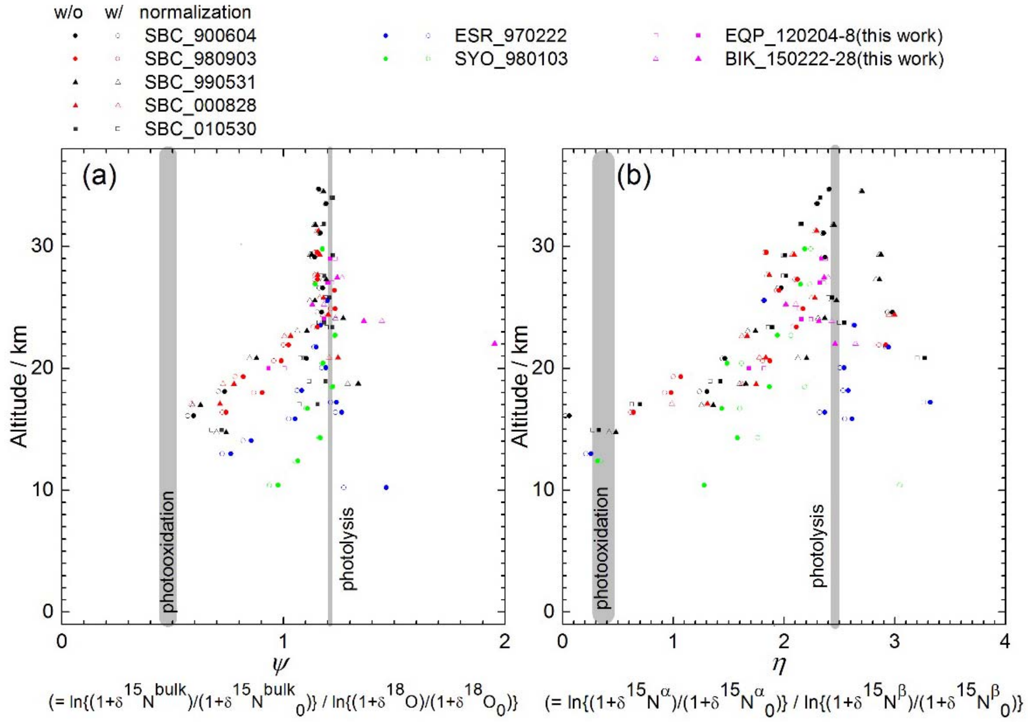
Transport processes accompanied by mixing of variously aged stratospheric air has been considered as the major cause of lower $|\varepsilon|$ value in the stratosphere than in the laboratory photochemical decomposition (Park et al., 2004; Kaiser et al., 2006). Our new observation revealed that all the N_2O isotopocules are fractionated by the almost ideal Rayleigh process in the middle stratosphere over the deep tropics where the stratosphere is effectively the most isolated relative to all other regions. This underlines how much transport and mixing affect the apparent ε value.

We then consider the effect of transport on the apparent ε at different latitudes with a conceptual two-dimensional circulation model in the tropical and extra-tropical stratosphere that was proposed to explain tracer–tracer correlation (Plumb, 2002). …

5. After many years of debate with this community using all our datasets in common and often coming to opposite conclusions, I still do not find the evidence that others cite – and including the analysis of the new data here in Section 3.4 ("Share of photolysis and photooxidation) – that the N2O isotopic compositions suggest that O(1D) accounts for a significantly larger share of N2O destruction at low altitudes.

(a) As the authors themselves point out, the 'normalization' and/or 'age correction' will have the largest noise and uncertainty in the lower stratosphere. Much of the variations in Figure 10 could be noise.

The larger errors in ψ and η at lower altitudes are not introduced by the normalization, but the small difference in δ values between the stratosphere and troposphere. Effect of the normalization is smaller than the error bars in Fig. 10 as shown below.



(b) I do not find Figure S3b to be convincing or perhaps even relevant. It is not the ‘share’ of N2O destruction by photolysis versus reaction with O(1D) that is relevant (which is what is plotted in Fig S3b), if the lifetime of N2O with respect to destruction to both processes is 70 years. 70 years is the ‘in situ’ N2O lifetime at 18 km in the tropics, for example. Thus, the decrease in N2O mixing ratios observed just above the tropical tropopause is due to photochemical destruction elsewhere: photochemically aged air from middle latitudes (which itself came from higher altitudes) is transported into thelower tropical stratosphere. . .. In other words, if essentially no N2O destruction is occurring in the lower stratosphere, then what does it matter if the share of photooxidation by O(1D) is >70% according to the ratio of their rate constants/J-values (as in Figure S3b)? Likewise, what does it mean in Figure S3b in February above the Arctic Circle when and where it is completely dark to show the relative rates of destruction of N2O by photolysis and by O(1D)? And, finally, the tropical tropopause is at 18+ km in the deep tropics, so the share of O(1D) photoxidation below 18 km doesn’t really matter, does it, if this tropospheric air keeps being ‘reset’ by tropospheric N2O? Hence, I don’t see the relevance of Fig S3b, unless it is also accompanied with a plot of the total rate of destruction of N2O as a function of latitude and altitude to be able to better interpret Fig S3b and the point the authors are trying to make.

We thank the referee for this critical comment. We have added a supplementary graph of total loss rate constant of N_2O as a function of altitude (Fig. S6a, note that figure number has been changed from S3) and deleted a part of the plots of tropics and all the plots of February Arctic region so that the plots show the parameters in the region where photochemical N_2O loss really occurs. We agree that the loss rate of N_2O in the lower stratosphere is very slow and therefore the larger share of $O(^1D)$ sink in *in situ* total loss below 25 km is not directly reflected on the observed isotopocule ratios. However, we consider the decrease in ψ and η in the lower stratosphere cannot be explained solely by transport and mixing based on an example using a conceptual 2D model (see our response to the comment #5(c) below). As the referee pointed out, majority of N_2O injected into the stratosphere is destructed in the middle stratosphere and the photochemically aged air mass must be transported into the lower stratosphere. But we consider there is a possibility of additional decomposition of remaining N_2O during the transport (which should be slower than that of the tropical upwelling) and the isotopic signature of $O(^1D)$ pathway could be imprinted. Sentences in the last half of section 3.4 have been revised as follows.

P11, L13–22

> Although the loss rate of N_2O in the lower stratosphere is very slow and the majority of N_2O injected into the stratosphere is photolyzed in the middle stratosphere as noted by Park et al. (2004), the share of photooxidation in *in situ* total loss increases in the lower stratosphere (Fig. S6b). Therefore, there is a possibility of additional decomposition of remaining N_2O during the transport (which should be slower than that of the tropical upwelling) and the isotopic signature of $O(^1D)$ pathway could be imprinted, and the photochemically aged air mass must be transported into the lower stratosphere of the tropics and extratropics. However, Morgan et al. (2003) reported that inclusion of isotope fractionation for photooxidation into their 2D model does not make a significant contribution to overall fractionation in the stratosphere, and Park et al. (2004) discussed an alternative modelling

approach with and without O(^{1}D) sink to test the importance of O(^{1}D) reaction. Further studies using 3D model would be necessary to solve this controversial problem.

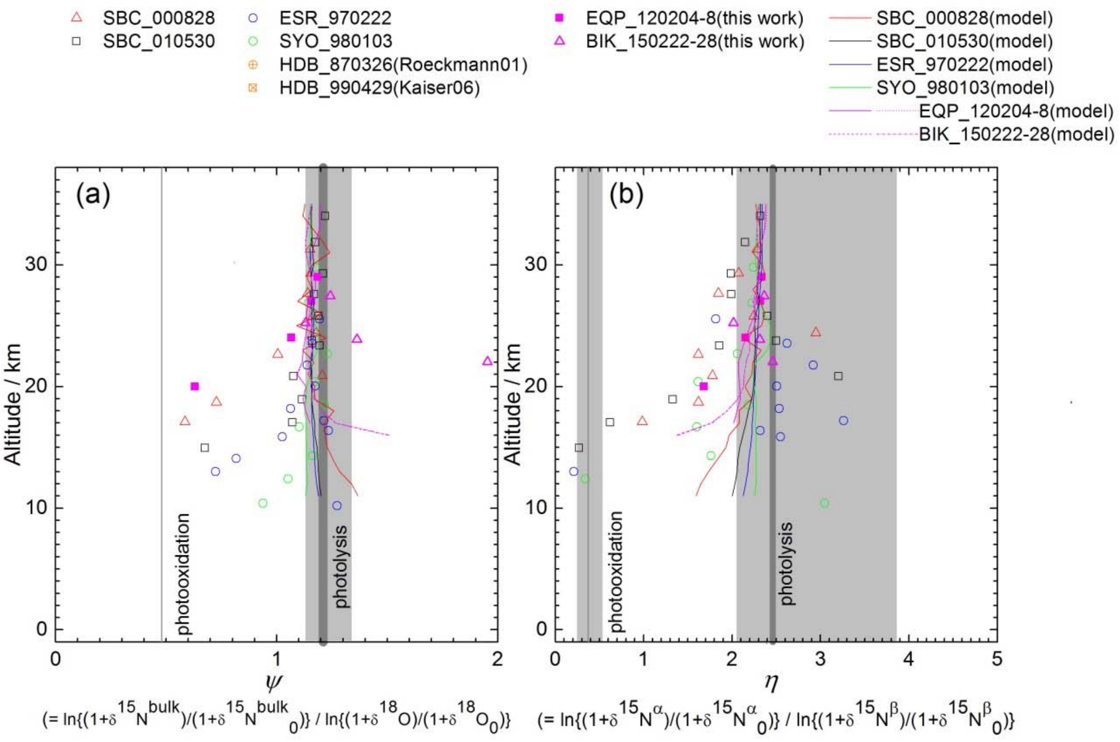
(c) Another reason why the datapoints may shift nominally toward the 'photooxidation' fractionation line in Figure 10 at the lowest altitudes is that some of these samples were likely collected in 'lowermost stratosphere' (potential temperature < 380K) where there is substantial mixing with tropospheric air that has not entered the stratospheric overworld across the tropical tropopause (or theta>380K). The epsilon apparent could be even LOWER, without resorting to invoking oxidation by O(1D) – if it's just mixing with tropospheric air. In this case, it might not be true that the ratios of epsilon apparent values are really independent of transport. I am not claiming that all the deviations are from the lowermost stratosphere but I would just caution that there are several reasons (a, b, and c) that I would be very careful about and try to rule out, if possible, when interpreting the data points and their spread in Figure 10.

We agree that apparent epsilon values in the lower stratosphere could be decreased by mixing with tropospheric air, but we cannot agree that the ratios of apparent epsilon values might depend on transport. For example, if we make the 2D simulation shown in Fig. 7 with different epsilon value (e.g., −40 permil) and calculate the ratio of apparent epsilons obtained for the black stars by the two different simulations, we obtain exactly the same ratios for all data points. As the referee points out below, 3D simulation might be needed to further ascertain this, but we consider it is beyond the scope of this paper.

(d) What I would find most convincing (in addition to being very careful about the possibilities in a-c) is the following: Use the 3D model and try two things. 1. Set the O(1D) KIEs in the model to 1 and see if the model shows anything different for the ratio of epsilon apparents for different N2O isotopes vs N2O mixing ratio relationships (best) or the ratio of epsilon apparents for different N2O isotope versus altitude relationships (ok) without any isotope fractionation for N2O+O(1D) versus their normal isotope runs. If the results for the two different types of runs look the same, then O(1D) isotope fractionation could not have been contributing anything in the lower stratosphere. Indeed, Morgan et al. [2004] did just this and didn't find any evidence in the modeled N2O isotopes for an increased fraction of N2O destruction by reaction with O(1D). I think this is significant. 2. Another thing to try is what Park et al. [2004] suggested; they agreed with McLinden [2003] and a number of non-isotope N2O studies and models that suggest there is not a larger role for N2O destruction in the lower stratosphere beyond about 10% of the total destruction. However, because the KIEs for O(1D)+N2O are quite small, perhaps an increased contribution could be in the noise also in comparing the model results for the two different scenarios with and without O(1D) KIEs. Park et al suggested that another complementary model test of this idea would be to compare the ratios of epsilon values in regular model results versus model results in which O(1D) photooxidation had been removed all together and to examine any differences in the lower stratosphere, in combination with model results with the O(1D) KIEs set to 1.

We appreciate the referee for the constructive comment. Before considering his/her suggestion, we have examined how the ψ and η values calculated from the data simulated by the 3D model are compared with those from observation. As shown below, η_{model} shows similar vertical trend as η_{obs} although its range is smaller. In contrast, ψ_{model} is almost independent of the altitude and shows larger value in the tropical lower stratosphere. We also confirmed that ψ and η calculated from ε values based on in situ J values do not depend on latitude nor altitude. Therefore, we recognize that there is a possibility that ψ and η might be affected by factors other than the relative share of photolysis and photooxidation.

We then examined the procedure how to conduct the simulations suggested by the referee. Unlike the simpler 2D model of Morgan et al. (2004), our 3D model optimizes emissions from the individual surface N_2O sources using several emission scenarios to simulate the tropospheric N_2O mixing ratio and isotopocule ratios. Therefore, if we change epsilon for photooxidation to 0‰ (i.e., KIE = 1) or if we remove the photooxidation sink, tropospheric (and hence tropical lower stratospheric) mixing ratios and isotopoule ratios and their trends will be also changed. To keep the tropospheric values close to the realistic ones, additional optimization of the surface emission are needed and this will cost huge computational resources (output data size will be 3.4TB for each simulation) and time (more than three weeks for each simulation). We consider that this is too much task to revise our current manuscript and that it should be done as a separate work.



6. Finally, as noted above, the authors could provide some more background and motivation for why tropical data is exciting and interesting as well as any practical applications throughout. Some more specific suggestions:

6-1) It would be beneficial for reproducibility and contribution to the scientific community if the authors included a table in the supplementary information of their data and a table of derived epsilon values and uncertainties.

We have added two supplementary tables. Raw and normalized isotopic data are listed in Table S3. Derived epsilon values are listed in Table S4.

6-2) Isotope Ratio Mass Spectrometry (there's not really any 'Monitoring' in this, yet 'monitoring appears in several places in this acronym).

We have revised the sentence as follows.

P5, L10–12

> The isotopocule ratios, … using gas chromatography – isotope ratio mass spectrometry.

6-3) In Methods, a few more details could be more explicit: -> there is only one or later two samples per small balloon flight

We have revised the sentences as follows.

P4, L25–27

> For each balloon flight, a 5–8 L STP of air sample was collected by a single sampler at programmed altitude of 19–29 km.

P4, L30–31

> For each balloon flight, two samplers integrated into a single gondola were launched from …

6-4) -> the fact that a sample covers an altitude range rather than one altitude needs to be included explicitly in the methods section, and what a typical altitude range is (and if it depends on altitude).

We have added the following sentences.

P5, L4–6

> Sampling was conducted while the balloon was ascending except the flight on Feb 5, 2012. Typical altitude range was about 2 km, and we took the central value of the range as the sampling altitude.

6-5) _> The Griffith et al FTIR is technically a 'remote' measurement, not 'in situ'. They are retrieving information rather far from the gondola, even though the gondola is flying on a huge balloon in the stratosphere.

We have revised the sentence as follows.

P3, L1–5

> For balloon observations, … (b) remote measurements are conducted ….

6-6) The 'age corrections': beware the seasonal cycle of CO2 that propagates from the troposphere. This can give a large error in the estimate mean age [e.g., Andrews et al., 1999, 2001].

According to Andrews et al. (2001), errors for the mean age associated with the tropospheric CO_2 seasonal cycle is less than 0.3–0.5 years. This is translated to error of 0.2–0.4 nmol mol^{-1} in the correction for N_2O

mixing ratio at the time of the air mass's entry into the stratosphere because annual trend of tropospheric N_2O is ~0.7 nmol mol^{-1}/yr. This error is about 25–50% and 5–10% of the correction value in the lower stratosphere (~1.5 nmol mol^{-1}) and in the middle stratosphere (1.5–4 nmol mol^{-1}), respectively. But in the final logarithmic form of $\ln\{[N_2O]/[N_2O]_0\}$, it is less than 0.001. Therefore, the effect of seasonal cycle of CO_2 is insignificant in the analysis of present study.

We added the following sentences at the end of section 2.2 to explain the effect of the normalization and possible errors introduced by the data conversion.

P6, L11–16

> In Table S3 we compare how much this correction regarding the age of air changed the position of each data point in Figs. 3 and 5. Typically, the term related to mixing ratio ($-\ln\{[N_2O]/[N_2O]_{trp}\}$) is decreased by 0.2–3% when we use $[N_2O]_0$, the value when the air mass actually entered into the stratosphere, instead of the value at the same time of the observation, $[N_2O]_{trp}$. The isotopic terms ($\ln\{(1+\delta)/(1+\delta_{trp})\}$) are either increased or decreased depending on their secular trends, and they are changed by 0.2–3%.

6-7) Air enters the stratosphere from the tropics, and, based on CO2 mixing ratio measurements taken over a very long time period (years) in both hemispheres, the air has a composition reflecting an admixture of NH and SH air [e.g, Boering et al. 1996, Andrews et al. 1999, 2001]. To take Cape Grim as the 'boundary condition' for SH stratosphere measurements and Mace Head for NH stratosphere measurements and a tropical site for tropical stratosphere measurements seems unduly complicated (if this correction is small) or simply introduces more error (if this 'correction' is actually significant). As noted above, also, it would be nice to have the raw data in supplementary materials as well as the 'corrected' and 'normalized' data used in the analyses.

As the referee points out, our selection of tropospheric reference value is somewhat arbitrary and the corrections are comparable or small relative to the measurement error. Nevertheless, we consider it is better approach to make a closer analogy to a Rayleigh fractionation system as noted by Kasier et al. (2006). We added Table S3 to present raw data as well as the converted data. See also our reply to the comment #6-6).

6-8) Section 2.3 model details: This section is difficult to read and to follow what is the same from earlier publications and what is different.

The differences from earlier publications are (1) avoiding the optimization of photolytic enrichment factors, (2) meteorological reanalysis data for nudging, and (3) modified surface emissions. The last paragraph in section 2.3 has been revised as follows.

P7, L4–11

> While both the surface emissions and the photolytic isotopocule fractionations were optimized in the earlier work by Ishijima et al. (2015), only the former was optimized in the present study. This is because we considered that it would be better to keep the experimentally determined original isotopocule enrichment factors for the purpose of comparison between the model and the

> observations in the stratosphere. Moreover, we found that apparent isotopocule enrichment factors obtained by the model simulation become much closer to those by the balloon observations by replacing the meteorological data from JRA-25 (Onogi et al., 2007) with those from ERA-interim. This is probably because dynamics and chemical reactions in the model was improved by the replacement of the meteorological reanalysis data for nudging. Surface emissions ….

6-9) Page 5, Lines 28-30: Why aren't lab data used for 18O epsilon values? This passages makes it sound like they are derived from stratospheric observations, or am I misunderstanding something? "Fractionation of N2O isotopocules was simulated using wavelength-dependent and temperature-dependent enrichment factors for 14N15N16O and 15N14N16O of von Hessberg et al. (2004) and that of 14N14N18O estimated from the relation 30 between apparent epsilon for each isotopocule observed in the stratosphere."

The referee correctly understands. In our model, epsilon values are incorporated as function of wavelength and temperature. Von Hessberg et al. (2004) presented ε values with wave length resolution of about 1 nm and at two different temperatures, which is suitable for our purpose. However, they did not report on $NN^{18}O$ isotopocule, and we could not find any other reports on wavelength and temperature dependency of $\varepsilon(^{18}O)$ as precise as that of von Hessberg et al. (2004). Therefore, we assumed the constant relationship between $\varepsilon(^{18}O)$, $\varepsilon(^{15}N^{\alpha})$, and $\varepsilon(^{15}N^{\beta})$ based on our previous observations (Toyoda et al., 2004) and approximated $\varepsilon(^{18}O)$. Detailed procedure to determine the $\varepsilon(^{18}O)$ value is described in Ishijima et al (2015). We slightly modified the following sentence.

P6, L27–31

> Fractionation of N_2O isotopocules was simulated using wavelength-dependent and temperature-dependent enrichment factors (ε) for $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ reported by von Hessberg et al. (2004) although the ε for $^{14}N^{14}N^{18}O$ was estimated from the relation between apparent ε for each isotopocule observed in the stratosphere due to the lack of suitable experimental reports.

6-10) Page 7, Line 1: why are the other isotopes not plotted? Could they be put in supplementary figures?

The Rayleigh plots for other isotopocules were omitted because they looked similar to that for $^{15}N^{bulk}$. We have added them as Figures S3, S4, and S5.

6-11) Page 7, Line 7: It should be clarified that these three data points are exactly what would be expected for tropical high altitude data – epsilon effective epsilon sink and why. . ..

Although we consider this was described in the next paragraph, we revised it taking account of the comment #6-12).

6-12) Page 7, Lines 15-20: This has been noted in many studies before. Here and in other places, the manuscript could be more complete in referencing previous studies, their conclusions, and similarities and differences with this study.

We added the following sentences in this paragraph.

P8, L22–25

> Although the similar latitudinal and altitudinal dependence of ε has been reported previously for the latitudes ranging from 18°N to 89°N (Park et al., 2004; Kaiser et al., 2006), our equatorial data showed that the change in ε occurs at altitude with higher N_2O mixing ratio and the ε value is exactly what would be expected during the N_2O photolysis.

6-13) Page 7, Line 19: Could the values in Fig 4 (and the additional breakdown of the Esrange Sweden flight to "M" and "L") be given as a table (with error bars) in supplementary materials? I'd like to see the numbers, for comparison with error bars and for comparison with future and past studies (e.g., with past aircraft samples in Park et al. [2004] and Kaiser et al [2006] that are not included in this manuscript). Also, why do the 17N data (HBD) not appear in the figure? [In addition, the gold color for photolysis was a bit confusing, because gold was used in the previous figures for the subtropical 17N data!]

Figure 4 has been revised as we described in response to the comment #3. Also we corrected a mistake in plotting epsilon values for photolysis. The values in the figure are given in newly added Table S4. The HDB data were not included because the highest sampling altitude is lower than other observations and it was difficult to estimate epsilon value for middle stratosphere.

6-14) Section 3.3: (in addition to major comments above): More discussion (even if very brief) of previous studies and their conclusions that agree with, or do not, with this study is needed.

The first paragraph in section 3.3.2 has been revised referring to two previous studies (see our response to the comment #4).

The last sentence in section 3.3.3 has been revised as follows.

P10, L27–30

> Because in situ $\varepsilon_{\mathrm{photolysis}}$ used in the model calculation is nearly the same between low and high latitudes (Fig. S6c), this agreement supports the inference that the major causes of the difference are transport and mixing, which was previously suggested by observations in the high latitudes (Park et al., 2004) and by 1D or 3D model studies (McLinden et al., 2003; Morgan et al., 2003).

6-15) Page 8, Line 1-4: "There is no bending or curved structure apparent in the Rayleigh diagram, which suggests that chemical processes are not variable, although the small fluctuation in the lower left region in Fig. 5a will be discussed later." First, "chemical processes are not variable" will not be clear to many readers as to what the authors are trying to communicate regarding the variability of the processes involved. Second, in addition to my not agreeing that the lower left region of Fig 5a means something about O(1D) chemistry dominating photolysis (see above major comments), I also find this statement misleading: Chemical processes can vary throughout the stratosphere but the isotopic composition of N2O – being a long-lived tracer – is not necessarily going to retain a ‘memory’ of this since air with many different transport histories (and chemical histories) are mixed together; in fact, N2O destruction is dominated by photolysis in upper stratosphere, and then the remaining N2O is redistributed from the upper stratospheric sink region. So I don’t think the authors can make the inference the other way around – that if there is no bending or curvature in the Rayleigh plot, that that means that chemistry and relative chemical time scales do not vary throughout the stratosphere.

We agree that the sentences are not clear and misleading. They have been revised as follows.

P9, L9–14

> Especially in Fig. 5b, almost all data show a compact linear relation without bending or curved structure apparent in the Rayleigh diagram. The slope, which corresponds to the ratio of ε values, is very close to the one expected for photolysis. This confirms that photochemical decomposition of N_2O is mainly caused by photolysis, although the small fluctuation in the lower left region in Fig. 5a will be discussed later.

6-16) If the authors do wind up using their data to support a large relative role for photooxidation in the lower stratosphere, then they need to more explicitly differentiate their comments on Page 9, line 25 that “transport and mixing” are discussed as the difference between the epsilon values at different the latitudes, from those on Page 10, Line 4 that photooxidation is cited as having a major influence in the lower stratosphere (for which it is the ratios of epsilon values are assumed to be independent of transport of mixing); this is confusing without clarification (for which background is lacking in general for this “ratio of ratio” approach).

Sentences in the last half of section 3.4 have been revised. See our response to the comment #5(b).

6-17) Throughout: “Transport” is the term used to describe air mass or tracer transport (while transportation is buses, cars, airplanes, etc.)

"transportation" has been replaced with "transport", as suggested.

6-18) By the way, the so-called “transport barrier” is not really a barrier – it just looks like one in satellite views of tracers like the aerosol from the Mt Pinatubo eruption! It ‘looks’ and ‘acts’ like a barrier because, between 22 and 28 km, the vertical ascent rates in the tropics are much faster than quasi-horizontal transport rates out of the tropics to the midlatitudes, which in turn are much much faster then quasi-horizontal rates from the midlatitudes into the tropics (and contrasting with the rate of transport and mixing into the tropics below 22 km, which your data here, and many other types of tracer studies, are completely consistent with!). Alan Plumb discusses this quite a bit, as ‘barrier’ is a bit of a misnomer when one is contemplating the dynamics and transport.

The sentence has been revised as follows.

P9, L26–28

> Because the vertical ascent rate in the tropics is much faster than quasi-horizontal transport, there is

an apparent transport barrier between the tropics and extratropics (Plumb, 2007). Nevertheless, entrainment of air mass Yi ….

Reply to co-editor

Co-editor's comment is typed in blue, authors' response is typed in black.

I have one more scientific comment that you may want to consider already, although I do not require any changes now. It may also be addressed in the public discussion later. It relates to the value of your 2-D mixing model

1) Is it realistic to assume an end member with only 5 ppb N2O in the tropical region?

It is true that the mixing ratio we observed at about 30 km height is much higher than 5 ppb. But at higher altitudes in the middle/higher stratosphere (40–50 km), it would approach to 5 ppb. This can be seen in the 3-D model simulation results (Fig. 8a).

2) Conceptually, you develop an additional model to explain the shape of the curve in mid latitudes, which can already be successfully explained by the 1D model. But your model does not provide any evidence that the epsilon values in the equatorial mid stratosphere, where you present the new data, are so much higher. So in the present text I am not really convinced about the additional value of this simple model. The 3D model result on the other hand is very valuable!

The referee #2 pointed out that the discussion with the 1-D model is misleading and even incorrect. We decided to delete the 1-D model part and leave the discussion with the conceptual 2-D model according to the referee's comment.

Vertical distributions of N_2O isotopocules in the equatorial stratosphere

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Abstract. Vertical profiles of nitrous oxide (N_2O) and its isotopocules, isotopically substituted molecules, were obtained over the equator at altitudes of 16–30 km. Whole air samples were collected using newly developed balloon-borne compact cryogenic samplers over the Eastern Equatorial Pacific in 2012 and Biak Island, Indonesia in 2015. They were examined in the laboratory using gas chromatography and mass spectrometry. The mixing ratio and isotopocule ratios of N_2O in the equatorial stratosphere showed a weaker vertical gradient than the previously reported profiles in the subtropical and mid-latitude and high-latitude stratosphere. From the relation between the mixing ratio and isotopocule ratios, further distinct characteristics were found over the equator: (1) Observed isotopocule enrichment factors (ε values) in the middle stratosphere (25–30 km or $[N_2O]$ < ca. 260 nmol mol^{-1}) are almost equal to ε values reported from broadband photolysis experiments conducted in the laboratory. (2) ε values in the lower stratosphere (< ca. 25 km or $[N_2O]$ > ca. 260 nmol mol^{-1}) are about half of the experimentally obtained values, being slightly larger than those observed in the mid-latitude and high-latitude lower stratosphere~~.~~ ($[N_2O]$ > ca. 170 nmol mol^{-1}). These results suggest the following. (1) The time scale of horizontal mixing in the tropical middle stratosphere is sufficiently large for in-situ photolysis of N_2O, mainly because of strong upwelling and transport barrier between the tropics and extratropics. (2) The air in the tropical lower stratosphere is exchanged with extratropical air on a time scale that is shorter than that of photochemical decomposition of N_2O. Previously observed ε values, which are invariably smaller than those of photolysis, can be explained qualitatively using a three-dimensional chemical transport model and using a simple model that assumes mixing of ‘aged’ tropical air and extratropical air during residual circulation. Results show that isotopocule ratios are useful to examine the stratospheric transport scheme deduced from tracer–tracer relations.

Keywords. nitrous oxide, stable isotopes, tropical stratosphere, cryogenic sampling, stratospheric transport, stratospheric photochemistry

1 Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas and stratospheric ozone depleting substance emitted from various sources on the Earth surface. It is injected into the stratosphere in tropical upwelling regions. In the stratosphere, it is transported meridionally by so-called Brewer–Dobson circulation and is decomposed by photolysis (Eq. 1) and photooxidation (Eq. 2) with approximate shares of 90% and 10%, respectively (Minschwaner et al., 1993).

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \qquad (1)$$

$$N_2O + O(^1D) \rightarrow 2NO \qquad (2a)$$

$$\rightarrow N_2 + O_2 \qquad (2b)$$

~~To~~Mixing ratios of trace gases such as N_2O and their interrelationships are regarded as useful tools to establish a detailed picture of stratospheric circulation~~, concentrations and isotopic information of trace gases such as N_2O are regarded as useful tools.~~ (Plumb, 2007), and previous observations showed compact tracer relationships that depend on latitude (e.g, Michelsen et al., 1998). Natural abundance ratios of N_2O isotopocules, molecular species that only differ in either the number or position of isotopic substitutions (Coplen, 2011), are useful tracers for elucidating the sources and physicochemical records of N_2O because isotopocule ratios reflect the isotopic compositions of source materials, isotope effects specific to each chemical and physical process relevant to formation, transportation, and decomposition of N_2O, and mixing of various air and water masses (Toyoda et al., 2015). In the context of stratospheric distribution, isotopocule ratios are unique in their ability to provide the degree of photochemical decomposition and the relative importance of the above-mentioned two decomposition pathways (Toyoda et al., 2001; Röckmann et al., 2001).

Stratospheric distributions of N_2O isotopocules have been studied using scientific balloons and aircraft. For balloon observations, (a) whole air samples are collected using cryogenic samplers and are evaluated using isotope ratio monitoring mass spectrometry (IRMS) (Kim and Craig, 1993; Rahn and Wahlen, 1997; Röckmann et al., 2001; Toyoda et al., 2001; Toyoda et al., 2004; Kaiser et al., 2006); alternatively, (b) ~~in situ~~remote measurements are conducted using Fourier-transform infrared spectrometry (Griffith et al., 2000). Such observations have revealed vertical profiles up to 35 km altitude. For aircraft observations, whole air samples are collected using pressurizing pumps, with subsequent evaluation by IRMS (Rahn and Wahlen, 1997; Park et al., 2004; Kaiser et al., 2006). Although these observations are limited to ca. 20 km altitude, vertical profiles can be obtained for horizontally wide areas such as Arctic polar vortexes.

Earlier studies showed that a decrease in the mixing ratio of N_2O with altitude is accompanied by enrichment of isotopocules of N_2O heavier than the major one ($^{14}N^{14}N^{16}O$~~).~~) (Kim and Craig, 1993; Rahn and Wahlen, 1997). The results were consistent with the expected isotopocule fractionation during photolysis~~,~~ (Yung and Miller, 1997), but the apparent degrees of fractionation (isotopocule enrichment factor, ε) differed between those of the lower (< 20–25 km where N_2O mixing ratio > 180-250 nmol mol^{-1}) and middle (> 20–25 km or < 180-250 nmol mol^{-1}) stratosphere~~.~~ (Toyoda et al., 2001; Röckmann et al., 2001; Kaiser et al., 2006; Park et al., 2004). They are always smaller than that obtained from laboratory photolysis experiments~~.~~ (Röckmann et al., 2000; Turatti et al., 2000; Zhang et al., 2000; Kaiser et al., 2002b; 2003) or absorption spectra (von Hessberg et al., 2004). Moreover, the values of ε for the middle stratosphere were found to depend on the latitude and season~~.~~ (Toyoda et al., 2004; Kaiser et al., 2006; Park et al., 2004). Such variation has been regarded as a result of photochemical and transport processes (McLinden et al., 2003; Park et al., 2004; Kaiser et al., 2006), but it has not been fully examined because of the lack of measurements taken over the ~~equatorial~~tropicalupwelling regions. As noted above, tropical stratosphere is the starting point of meridional transportation of N_2O injected from the troposphere and the rates of photochemical reactions are faster than those in the extratropics because of stronger actinic flux. Although there are a few reports on vertical profiles of N_2O isotopocules over India (18°N) (Röckmann et al., 2001; Kaiser et al., 2006), isotopic composition of N_2O in upwelling ~~region~~tropical air has not been characterized.

Another controversial problem about the stratospheric N_2O is whether the photooxidation sink (Eq. 2) has larger contribution than 10% in the lower stratosphere. Kaiser and coworkers found that the ratios of enrichment factors of isotopocule during photolysis and photooxidation are distinct (Kaiser et al., 2002a) and they estimated that a much larger fraction than 10% is removed by photooxidation at least in the lower stratosphere (N_2O mixing raitos > 300 nmol mol^{-1}) (Kaiser et al., 2006). However, similar but a little simplified analyses by Park et al. (2004) and Toyoda et al. (2004) could not detect significant differences in the enrichment factor ratios between the lower and middle stratospheres, and Park et al. (2004) speculated that the enrichment factor ratios could be affected not only by the relative share of the two sink pathways but also by other factors such as transport.

This study was conducted to ascertain the vertical profiles of N_2O and its isotopocules over the equator and to examine the factors that control the apparent isotopic fractionation in the stratosphere by comparing results from earlier studies and three-dimentional chemical transport model simulation.

2 Experiments and model simulation

2.1 Whole air sampling over the equator

Stratospheric air samples were collected using balloon-borne compact cryogenic samplers (J-T samplers) (Morimoto et al., 2009). The sampler consists of an evacuated 800 cm^3 stainless steel sample flask (SUS304), a cooling device called a Joule–Thomson (J-T) mini cooler, a two-liter high-pressure neon gas cylinder, pneumatic valves, solenoid valves, a 100 cm^3 high-pressure N_2 gas cylinder for actuation of pneumatic valves, an electronic controller with a GPS receiver, a telemetry transmitter, and batteries. The J-T mini cooler can produce liquid neon from high-pressure neon gas that is pre-cooled by liquid nitrogen. The liquid neon is used as refrigerant to solidify or liquefy the stratospheric air. Contrasted against the larger sampling system used in our previous observations, which was about 250 kg with 12 sample flasks in a Dewar flask filled with liquid helium, the J-T sampler is ca. 20 kg, with operational and logistic advantages at remote sites such as remote islands or polar regions.

Sampling over the eastern equatorial Pacific (0°N, 105°W−115°W) was conducted on February 4, 5, 7, and 8, 2012 during the KH-12-1 cruise of R/V Hakuho-maru, JAMSTEC as a part of the Equatorial Pacific Ocean and Stratospheric/tropospheric Atmosphere Study Program. For each ~~experiment~~balloon flight, a 5−8 L STP of air sample was collected by a single sampler at programmed altitude of 19–29 km. The sampler then descended by parachute. It was later recovered on the sea.

Another sampling campaign was conducted at Biak Island, Indonesia (1°S, 136°E) on February 22, 24, 26, and 28, 2015 as a part of Small-Size Project by ISAS / JAXA (Hasebe et al., submitted). For each ~~experiment~~balloon flight, two samplers integrated into a single gondola were launched from the observatory of National Institute of Aeronautics and Space of the Republic of Indonesia (LAPAN). Samples were collected at two altitudes. Therefore, in total, we obtained seven samples: two samples on each of four flights, with one failed sampling. ~~Locations of launching sites are shown in Figure 1. Balloon trajectories are portrayed in Figure S2.~~

Locations of launching sites are shown in Figure 1. Balloon trajectories are portrayed in Figure S2. Sampling was conducted while the balloon was ascending except the flight on Feb 5, 2012. Typical altitude range was about 2 km, and we took the central value of the range as the sampling altitude.

2.2 Analysis of mixing ratio and isotopocule ratios

At Tohoku University, the mixing ratio of N_2O was measured using gas chromatography with electron capture detection (GC-ECD) with precision of 1 nmol mol^{-1} (Ishijima et al., 2001). The isotopocule ratios, defined as follows, were measured at Tokyo Institute of Technology using gas chromatography – isotope ratio ~~monitoring~~ mass spectrometry (Toyoda et al., 2004; Toyoda and Yoshida, 2016).

$$\delta X = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}, \tag{3}$$

Therein, X denotes $^{15}N^{\alpha}$, $^{15}N^{\beta}$ or ^{18}O, and where R denotes $^{14}N^{15}N^{16}O/^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O/^{14}N^{14}N^{16}O$ or $^{14}N^{14}N^{18}O/^{14}N^{14}N^{16}O$ of the sample and standards (Toyoda and Yoshida, 1999). The δ value is expressed as the permil (‰) deviation relative to atmospheric N_2, and Vienna Standard Mean Ocean Water (VSMOW), respectively, for nitrogen and oxygen. In addition to $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$, the δ value for bulk N and ^{15}N-site preference (SP) are often used as illustrative parameters:

$$\delta^{15}N^{\text{bulk}} = (\delta^{15}N^{\alpha} + \delta^{15}N^{\beta}) / 2 \tag{4}$$

$$SP = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta}. \tag{5}$$

Duplicate analyses were made for a set of two runs: monitoring of molecular ion for determination of $\delta^{15}N^{\text{bulk}}$ and $\delta^{18}O$ and NO^+ fragment ion for determination of $\delta^{15}N^{\alpha}$. A 300–400 cm^3 STP aliquot of the sample air was introduced into the analytical system from the sample flask in a single run. Typical precisions of the isotopic analyses are < 0.1‰ for $\delta^{15}N^{\text{bulk}}$, < 0.2‰ for $\delta^{18}O$, and < 0.5‰ for $\delta^{15}N^{\alpha}$, although they were slightly worse for samples collected at higher altitudes because of the lower N_2O mixing ratio.

To analyze the relation between the N_2O mixing ratio ($[N_2O]$) and isotopocule ratio (δ) in a Rayleigh fractionation scheme (Eq. 6), measured values must be normalized with respect to the values before the air mass enters the stratosphere.

$$(1+\delta)/(1+\delta_0) = \{[N_2O]/[N_2O]_0\}^{\varepsilon} \quad (6)$$

In Eq. 6, subscript 0 signifies a tropospheric value; ε is the enrichment factor. Because the tropospheric mixing ratio and isotopocule ratios are known to have secular trends, $[N_2O]_0$ and δ_0 were estimated as follows. First, the age of the measured air mass was estimated based on the mixing ratio of CO_2, which was also measured for the same air sample (Engel et al., 2009). Then, the N_2O mixing ratio at the time when the air mass was in the troposphere was calculated using the estimated age of air and the secular trend of tropospheric mixing ratio observed by the ALE/GAGE/AGAGE project (Prinn et al., 2000). We used AGAGE data from Mace Head (Ireland) to calculate $[N_2O]_0$ for stratospheric air in the tropics (this study) and the Northern Hemisphere (in which our previous observations were conducted) and those from Cape Grim (Tasmania) for the Southern Hemisphere (our previous observation in Antarctica). For calculating δ_0, the secular trends observed at Hateruma island, Japan (Toyoda et al., 2013) and Cape Grim (Park et al., 2012) were used, respectively, for the tropics/Northern Hemisphere and the Southern Hemisphere. In Table S3 we compare how much this correction regarding the age of air changed the position of each data point in Figs. 3 and 5. Typically, the term related to mixing ratio ($-\ln\{[N_2O]/[N_2O]_{trp}\}$) is decreased by 0.2–3% when we use $[N_2O]_0$, the value when the air mass actually entered into the stratosphere, instead of the value at the same time of the observation, $[N_2O]_{trp}$. The isotopic terms ($\ln\{(1+\delta)/(1+\delta_{trp})\}$) are either increased or decreased depending on their secular trends, and they are changed by 0.2–3%.

2.3 Simulation using a three-dimensional chemical transport model

To examine the factors controlling the stratospheric distributions of N_2O isotopocules, a numerical simulation was conducted using the Center for Climate System Research/National Institute for Environmental Studies/Frontier Research Center for Global Change atmospheric general circulation model with chemical reactions (CCSR/NIES/FRCGC ACTM) (Ishijima et al., 2010; Ishijima et al., 2015). Because Ishijima et al. (2015) have already given a detailed description of the N_2O isotopocule model, we briefly explain it here.

The N_2O photolysis rate was calculated for 15 bins from 178 to 200 nm and for 3 bins from 200 to 278 nm using a scheme incorporating the parameterization of Minschwaner et al. (1993) (Akiyoshi et al., 2009) and by a main radiation – photolysis scheme of the ACTM (Sekiguchi and Nakajima, 2008). Fractionation of N_2O isotopocules was simulated using wavelength-dependent and temperature-dependent enrichment factors (ε) for $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ ~~of~~reported by von Hessberg et al. (2004) ~~and that of~~ although the ε for $^{14}N^{14}N^{18}O$ was estimated from the relation between apparent ε for each isotopocule observed in the stratosphere due to the lack of suitable experimental reports. The model transport was nudged to ERA-interim reanalysis (Dee et al., 2011) for horizontal winds and temperature at 6-hourly time intervals. Regarding the photooxidation sink of N_2O, the concentration of $O(^1D)$ was calculated online in the ACTM; ε values were calculated as described by Kaiser et al. (2002a).

~~The main difference of the simulation settings from those in an earlier report (Ishijima et al., 2015) is that the present study did not optimize the photolytic isotopocule fractionation. Therefore, the kinetic fractionations for N_2O isotopocules were provided by the original calculation results obtained using the model chemistry scheme containing experimentally determined enrichment factors described above. However, surface~~While both the surface emissions and the photolytic isotopocule fractionations were optimized in the earlier work by Ishijima et al. (2015), only the former was optimized in the present study. This is because we considered that it would be better to keep the experimentally determined original isotopocule enrichment factors for the purpose of comparison between the model and the observations in the stratosphere. Moreover, we found that apparent isotopocule enrichment factors obtained by the model simulation become much closer to those by the balloon observations by replacing the meteorological data from JRA-25 (Onogi et al., 2007) with those from ERA-interim. This is probably because dynamics and chemical reactions in the model was improved by the replacement of the meteorological reanalysis data for nudging. Surface emissions of the four N_2O isotopocules were optimized in the manner described in an earlier report (Ishijima et al., 2015), with emissions modified to reproduce observed trends (Röckmann and Levin, 2005) and interhemispheric differences (Ishijima et al., 2007) of atmospheric N_2O isotopocule mixing ratios. Consequently, the estimated emissions were used for a forward simulation of four N_2O isotopocules in the atmosphere from the surface to the stratosphere in this study. The emissions and tropospheric values are reasonable (see Supplemental Information) compared to those of past studies (e.g., Toyoda et al., 2013; Toyoda et al., 2015) in terms of the necessary order of precision for analysis of the large vertical profiles in the stratosphere in this study.

3 Results and discussion

3.1 Vertical profiles of the N_2O mixing ratio and isotopocule ratios over the Equator

In all, 11 samples (4 from the eastern Pacific, 7 at Biak Island) were collected at target altitudes; of them, 10 were measured for N_2O isotopocules. Figure 2 presents vertical profiles of the N_2O mixing ratio, $\delta^{15}N^{bulk}$, SP, and $\delta^{18}O$ observed over the equator. Data from our previous observations over Japan, Sweden, and Antarctica and those from observations by Röckmann et al. (2000) and Kaiser et al. (2006) conducted over India are also shown. The height of the tropical tropopause layer (TTL) was 14–18.5 km (Fueglistaler et al., 2009), whereas the tropopause height was 12–16 km over Japan and 9 or 10 km over Sweden and Antarctica (Table S1). As observed at mid-latitudes and high latitudes, the mixing ratio decreases with height; isotopocule ratios increase with height over the equator. However, the vertical gradient is weaker at lower latitudes. Our observation over the equator shows the weakest gradient. Although a slight difference in mixing ratio was observed for 20–25 km, the two equatorial profiles obtained at different longitudes over the equator agreed quite well. We combined the two datasets as a single one for further examinations.

3.2 Correlation between mixing ratio and isotopocule ratios: apparent isotopocule enrichment factors

In Fig. 3 and Figs. S3–S5, the ~~normalized $\delta^{15}N^{bulk}$ is~~ isotopocule ratios are shown against the ~~normalized~~ N_2O mixing ratio after the normalization described in Eq. 6 (Rayleigh plot). The equatorial data for lower altitudes ~~(< 25 km~~($-\ln\{[N_2O]/[N_2O]_0\} < 0.2$ or $[N_2O] >$ ca. 260 nmol mol^{-1}) are on the line defined by the data for lower altitudes ~~(< 22–27 km~~($-\ln\{[N_2O]/[N_2O]_0\} < 0.6$ or $[N_2O] > 170$ nmol mol^{-1}) over middle latitudes and high latitudes. The linear relation is consistent with isotopocule fractionation during the decomposition of N_2O in a closed system, although the slope of the line, which corresponds to isotopic enrichment factor (ε), is markedly lower than that obtained by laboratory photolysis experiments (see below). However, the three data points obtained at altitudes ~~higher than 25 km~~corresponding to $-\ln\{[N_2O]/[N_2O]_0\} > 0.2$ ($[N_2O] <$ ca. 260 nmol mol^{-1}) show systematic deviation from the line and seem to define another line (Fig. 3b). A similar deviation or *bending* structure of the Rayleigh plot has also been observed at middle to high latitudes (Fig. 3a, from the points where the *x* axis value is ca. 0.5) (Toyoda et al., 2004). We therefore compare the slope of the lines obtained for observations at various latitudes and for laboratory simulation experiments.

As portrayed in Fig. 4, absolute values of ε ($|\varepsilon|$) for $^{15}N^{bulk}$, $^{15}N^{\alpha}$, and ^{18}O in the equatorial lower stratosphere are slightly higher than those of middle latitude and high latitude lower stratosphere, but they are still only about half of the ε obtained by broadband photolysis experiments (Kaiser et al., 2002b; Kaiser et al., 2003). In contrast, $|\varepsilon|$ in the higher region (or middle stratosphere) show larger values. They are the largest over the equator except for $\varepsilon(^{18}O)$. The equatorial values of ε almost coincide with those of photolysis. It is also noteworthy that $|\varepsilon|$ in the middle stratosphere in the arctic polar vortex (Sweden) is as small as that in the lower stratosphere and that latitudinal and year-to-year or seasonal variation are slight compared to those of the middle stratosphere in the lower stratosphere. Although the similar latitudinal and altitudinal dependence of ε has been reported previously for the latitudes ranging from 18°N to 89°N (Park et al., 2004; Kaiser et al., 2006), our equatorial data showed that the change in ε at altitude with higher N_2O mixing ratio and the ε value is exactly what would be expected during the N_2O photolysis.

3.3 Cause of the variation of stratospheric ε

We then discuss causes of (1) lower $|\varepsilon|$ value in the lower stratosphere, (2) increase of $|\varepsilon|$ in the middle stratosphere, and (3) the largest $|\varepsilon|$ in the equatorial middle stratosphere based on two factors: photochemical and transport processes.

3.3.1 Photochemical processes

During photochemical decomposition of N_2O, ε reportedly depends on the wavelength that photolyzes N_2O, the relative share of photolysis and photooxidation pathways (Eqs. 1 and 2), and temperature (Toyoda et al., 2004; Kaiser et al., 2006). ~~The difference in~~Moreover, because of transport processes the stratosphere cannot be always treated as an isolated system which is a prerequisite for Rayleigh fractionation model. The ratio of ε values ~~or normalized δ values~~ for independent isotopocules (e.g., $\varepsilon(^{15}N^{bulk})/\varepsilon(^{18}O$~~) or $\delta^{15}N^{bulk}_{norm}/\delta^{18}O_{norm}$)~~)), however, has been identified as a useful parameter to distinguish photolysis and photooxidation (Kaiser et al., 2002a) because its sensitivity to wavelength and temperature is small~~. In Fig.~~ and it is not affected by mixing process. Figure 5~~, we plot~~ shows the ~~normalized δ values~~ data obtained in this study and some previous ones~~.~~ in δ–δ space after the normalization described in Eq. 6. Especially in Fig. 5b, almost all data show a compact linear relation~~. There is no~~ without bending or curved structure apparent in the Rayleigh diagram. The slope, which ~~suggests~~corresponds to the ratio of ε values, is very close to the one expected for photolysis. This confirms that ~~chemical processes are not variable,~~photochemical decomposition of N_2O is mainly caused by photolysis (Minshwaner et al., 1993), although the small fluctuation in the lower left region in Fig. 5a will be discussed later.

3.3.2 Transport processes

~~As for transport, Kaiser et al. (2006) pointed out that in a simple 1D reaction–diffusion scheme, apparent or effective ε can be reduced from ε for the intrinsic sink reaction depending on the ratio of time scales for transport and chemistry as follows:~~

~~$\varepsilon_{eff} \approx \frac{1}{2}\varepsilon_{sink}\left(1 + \frac{1}{\sqrt{1 + \tau_{trans}/\tau_{chem}}}\right) \qquad . \qquad (7)$~~

~~In Eq. 7, τ_{trans} and τ_{chem} respectively denote the time scales for transport and chemistry; $\tau_{trans} = 4H^2/K$ and $\tau_{chem} = 1/k$, where H, K, and k respectively represent the scale height, the vertical eddy diffusion constant, and the rate constant of chemical decomposition of N_2O. If N_2O decomposition is limited by transportation rather than by photolysis, then ratio τ_{trans}/τ_{chem} is high. Consequently, ε_{eff} approaches to about half of ε_{sink} for the photolysis.~~

~~Conversely, if N_2O decomposition is limited by photolysis rather than transportation, then τ_{trans}/τ_{chem} is small and ε_{eff} approaches to ε_{sink}. Based on this simple scheme, Kaiser et al. (2006) explained qualitatively the vertical and meridional trends in ε obtained over latitudes ranging from 18° to 80° (N or S). Results of this study demonstrate that ε_{eff} indeed equals to ε_{sink} in the equatorial middle stratosphere, indicating that the time scale of photochemistry is sufficiently larger than that of vertical transport.~~

Transport processes accompanied by mixing of variously aged stratospheric air has been considered as the major cause of lower $|\varepsilon|$ value in the stratosphere than in the laboratory photochemical decomposition (Park et al., 2004; Kaiser et al., 2006). Our new observation revealed that all the N_2O isotopocules are fractionated by the almost ideal Rayleigh process in the middle stratosphere over the deep tropics where the stratosphere is effectively the most isolated relative to all other regions. This underlines how much transport and mixing affect the apparent ε value.

We then consider the effect of ~~transportation~~ transport on the apparent ε at different latitudes with a conceptual ~~mixing model extending the 1D scheme to 2D, based on a simplified~~ two-dimensional circulation model in the tropical and extra-tropical stratosphere that was proposed to explain tracer–tracer correlation (Plumb, 2002). In the tropics, N_2O is decomposed gradually during upwelling of the air mass injected from the troposphere. The uppermost tropical air mass X_0 is then transported to middle latitudes and higher latitudes, where it begins downwelling. ~~Although a~~Because the vertical ascent rate in the tropics is much faster than quasi-horizontal transport, there is an apparent transport barrier ~~exists~~ between the tropics and ~~mid-latitudes and high latitudes,~~extratropics (Plumb, 2007). Nevertheless, entrainment of air mass Y_i across the subtropical edge separating the two regions must occur to compensate mass flux in the lower region (Fig. 6).

If we assume tropical profiles of N_2O and its isotopocule ratios (e.g., $\delta^{15}N^{bulk}$) are determined purely by photochemistry with initial mixing ratio of 320 ppb, a delta value of 0‰ and a ε_{sink} of −50‰, then tropical air masses vertically divided from Y_8 through Y_1 and X_0 are expected to line up on a solid line as portrayed in Fig. 7. Next, let us consider that air mass X_0 is mixed with Y_1 to form X_1. Based on the mass balance of isotopocules before and after mixing, the resulting composition of X_1 is obtained as a curve, as shown in red in Fig. 7. Assuming arbitrarily that the mixing ratio of Y_1 to X_1 is 0.1, and repeating such mixing stepwise, then we obtain mixing ratio and isotope ratios of N_2O in X_1 through X_8 as black stars in Fig. 6. This hypothetical, continuous mixing produces a curve that is qualitatively consistent with observations made over the mid-latitudes or high latitudes.

The mixing effect must also be the cause of smaller ε in the equatorial lower stratosphere (Fig. 4). The mean age of air deduced from CO_2 mixing ratio is known to be significantly larger than the phase lag of the water vapor mixing ratio, a so-called tape recorder signal, in the tropical stratosphere, which is explainable by mixing of old air from the extratropics into the tropics (Waugh and Hall, 2002). In addition, the difference in age between the equator and mid-latitude (over Japan) decreases concomitantly with decreasing altitude (Sugawara et al., unpublished data), suggesting that the time scale of meridional mixing or transport is smaller in the lower stratosphere than in the middle stratosphere, as suggested by results of an earlier study (Boering et al., 1996).

3.3.3 Comparison with chemical transport model (ACTM) simulation

We further examined the importance of transport using ACTM. Figure 8 presents results of ACTM simulation with observational data. Although the model approximates the photolysis of N_2O in the longer wavelength region (λ > 200 nm) with lower spectral resolution, profiles of the N_2O mixing ratio and isotopocule ratios were reproduced well, except in the winter polar stratosphere, where dynamic processes specific to the polar vortex might not be simulated appropriately in the model. In Fig. 9, the model simulation and observations are compared on a Rayleigh plot. Again, the model reproduced the difference between tropical and mid-latitudes or high latitudes. Because in situ $\varepsilon_{\text{photolysis}}$ used in the model calculation is nearly the same between low and high latitudes (Fig. ~~S3a~~S6c), this agreement supports the inference that the major causes of the difference are transport and mixing~~.~~, which was previously suggested by observations in the high latitudes (Park et al., 2004) and by 1D or 3D model studies (McLinden et al., 2003; Morgan et al., 2003).

3.4 Share of photolysis and photooxidation

Kaiser et al. (2006) used the ratio of ~~normalized δ~~ε values for $^{15}N^{\text{bulk}}$ and ~~δ~~^{18}O (ψ) and the ratio of ~~normalized δ~~ε values for $^{15}N^{\alpha}$ and ~~δ~~$^{15}N^{\beta}$ (η) to estimate the relative share of photolysis and photooxidation based on the fact that ψ and η are almost independent of transport processes and are significantly different between the two decomposition processes. ~~In Fig. 10, we show ψ and η values for data in Fig. 2.~~They computed ψ and η values directly for each individual sample in order to avoid statistical errors associated with linear regression to the δ–δ plot which was adopted by Toyoda et al. (2004) and Park et al. (2004). In Fig. 10, we show ψ and η values calculated using the data presented in Fig. 2 in the manner similar to that of Kaiser et al. (2006) except that we used individual date of stratospheric entry for each data to normalize the δ values instead of using a single tropopause date. Although it is noteworthy that errors in ψ and η values increase concomitantly with decreasing altitude because of the decrease in the ~~normalized~~ δ values, low values are obtained near the TTL over the Equator just as they are at other latitudes. This result confirms the indication by Kaiser et al. (2006) that the photooxidation sink has a much larger fraction than 10% in the lower stratosphere. ~~A rapid increase of the share of photooxidation in the lower stratosphere is also predicted in the ACTM used for this study (Fig. S3b). Because O(^{1}D) is more abundant in the tropical stratosphere than in the middle latitude and high latitude stratosphere because of stronger solar irradiation, the signal of photooxidation sink can propagate from the tropics to the extratropics by transport~~Although the loss rate of N_2O in the lower stratosphere is very slow and the majority of N_2O injected into the stratosphere is photolyzed in the middle stratosphere as noted by Park et al. (2004), the share of photooxidation in *in situ* total loss increases in the lower stratosphere (Fig. S6b). Therefore, there is a possibility of additional decomposition of remaining N_2O during the transport (which should be slower than that of the tropical upwelling) and the isotopic signature of O(^{1}D) pathway could be imprinted, and the photochemically aged air mass must be transported into the lower stratosphere of the tropics and extratropics. However, Morgan et al. (2003) reported that inclusion of isotope fractionation for photooxidation into their 2D model does not make a significant contribution to overall fractionation in the stratosphere, and Park et al. (2004) discussed an alternative modelling approach with and without O(^{1}D) sink to test the importance of O(^{1}D) reaction. Further studies using 3D model would be necessary to solve this controversial problem.

4 Conclusions

Vertical profiles of isotopocule ratios of N_2O in the equatorial stratosphere are found using balloon-borne compact cryogenic samplers and mass spectrometry in the laboratory. This report of the relevant literature is the first describing observations of them over the equator. ~~Enrichment~~Unlike other region of the stratosphere, enrichment factors for isotopocules in the middle equatorial stratosphere (25–30 km, or *[N_2O] < 260 nmol mol^{-1}*) agreed with those obtained with laboratory photolysis experiments, suggesting that the isotopocule ratios are determined mainly by photolysis because of weak vertical or horizontal mixing in the tropical upwelling. In the lower equatorial stratosphere (< ca. 25 km~~),~~ or *[N_2O* ~~is likely to be decomposed by photochemical processes with a larger contribution from photooxidation than~~*]* > 260 nmol mol^{-1}), isotopocule ratios suggest that ~~estimated for the whole stratosphere. It is latitudinally well~~differently aged air masses are mixed ~~in the lower stratosphere. Distribution~~because of the meridional transport and that decomposition by photooxidation might also plays a significant role. Vertical and latitudinal distributions of N_2O and its isotopocules are found to be a unique tool to diagnose the relationship between photochemistry and transport in the ~~middle~~ stratosphere~~ depends on mixing during meridional circulation~~. Further observations of temporal variations and comparison with ACTM simulation will ~~make isotopocules an effective tool for probing of variation in transport processes and decomposition processes~~be needed to examine the change in the meridional circulation and obtain the quantitative estimate of the importance of photooxidation pathway.

Competing interests. The authors declare that they have no conflict of interest.

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Figure captions

Figure 1: Map showing balloon launching sites.

Figure 2: Vertical profiles of mixing ratio (a), $\delta^{15}N^{bulk}$ (b), *SP* (c), and $\delta^{18}O$ (d), of N_2O observed over the equator (pink symbols). Previously published results obtained over Japan (black and red symbols), Sweden (blue), and Antarctica (green) (Toyoda et al., 2001; 2004), and India (orange, Kaiser et al., 2016; Röckmann et al. 2001) are also shown. In the legend, launch sites and dates are shown, respectively, by three characters and six digits in yymmdd format. SBC, Sanriku Balloon Center, Japan; ESR, Esrange, Kiruna, Sweden; SYO, Syowa station, Antarctica; HDB, Hyderabad, India; EQP, Eastern equatorial Pacific; BIK, Biak island, Indonesia. See also Table S2 for details.

Figure 3: Correlation between mixing ratio and $\delta^{15}N^{bulk}$ of N_2O (Rayleigh plot). The high mixing ratio range (> ca. 120 nmol mol^{-1}) in (a) is enlarged in (b). Both parameters are normalized to their values at the time when the corresponding air mass entered the stratosphere (see Eq. 6 in the text). Grey solid and broken lines show slopes obtained respectively from laboratory broadband photolysis experiments (Kaiser et al., 2002; 2003) and photooxidation experiments (Kaiser et al., 2002; Toyoda et al., 2004).

Figure 4: Comparison of absolute values of the isotopocule enrichment factor ($|\varepsilon|$) for $^{15}N^{bulk}$, $^{15}N^{\alpha}$, and ^{18}O of N_2O between observations and laboratory experiments. L and M respectively refer to the lower and middle stratosphere with boundary ~~altitude~~mixing ratio of ~~20–27 km~~about 170 nmol mol^{-1} ($-\ln\{[N_2O]/[N_2O]_0\} = 0.6$) and 260 nmol mol^{-1} ($-\ln\{[N_2O]/[N_2O]_0\} = 0.2$) for extratropics and tropics, respectively, based on the Rayleigh plot shape (Fig. 3). The respective $|\varepsilon|$ for Japan, Sweden, and Antarctica are from Toyoda et al. (2004). Those for photolysis and photooxidation experiments are referred from reports by Kaiser et al. (2002; 2003) and Toyoda et al. (2004). Error bars show either the standard deviation for the mean value (observation over Japan and photooxidation experiments), standard error associated with linear regression in Rayleigh plot (observations except Japan), or the possible range for stratospheric conditions (photolysis experiments).

Figure 5: Correlations between $\delta^{15}N^{\beta}$ and $\delta^{15}N^{\alpha}$ of N_2O (a) and between $\delta^{18}O$ and $\delta^{15}N^{bulk}$ of N_2O (b). The δ values are normalized as noted in the text. Grey solid and broken lines show slopes obtained respectively from laboratory broadband photolysis experiments (Kaiser et al., 2002; 2003) and photooxidation experiments (Kaiser et al., 2002; Toyoda et al., 2004).

Figure 6: Conceptual two-dimensional circulation model to analyze mixing processes between tropics and extratropics (from Plumb, 2002). The X_0 is the uppermost tropical stratospheric air mass, X_i (i = 1–8) are air masses formed by mixing of X_{i-1} and Y_i.

Figure 7: Presentation of X_i (black stars) obtained using the mixing model with assumed Y_i in the Rayleigh plot. The straight line shows tropical vertical isotopocule fractionation without transport/mixing effect. Curves show mixing between X_{i-1} and Y_i where mixing ratio Y_i/X_i is assumed to be 0.1.

Figure 8: Comparison of vertical profiles of mixing ratio (a) and $\delta^{15}N^{bulk}$ (b) of N_2O between observations and simulation by the ACTM. Model simulations for equatorial profiles were conducted for two dates because the observations were conducted during a 5-day or 7-day period.

Figure 9: Comparison of results of ACTM simulation and stratospheric observation in Rayleigh plot. The square region shown by broken lines in panel (a) is enlarged in panel (b).

Figure 10: Vertical profiles of ratio of ~~normalized δ~~ε values for $^{15}N^{bulk}$ and ~~δ~~^{18}O (ψ) and the ratio of ~~normalized δ~~ε values for $^{15}N^{\alpha}$ and ~~δ~~$^{15}N^{\beta}$ ~~(η).~~(η) calculated in the manner similar to that of Kaiser et al. (2006). Grey bands show values obtained by laboratory broadband photolysis experiments (Kaiser et al., 2002; 2003) and photooxidation experiments (Kaiser et al., 2002; Toyoda et al., 2004) with widths representing their uncertainty. For photolysis, uncertainties associated with temperature (190–240 K) and wavelength (190–220 nm) dependency are shown with dark and light gray, respectively.