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Atmospheric
Chemistry
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Discussions

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.

J. Kaiser et al.

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We thank the referee for the constructive and helpful comments on our manuscript.

Response to general comments:

A table with station information, N_2O mixing and isotope ratios is available on request from the authors, for modelling or other purposes. A corresponding remark will be added to the revised version of the paper. However, we are reluctant to make the data fully available in the public domain as we are still in the process of writing up publications that are using these data.

We don't think that a complete separation of results and discussion will lead to an improved structure of the manuscript. Instead, we would like to keep the discussion closely associated with the results, so as to avoid unnecessary skipping between different parts of the paper. We also note that Referee #2 found the paper well structured and clear. Bearing this in mind, we have left the structure of the paper as it was, but have tried to remove any inconsistencies that might have existed and any ambiguities that might have made it difficult to separate results and discussion.

1) In the paper, we are testing the limits of three simple models used to describe isotope fractionation in the stratosphere, i.e., Rayleigh fractionation in a vertically diffusive atmosphere, end-member mixing and continuous weak mixing. We show to what extent these models can explain the observations and where they fail. As we explain in the paper, some features in the data (e.g., those for N_2O mixing ratios >200 nmol mol^{-1}) can be explained sucessfully by more than one model. This should not be mis-construed as a “change of argument” or “inconsistent description”. Rather, it is a reflection of the complex reality. For example, the change of the apparent fractionation constant with latitude could be explained by a change of the photochemical and transport parameters in a vertically diffusive Rayleigh fractionation model. However, the change of $\varepsilon_{\mathrm{app}}$ with altitude cannot be explained in such a way, as it is contrary to the known eddy diffusion coefficients and N_2O loss rates. This is our argument in Sect. 3.3.3. In view of the confusion of the reviewer, we have clarified this section of the paper in the revised version and have tried to remove any remaining ambiguities elsewhere.

2) Following a similar comment by referee #2, we have now enhanced section 3.5 of the paper and backup our results with detailed equations and an additional figure. The statement in the abstract about the contribution of photo-oxidation has been changed to “possibly up to 100% for N_2O mixing ratios above 300 nmol mol^{-1}).” A more detailed description will be available in the revised version of section 3.5

3) We note that the interpretation of a mixing plot (δ vs. μ^{-1}) is not dependent on the choice of the end-member, be it tropospherica air, extravortex air, or anything else (cf. Eq. 5 in the paper). We disagree with the referee that end-member mixing is a

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suitable explanation for the curved in lines in Figs. 9 and 10 (e.g., for SOLVE or EUPLEX). Of course, any two points on a curve can be connected by a “mixing line”, but this can hardly be interpreted as a physical explanation. We have already discussed (section 3.3.2) that end-member mixing is to some extent successful in explaining the mid-latitude results, but the deviations from a mixing line are nevertheless more pronounced than the analytical errors. Regarding the continuous weak mixing model, we do not expect it to quantitatively explain the features of the observation. It is merely a conceptual model and we wanted to highlight its qualitative merit of showing an increase of the apparent fractionation constant in a Rayleigh fractionation plot, which a simple vertically diffusive model fails to capture successfully. Likewise, the proximity of the data points to the $r = 0$ curve (center of vortex) is a mere coincidence. Note that most points for $r < 0.3$ (intra-vortex) are very close to the observations, not only those for $r = 0$. We have tried to make this clear in the ACPD version of the paper, but have made additional clarifying statements in the ACP version. Figures 12–14 have now been merged into one figure with six panels and the same symbols as for the Kiruna flights have been used. We don’t mean to explain the mesospheric intrusions, but have shown all data points for comparison and have re-iterated that this is merely an illustration, not a quantitative comparison.

Response to specific comments:

p. 4274, l. 9-13: Sentence deleted.

p. 4284, l. 6: Corrected to "up to about 30 per mille"

p. 4284, l. 9: Corrected to "isolation of the polar vortex from mid-latitude air masses" and deleted the confusing reference to "more complicated mixing effects".

p. 4284, l. 16: ϵ is defined in the previous line and μ_{T} has been defined now as the N_2O mixing ratio at the tropopause.

p. 4284, l. 20: Indeed. This is discussed on p. 4285, l. 20.

p. 4285, l. 19: We have now added an explanation at the end of section 3.2.2: “A comparison of the $\varepsilon_{\mathrm{app}}$ values derived from the normalized N_2O isotope and mixing ratios with $\varepsilon_{\mathrm{app}}$ values derived from the non-normalized data shows differences between -0.4 and +0.2 per mille for ε^{15}N. The corrections described in Sect. 3.2.1 are therefore of minor importance for the $\varepsilon_{\mathrm{app}}$ values, but the isotope ratio corrections turn out to be significant for the study of correlations between different intramolecular isotope signatures in the lower stratosphere (Sect. 3.5).”

p. 4289, l. 7: We have added statistical indicators, so that the sentence now reads: “Specifically, average $\varepsilon^{15}\mathrm{N}_{\mathrm{app}}$ values at ln(μ/μ_{T})$>$ –0.6 are (-18.5 ± 0.9) per mille at tropical latitudes, (-16.9 ± 0.6) per mille at mid-latitudes and (-15.5 ± 0.6) per mille at polar latitudes. The pairwise differences are only significant at the 1σ level, but all $|\varepsilon^{15}\mathrm{N}_{\mathrm{app}}|$ values are clearly less than half the absolute magnitude of the intrinsic fractionation constant of about -50 per mille at a lower stratospheric temperature of 217 K (Kaiser et al., 2002b), estimated from broadband N_2O photolysis with an ultraviolet (UV) lamp that simulates the solar spectrum at stratospheric altitudes. ”

p. 4289, l. 23: We have now merged this paragraph with the discussion in the first paragraph of the section, where this paragraph belongs.

p. 4290, l. 7: We can’t follow the potential discrepancy the reviewer has seen between the text and Table 2. Except for the lower stratospheric results, all Gap 06/99 values are smaller than the fall ASA values (i.e. for ln(μ/μ_{T}) = –1.0, –1.5, and –2.0), just as written in the text.

p. 4295, l. 10: We have now added the reasoning, on which we base our statement to the last sentence of the section: “Based on Fig. 9, a similar event must have occurred in the winter of 1992, because also then, similar δ^{15}N were observed over a large range of mixing ratios in the middle stratosphere.”

p. 4296, l. 10: This should indeed read “$0.1 < z < 0.2$” and has been corrected.

p. 4296, l. 15: This typo has been corrected.

p. 4307, Table 1: This typo has been corrected.

p. 4311, Fig. 2 and p. 4281: Figure 2 now shows absolute differences and the offending black line has been deleted as it just led to confusion and is not necessary. The text on p. 4281 has been amended to reflect the changed Figure without losing emphasis on the argument that it is the relative differences that matter for the derivation of stratospheric apparent fractionation constants. The text now reads: “Figure 1 shows that they follow a 1:1 relationship very closely, with the NO^+-derived mixing ratio being on average (1.3±2.1) nmol mol^{-1} higher. The average relative difference, which is more important for the derivation of stratospheric apparent fractionation constants, is (0.7±1.1)% (excluding five outliers of $-$15%, $-$7%, 8%, 10%, and 46%). We adopt the mean of the N_2O^+- and the NO^+-derived mixing ratio as the mixing ratio of the individual sample. For a subset of 47 samples, we have compared this mixing ratio to independent GC-ECD measurements at the Institute for Meteorology and Geophysics of the University of Frankfurt (Fig. 2). The average difference between these two values is $-$(0.2±2.4) nmol mol^{-1}, and the average relative difference is ($-$0.3±2.1)% (excluding two outliers of $-$18% and 11%), with relative differences of 1% or smaller for larger mixing ratios and larger relative differences for smaller mixing ratios.”

p. 4316, Fig. 7: The errors in figure and figure caption have been corrected.

p. 4318, Figs. 9 & 10: We don’t understand the comments of the reviewer. The end-member mixing line does not and should not pass through zero. If it was passing through zero, this would indicate a δ^{15}N value of 0 per mille at infinitely large mixing ratios. Rather, δ^{15}N equals 0 for tropospheric mixing ratios of about 320 nmol mol^{-1}.

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