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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Probing stratospheric transport and chemistry with new balloon and aircraft observations of the meridional and vertical N_2O isotope distribution" *by* J. Kaiser et al.

Anonymous Referee #1

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This manuscript reports a large number of measurements of the N_2O isotope ratios in various areas of the stratosphere, providing new materials to investigate processes relevant to the variabilities of the N_2O isotopologues, which is in turn related to stratospheric photochemistry and dynamics. The number of measurements (220 samples) outweighs the total number of previous observations reported in literature, which may well recommend publication for the measurements to be available for further research on the relevant scientific areas, e.g. validation of modeling study. In view of this, I strongly recommend presenting all data used in the figures and calculations in the text in a tabular form. In addition, the structure of the manuscript needs to be improved to describe clearly results from the observations and discussion from which conclusions are drawn. As commented below, I often found it confused whether the authors describe results or discuss the authors' argument.

General comments:

1. N_2O distribution in the lower stratosphere

The authors divided the stratosphere into two regimes with respect to several different surfaces of N_2O mixing ratios, e.g., 200 or 70 ppb, or ln(μ/μ_T) = -0.6 (corresponding to $\sim$170 ppb) depending on the argument. However, the interpretation of processes in the lower stratosphere is not consistent along the discussion in the text. Based on 200 ppb surface, the authors agreed with Park et al. (2004)'s finding that atmospheric mixing results in such a compact linear relationship between δ and μ (Sect. 3.2, Fig. 5). Segregation of the lower stratosphere at 70 ppb surface appears to require atmospheric mixing, which is also supported by δ-μ^{-1} space such that the EUPLEX observation can be explained by end-member mixing for the mixing ratios above 200 ppb and probably by continuous weak mixing for that below 200 ppb (Sect. 3.3.3, Fig. 10 and 11). However, the authors interpret the variation of δ and μ in the low stratosphere, as being segregated at the surface of $\sim$170 ppb mixing ratio, by the Rayleigh fractionation, which is governed by photochemistry (Sect. 3.2.3 and Fig. 7). Furthermore, the authors grouped and calculated ϵ in three latitude regions of the lower stratosphere, and argued that the decrease of absolute value of ϵ (which I think needs vigorous statistical test) would be due to competition between reaction and diffusion as well as partly to the reaction with $O(^1D)$. But, the authors changed this argument in Sect. 3.3.3 and stated that Rayleigh process is not sufficient to explain the observation. Notwithstanding, the authors described in Abstract that the compact linear relationship between δ and μ for the N_2O mixing ratios above 200 ppb can be explained by Rayleigh fractionation as well. I find such inconsistent interpretation of data leading to suspicion on the conclusion drawn in the manuscript.

2. Contribution of $O(^1D)$ reaction to N_2O sink in the lower stratosphere

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The authors argued that a significant fraction of the lower stratospheric N_2O are destructed by the reaction with $O(^1D)$. In this argument, the authors again revealed inconsistent argument. In Sect. 3.2.3, fraction of the N_2O reacted with $O(^1D)$ is estimated to be 25 % at least but much less than 70 %, a value Toyoda et al. (2004) estimated. However, in Sect. 3.5 the authors argued that a predominant fraction of N_2O is reacted with $O(^1D)$ in the lower stratosphere, where the N_2O mixing ratio is high, on the basis of the comparison of the values of η and ψ calculated at several levels of N_2O mixing ratios (Fig. 15). This is stated quantitatively in Abstract such that "up to 100 %" of N_2O is destructed by the reaction with $O(^1D)$, which is in contrast to what the authors argued in Sect 3.2.3. The authors should resolve this contradiction. In addition, almost 100 % destruction of total N_2O by reacting with $O(^1D)$ stems from the values of η and ψ obtained at a single bin of data whose N_2O mixing ratios are over 300 ppb (Fig. 15). Except this single bin, others result in the values of η and ψ that are far larger than the values expected from the reaction with $O(^1D)$. Thus, I doubt the conclusion that a large fraction of N_2O in the lower stratosphere is destructed by $O(^1D)$. Furthermore, since the authors delimit the lower stratosphere as the region where N_2O mixing ratios are larger than 200 ppb, the high values of η and ψ at the bins between 200 and 300 ppb should be taken into account for the authors' argument.

3. End-member mixing and continuous weak mixing

According to the discussion in Sect. 3.3.2 and 3.3.3, the authors assumed the stratosphere to be a well-mixed one-box and the tropospheric air mass to be added continuously. Thus, curved line or deviation from the linear mixing line between air mass from the troposphere (near the origin in δ-μ^{-1} plot in Fig. 9 and 10) and a representative stratospheric air is assumed to indicate other than end-member mixing. However, the stratosphere is not a well-mixed regime. For instance, Fig. 9 and 10 show clearly end-member mixing line for the N_2O mixing ratios above $\sim$200 ppb while for the N_2O mixing ratios lower than 200 ppb several mixing lines could be possible as Park et al. (2004) demonstrated. As displayed in Fig. 11, the EUFLEX data can be explained with

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two end-member mixing lines: one for below 200 (or 170) ppb and the other for above 200 ppb. Consequently, end-member mixing could explain the curved line in the δ-μ^{-1} plot apart from the authors' argument. Regarding the continuous weak mixing model, I am wondering why all observations in the polar vortex region (Kiruna and EUFLEX) follow the model with r = 0, but not between r = 0 and r = 1. Since I do not expect all samples were collected at the center of vortex, it needs to be discussed more in detail. In addition, the EUFLEX and some Kiruna data points whose N_2O mixing ratios are lower than $\sim$170 ppb place below green line that represents the model with r = 0 in Fig. 12. I do not understand this because theoretically data points should place above or on green line as the model space limits between r = 0 and r = 1. This is opposite to the authors' argument that the continuous weak mixing could explain the EUFLEX data for the N_2O mixing ratio below 200 ppb. Furthermore, in Figs.12-14 the mesospheric intrusion events (Kiruna 03/03 and perhaps the flights in 1992 according to the authors' argument) are included although not being mentioned in the text and caption. I wonder whether the authors want to explain the mesospheric intrusion event by the continuous weak mixing model. This should be clarified. I recommend the use of the same symbols for Kiruna flights in Fig. 12, 13, and 14 as used in other Figures to avoid confusion.

Specific comments:

p.4274, L. 9 - 13: This sentence is very specific and not relative to any following statements. I suggest deletion of this sentence.
p.4284, L. 6: "The polar vortex samples show δ^{15}N variations of more than 25 permil for the same N_2O mixing ratio, ..." I do not see such large difference of δ^{15}N except at the N_2O mixing ratios of $\sim$10 ppb in Fig. 5.
p.4284, L.9: ".... dynamic isolation of the polar vortex ...." Why does the isolated air have a large variation of δ^{15}N? This phrase is in contrast to the next sentence, "In addition, mixing with upper stratospheric .... as well as more complicated mixing ...." Perhaps the air sampled is not an isolated air but on the line of mixing between the

vortex air and the surrounding stratospheric air or the descending mesospheric air.
p.4284, L.16: Define ϵ and μ_T.
p.4284, L.20: According to Fig. 5, the data for the N_2O mixing ratio between 100 ppb and 300 ppb place below the Rayleigh line with ϵ = -19.2 . In particular, the data from EUPLEX are excluded from these bounds of isotopic fractionation lines.
p.4285, L.19: μ and δ were corrected at a specific date of 15 Mar., 2002 in this section to calculate local ϵ_{app}. How much different are the values of ϵ_{app} with and without the corrections for μ and δ? For visualization, it would be useful to compare the corrected values at the same μ-δ^{15}N space shown in Fig. 5. Based on Fig. 6, I do not see significant difference after the correction such that for the N_2O mixing ratios above about 100 ppb data points place still below the Rayleigh line with ϵ = -19.2 .
p.4289, L.7: Are the values of $\epsilon^{15}N_{app}$ at the three regions of the lower stratosphere different significantly? It needs to be discussed rigorously in terms of statistics.
p.4289, L.23 - 28: What is this paragraph for? I wonder if the authors want to argue that the apparent fractionation at the mid-stratosphere is explained by pure vertical diffusion. This is, however, opposite to what the authors mentioned in line 3 on the same page.
p.4290, L.7: Table 2 does not support the authors' argument that the values of ϵ_{app} for Gap 06/99 are generally smaller than that for ASA. To the contrary, ϵ_{app} for ^{15}N and ^{18}O for ASA 09/93 are the same as that for Gap 06/99.
p.4295, L.10: I cannot follow this sentence. Why did the author expect a similar event in 1992?
p.4296, L.10: I suppose “0.1 <z<0.2” instead of “1<z<0.2”.
p.4296, L.15: I suppose “-(z-1.1)^{38}” instead of “-(z-1.1)38”
p.4307, Table 1: I suppose longitude of Kiruna, Sweden to be 21°E not 1°E under Griffith et al. (2000) compilation.
p.4311, Fig. 2: It would be better to plot as like Fig.1 rather than relative values at the vertical axis in order to compare the N_2O mixing ratios measured from two methods. Does solid line in the figure indicate the regression? What is this line for?

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p.4316, Fig. 7: An extrapolated value is not indicated for ln(μ/μ_T) > -0.6 in Table 2, but one is shown here. In addition, add logarithmic symbol "ln" before μ in the plot and the caption.
p.4318, Fig. 9 and p.4319, Fig. 10: Why does the end-member mixing line for the high N_2O mixing ratios not pass through the origin in the plot even though the values of μ and δ are normalized?

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 4273, 2006.

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