Referee #2

Review on "**The isotopic composition of atmospheric nitrous oxide observed at the high-altitude research station Jungfraujoch, Switzerland**".

This manuscript described the 5-year observations of nitrous oxide (N_2O) mixing ratios and their isotopic compositions at Jungfraujoch using laser spectroscopic technique for the first time. The long-term observations of N_2O isotopocules allow the authors to characterize the integrated isotopic signatures of anthropogenic sources that have been emitted since the industrial revolution and to identify the main processes governing the seasonality of N_2O. The authors utilized a two-box model and a Lagrangian particle dispersion model to characterize the isotope signatures of anthropogenic sources that contribute to the atmospheric increase of N_2O concentration. The unique observations of N_2O isotopocules in the middle of the European continent and the interesting interpretation of data makes worth publication. Notwithstanding, there are several hazy spots in the manuscript which needs to be revised in order to avoid any confusion.

Major issues:

1. Application of a two-box model assumes the data obtained at Jungfraujoch to represent the variability of N_2O mixing ratios and its isotopocules in the troposphere. This appear to contradict to the use of footprint model to characterize the isotopic signatures of the anthropogenic sources in the European continent. This is demonstrated in Table 2 and 3 that the isotopic signatures of the anthropogenic N_2O are different. In the text on the lines from 626 to 635, the authors ascribed it to the different isotopic signatures of N_2O source emissions in the model. However, as shown in Table 2 and mentioned in the text (on the line of 612), the single spot observation won't be representative the global scale of atmosphere, but would represent the regional characteristics of N_2O. The long-term trends of N_2O isotopocules listed in Table 1 also support that the observation at Jungfraujoch does not represent the tropospheric variability of N_2O. Contradict to the global trends of isotopocules shown in Figure 6, the observations of $\delta^{15}N^{SP}$ and $\delta^{18}O$ are positive trends at Jungfraujoch. In view of these contradict aspects revealed in the observation and the model, the isotopic signatures of the anthropogenic source will not help understand the contribution of anthropogenic source to the increase of atmospheric N_2O. I would suggest limiting the data interpretation in regional scale.

R: We thank the review for the critics and suggestions. Although the reviewer suggests to limit our data interpretation with respect to the global model, we argue that the air samples collected from Jungfraujoch Sphinx still represent the background troposphere, despite the contribution of regional emissions to the seasonal variability. The box model estimates for the emission strength and isotopic composition of the anthropogenic source are largely depending on the mean values of N_2O concentrations and isotopic composition at Jungfraujoch, and little affected by subtle temporal changes, which are shown in the seasonal variabilities. Based on the NO_y : CO criterion (Herrmann et al., 2015; Zellweger et al., 2003), which has been identified as an effective indicator for the (short) age of air mass, 110 out of 142 sample points were found to represent the free troposphere. To demonstrate that two-box model results are not affected by regional emissions, we re-ran the two-box model with the data filtered for free troposphere and got statistically identical results. The new results are now mentioned in section 4.4.

Regarding the reviewer's arguments referring to Table 2 and 3 as well as the texts in discussion, we believe that there are misinterpretations. In our discussion (LN 626-635), the differences in source isotopic signatures between Table 2 (two-box model) and Table 3 (bottom-up estimate) was largely attributed to the uncertainty in the estimated source isotopic signatures, which were used in the bottom-up model (Table S2; original version). This was further explained by comparing our bottom-up estimates with those from Toyoda et al. (2013), demonstrating that the selection of source isotopic signatures for distinct source categories from literature largely influence the isotopic composition of the anthropogenic source.

We are aware that a single-site study can be limited in determining long-term trends of N_2O isotopic signatures. As we discussed in the manuscript, extension of the study period at an even higher sampling frequency would reduce such uncertainties. Although the interannual trends of $\delta^{15}N^{SP}$ and $\delta^{18}O$ were positive in the first phase of our observation, we obtained insignificant trends for the whole dataset, which in return makes a minor influence on the model estimates. Given the relatively short study period, the mean isotopic signatures observed at Jungfraujoch is more important than the trends for determining isotopic signatures of anthropogenic sources from the NH background atmosphere.

2. The long-term observation at one station allowed seasonal variation to be explored. The authors argued the minimum N_2O concentration observed in late summer is driven by STE which is also evidenced by the enrichment of ^{15}N in the N_2O driven by the photochemical destruction in the stratosphere. On the other hand, $\delta^{15}N^{SP}$ and $\delta^{18}O$ did not seemingly synchronize the STE event, which, the authors argued, the N_2O emitted from the soil overwhelms the effect by STE. If these two processes govern the seasonality of the atmospheric N_2O, I would suggest quantifying how to compete these two processes along the year at Jungfraujoch.
R: The authors agree, as already mentioned in the manuscript, that N_2O isotopic composition at Jungfraujoch is controlled by stratospheric intrusions and uplift of polluted air masses. However, it is currently not possible to quantify the relative importance of these two mechanisms over time, given that temporally resolved isotopic signatures of stratospheric air and soil N_2O sources are not available for Jungfraujoch. We simulated the contribution of upper tropospheric air (15 km) to Jungfraujoch station, which is highest in the August. This acts as a qualitative indicator of the seasonal pattern of STE, which assists to explain the seasonal variability of $\delta^{15}N^{bulk}$ (added to the discussion 4.2). On the other hand, simulations of N_2O enhancements (on average 60% from soil) for 2017-2018 suggest that ground emissions of N_2O were highest in the early to middle summer (Fig. 5; original version). In August, when N_2O mixing ratios were lowest below baseline, the N_2O depletion due to mixing with stratospheric air clearly outcompeted the enhancement from ground emissions.
In a back-of-the-envelope calculation, we assume N_2O enhancement from ground-based emissions in August to be 0.15-0.20 nmol mol^{-1}, which is close with or slightly smaller than the maximum change of N_2O mixing ratio above baseline (0.20 nmol mol^{-1}; Fig. 1b). Then, given that the net minimum of N_2O mixing ratio in August is -0.2 nmol mol^{-1} below baseline, we can estimate the N_2O depletion due to STE as 0.35-0.40 nmol mol^{-1}. In addition, N_2O enhancement by soil emission (60% of total ground emission) can be calculated as 0.09-0.12 nmol mol^{-1}. With the isotopic effect associated with each mechanism from literature, we may estimate the combined effects of the two mechanisms on the maximum variabilities of $\delta^{15}N^{SP}$ in the late summer at Jungfraujoch. The net isotopic effect of mixing with stratospheric air is assumed to be about +5‰ for the lower stratosphere (higher isotopic signature but smaller mixing ratio for higher stratosphere) (Toyoda et al., 2018); the isotopic effect due to switch from nitrification to denitrification is assumed to be -30‰ (Sutka et al., 2006). Therefore, STE contributes N_2O depletion at a strength four times of that from soil emissions, while the isotopic effect of STE is only 1/6. Based on the estimates above, it is reasonable to suggest that soil emission would outcompete STE in regulating $\delta^{15}N^{SP}$ during the late summer. Nevertheless, our estimates may have large uncertainty, and require further validation with isotopic measurements of two individual processes. By contrast, given that the isotopic effects of soil processes are much smaller for $\delta^{15}N^{bulk}$ (Toyoda et al., 2011), STE stands out to control the variability of $\delta^{15}N^{bulk}$ during late summer. We have now implemented these estimates in the supplementary material and have included more discussion in the manuscript.

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Minor issues and technical comments:
1. L 52: The publication year of Tian et al. (2018) is 2019.
2. L 171: "gas chromatography" should be "gas chromatograph" in the context.
R: OK.

3. L 170 – 184: Since no references are given, I suggest describing the analytical methods in detail including the calibration of the system for the analysis of N_2O, CO, NO_y, and O_3 mole fractions perhaps in the section of Supporting Information.
R: Thanks for the suggestion. Additional details on the analytical method of N_2O is now implemented. The references for CO, NO_y and O_3 were given in the section 2.1 for atmospheric pollutant measurements at Jungfraujoch. In the revision, we have referred to specific publications for each pollutant giving more details on analytical methods.

4. L 217: Have you tested the mole fraction dependency of the isotope ratios of N_2O? Here, the amount of N_2O for the QCL is 45 ppm. However, Mohn et al. (2010, 2012) concentrated ambient air to > 60 ppm of N_2O.
R: Yes. The dependency of N_2O mole fraction on isotopic results was determined and corrected for (if necessary) during every batch of measurement. In addition, following identical-treatment principle, we fixed the N_2O mole fractions of calibration standards (CG1 and CG2) to the same level 45 ppm.

5. L 218: I think the citation of Harris et al. (2017) should be Harris et al. (2014).
R: Not true. Harris et al. (2014) described the laser spectroscopic technique that was developed in MIT for N_2O isotopic measurement; however, this study shares the same instrumentation as Harris et al. (2017) which was developed at Empa (Switzerland).

6. L 236: What are the matrix gases in CG1 and CG2 standards?
R: 78% N_2 and 21% O_2. This is now mentioned in the manuscript.

7. L 253: In Figure S2, the scattering of isotope ratios in the second phase look larger than that in the first phase, particularly for $\delta^{18}O$. Is it statistically insignificant?
R: Statistically, the difference is not significant.

8. L 313 – 314: T_{PI} and T_{PD} should be replaced to τ_{PI} and τ_{PD}.
R: OK

9. L 353: It's misleading. Fig. S3 shows the agreement improved since the year 2015 when GC-ECD was replaced to OA-ICOS, NOT in the second phase.
R: This is now revised. See section 3.1 for change.

10. L 358 – 361: Provide the ground that the N_2O growth rates of 0.880±0.001, 0.993±0.001, and 0.93 are in agreement. Statistically they are different each other unless standard deviation of the global growth rate of 0.93 (by NOAA) is larger than ~0.02.
R: We agree. The uncertainty of growth rates by NOAA is around 0.03 nmol mol^{-1} a^{-1}, suggesting that the global mean growth rate of 0.93 ± 0.03 nmol mol^{-1} a^{-1} is lower than retrieved from our measurements at Jungfraujoch, excluding GC-ECD measurements (2015-2018). This is now revised.

11. L 361: Add the literature (WMO, 2018) next "NOAA (0.93 nmol mol^{-1} a^{-1})".
R: OK.

12. L 362 – 364: The annual growth rate, 0.813±0.027 is not lower than the value 0.858±0.002 within 2 standard deviations.
R: This is now revised as "the absolute growth rate determined from the discrete gas samples was even lower albeit larger uncertainty (0.813 ± 0.027 nmol mol^{-1} a^{-1})".

13. L 376: The authors indicate the insignificant increasing trend of $\delta^{15}N^{SP}$ and $\delta^{18}O$. However, their standard deviations do suggest significant increase of them within 1 sd. It needs to be clarified.
R: In Table 1, we showed coefficients from linear regressions with 1 SD. However, as indicated in section 2.6, significance level for linear regression was set to $p < 0.01$ (confidence level of 99%). Hence, this would require coefficients to be larger than 3 times of SD.

14. L 383 – 391: It needs explanation why the trends of $\delta^{15}N^{SP}$ and $\delta^{18}O$ during the first phase is one order of magnitude larger than that in the second phase.
R: As stated in LN 386-388 (original version), the strong increasing trends for $\delta^{15}N^{SP}$ and $\delta^{18}O$ were most likely due to the unexpectedly low $\delta^{15}N^{SP}$ and $\delta^{18}O$ values in summer 2014 (Fig. 2). In addition, this has been discussed in section 4.3: "Nevertheless, our observation period is shorter than that of other studies, so the interannual trends determined here are more likely affected by year-to-year variability" (LN 540-542; original version).

15. L 438: I would suggest moving Fig. S7 onto the main text as it is the unique visualization to illustrate Lagrangian footprint of isotopic signatures of the sources.
R: Agree.

16. L 442 – 451: The section 4.1 does not seem to benefit the main theme of this manuscript. It rather makes the manuscript loose. Analytical quality has already mentioned in the section 2.4 Data analysis (see the lines 246, 252 – 253) and the excellent analytical repeatability for $\delta^{15}N^{SP}$ by QCL is well described in Mohn et al. (2014).
R: Although an excellent repeatability of singular measurements has been shown by (Mohn et al., 2014), it is important that repeated measurements of target gases show a good consistency, indicating long-term robustness of our measurements. This is crucial for isotopic measurements of background atmosphere, as target variabilities of our samples are most likely in a range that is only a few times larger than our analytical precision (Toyoda et al., 2013). Therefore, we would like to keep this section. To avoid confusion, we have now changed "analytical repeatability" to "target repeatability".

17. L 458: Decock and Six (2013) does not describe the STE process at all. Is it an error in citation?
R: The reviewer is right. We have now revised the citation.

18. L 459: Add superscript “bulk” next 15N.
R: Superscript "bulk" is used for $\delta^{15}N$ values, which refer to the average of $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$. Here, enrichment of ^{15}N is a general description, thus not requiring “bulk” notation.

19. L 461: Comparing Figure 3(a) in Toyota et al. (2013) with Figure 1a here, it does not look “almost identical”, but perhaps comparable. The monthly mixing ratio of N_2O at Jungfraujoch is at maximum in June while in April at Hateruma Island, Japan.
20. L 464: What are the underlying mechanisms?

21. L 511: Provide the regression coefficients in Figure S8.
R: They have been already embedded in each figure as red fonts.

22. L 514: $\delta^{15}N^{bulk}$ in Figure S7 is not particularly high in spite of potential influence of STE. It needs to be clarified.
R: This must be a misunderstanding. In Figure S7, we compared $\delta^{15}N^{bulk}$ for six air mass foot-print clusters but not showing air coming from stratosphere.

23. L 537: Add minus sigh before 0.06.
24. L 558 – 559: Rahn and Wahlen (2000) do not provide clear evidence on the influence soil water vapor to oxygen isotope in N_2O, but they speculated. Thus, it would appropriate to write "… assuming that …" instead of "… given that …".
R: OK

25. L 605: The authors' argument is not clear here. Based on the isotopic signatures of the anthropogenic N_2O, long-term observation at Jungfraujoch indicates the significant contribution of denitrification process in soil while the results from Park et al. (2012) or Prokopiou et al. (2017) favor nitrification process in soil. This is clearly contradicted each other.
R: Based on the difference between our and other studies in box-model estimates, we suggest that the isotopic signatures of anthropogenic sources may have shifted in recent decades. This would mean non-linear change of N_2O source isotopic signatures since preindustrial times. On the other hand, the uncertainty in measuring N_2O isotopic signatures in the background atmosphere and inter-comparability among laboratories may play a role in the discrepancy of the estimated source isotopic signatures. Further elaborations are incorporated now (section 4.4).

26. L 617: Figure 6 shows that $\delta^{15}N^{bulk}$ from Jungfraujoch are higher than any other values including Park et al. (2012) and even Toyota et al. (2013). Thus, this sentence does not help explain why $\delta^{15}N^{bulk}$ of the anthropogenic N_2O from the observation at Jungfraujoch is higher than the value by Park et al. (2012).
27. L 618: It is impossible to mention trends of $\delta^{15}N^{SP}$ as the data is too scattered. In addition, $\delta^{15}N^{SP}$ at Jungfraujoch shows positive trends, too (Table 1).
R: Thank you for the critical comments. We have now clarified these two points in the discussion. Below are some explanations.
The difference in $\delta^{15}N^{bulk}$ between our study and Toyoda et al. (2013) is relatively small (0.10-0.15‰ based on year-to-year comparison) compared with the difference between ours and Park et al. (2012) (0.40-0.5‰). Therefore, the $\delta^{15}N^{bulk}$ of anthropogenic source estimated with two-box model is much smaller in Park et al. (2012) than in ours and Toyoda et al. (2013). Even larger inter-laboratory differences in $\delta^{15}N^{bulk}$ have been observed in Ostrom et al. (2018) and can be explained by different anchoring to international scales (Air-N2).
As stated in section 4.4, the difference between current mean tropospheric isotopic values and preindustrial values (given in Table S1) are important in determining the trend of N_2O isotopic signatures in the model estimates. The trends mentioned here are referred to long-term trends since preindustrial times as simulated by the model, but not the observed trends in the "current" troposphere.

28. L 652: What do the authors mean the "higher-frequency temporal variation" for $\delta^{15}N^{SP}$ and $\delta^{18}O$? Is it relevant to soil emission? Please state it clearly.
R: This is not referred to soil emissions. The determined interannual trends for $\delta^{15}N^{SP}$ and $\delta^{18}O$ showed large uncertainties, which is possibly due to large temporal (seasonal) variabilities of $\delta^{15}N^{SP}$ and $\delta^{18}O$. We have reformulated this statement.

29. L 656: Table 2 clearly shows the isotope signatures from Jungfraujoch differ from the values obtained at other sites, opposite to the statement here.

R: Within model uncertainty, our model estimates of isotopic signatures for anthropogenic sources were largely in agreement with the other studies, except for the $\delta^{15}N^{bulk}$ and $\delta^{15}N^{SP}$ when compared with Park et al. (2012) and Prokopiou et al. (2017).

Reference

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