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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Vertical distributions of N_2O isotopocules in the equatorial stratosphere” *by* Sakae Toyoda et al.

Anonymous Referee #2

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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.

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.

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.

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 $>\sim$23 km and N2O mixing ratios $<\sim$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.

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 = $\frac{1}{2}$ 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 = $\frac{1}{2}$ epsilon sink. So also the opposite of the Equation 7 limits. Indeed, even Kaiser et

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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 reaction-diffiusion-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 $\frac{1}{2}$ 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-

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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.

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.

(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

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tropopause is due to photochemical destruction elsewhere: photochemically aged air from middle latitudes (which itself came from higher altitudes) is transported into the lower 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.

(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.

(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)

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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.

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:

* 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.

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

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

-> 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).

_> 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.

* 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].

* 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.

* 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.

* 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.”

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

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 $\sim$ epsilon sink and why. . ..

* 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.

* 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!]

* 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.

* 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.

* 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).

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

* 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.

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