Reply to the manuscript review by Anonymous Referee #1

We thank Anonymous Referee #1 for their perceptive and constructive review of our manuscript. Below, the Referee's comments (in bold) are followed by our response. Changes to the manuscript are highlighted in green.

Please note that, because we have moved a significant number of figures and tables to the Supplementary Materials, we have provided a list of the updated Figure, Table and Supplementary Material numbering at the end of this document.

Referee general comments and observations

The authors present a very comprehensive and thoughtfully planned study to evaluate the performance of the three common N2O isotope laser spectrometers, Picarro CRDS, Los Gatos ICOS, and Aerodyne QCLAS. Most importantly, they found that significant matrix and trace gas composition affected the precision and accuracy of all instruments with these interferences scaling with N2O mole fraction. The authors do a great service for the community by proposing a step-by-step workflow to properly deal with these interferences.

I really appreciated Table 4 overviewing the many experiments performed because it helped orient me as I read through Section 2.4. Testing of instruments. Although I hesitate to ask the authors to add any more to this already massive manuscript, I think that readers would benefit from an additional overview table summarizing the main findings for each of the three types of N2O isotope laser spectrometers. This would help readers implement step 1 of the proposed workflow, choosing the right laser spectrometer for one's application, and also help readers implement the general workflow as appropriate for the specific spectrometer type (e.g., dealing with CH4 interference is less important for QCLAS). Some readers may view this instrument intercomparison as an effort to determine which spectrometer outperforms the others. The addition of this summary table would also help convey the important point that there is not one spectrometer with superior performance across all applications. The manuscript is well-written, but given the complex and detailed nature of the study, the experimental set-ups and results were inherently confusing to wade through. I have inserted specific comments in the attached PDF supplement to help highlight the take-home messages from the experiments and to clarify some points for readers who may be less familiar with N2O isotope laser spectrometry.

Authors' response: Following your suggestion, we have incorporated Table 8 into the manuscript (please note that the original Tables 8, 9 and 10 have now been placed in the Supplementary). We anticipate that the information provided in Table 8 will assist readers in better understanding the advantages and limitations of each instrument when applied to certain measurement applications. It will be incorporated into the text on P60L4:

P60 L4: "A summary of results is presented in Table 8. Our results highlight that […]"

Table 8. Summary of main findings presented in this study.

Detection scheme (model; manufacturer)	OA-ICOS I (N2OIA-30e-EP)	CRDS I & II (G5131-i)	QCLAS I (CW-QC-TILDAS-SC-D)	TREX-QCLAS I (CW-QC-TILDAS-76-CS)
Allan precision (300 s) $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰] 326.5 ppb N_2O ~ 1000 ppb N_2O ~ 10000 ppb N_2O	0.79 – 1.69 0.28 – 0.67 0.12 – 0.17	0.32 – 0.46 0.21 – 0.89 n.d.	0.39 – 3.45 [a)] 0.19 – 0.83 [a)] 0.02 – 0.48 [a)]	n.d. n.d. n.d.
Repeatability (326.5 ppb N_2O) N_2O [ppb] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰]	0.07 1.19 – 2.17	0.26 – 0.30 0.52 – 0.83	0.16 5.35 – 8.57	1.29 0.37 – 0.60
Temperature effect (326.5 ppb N_2O) N_2O [ppb K^{-1}] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ K^{-1}]	0.01 0.36 – 2.60	0.02 0.25 – 0.65	0.10 31.29 – 37.32	n.d. n.d.
N_2O mole fraction dependence $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ ppb ($\Delta 1/N_2O$)]	-8296 – 2544	-458 – 1353	-66386 – 15833	n.d.
O_2 matrix effect (330 ppb N_2O) N_2O [ppb $\%^{-1}$ (ΔO_2)] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ $\%^{-1}$ (ΔO_2)]	-0.044 0.874 – 1.270	0.24 – 0.305 -0.279 – (-1.364)	0.351 -1.111	n.s. n.s.
CO_2 trace gas effects (330 ppb N_2O) N_2O [ppb ppm^{-1} (ΔCO_2)] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ ppm^{-1} (ΔCO_2)]	0.0011 -0.009 – 0.026	0.0005 n.s. – (-0.0019)	n.s. n.s. – 0.0154	n.s. n.s.
CH_4 trace gas effects (330 ppb N_2O) N_2O [ppb ppm^{-1} (ΔCH_4)] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ ppm^{-1} (ΔCH_4)]	n.s.[b)] 0.173	-0.039 – (-0.056) 0.085 – 2.50	n.s. n.s.	n.s. n.s.
CO trace gas effects (330 ppb N_2O) N_2O [ppb ppm^{-1} (ΔCO)] $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{18}O$ [‰ ppm^{-1} (ΔCO)]	-0.29 n.s.	-0.15 – (-0.24) -0.53 – (-2.41)	-0.19 n.s. – (-4.04)	n.s. n.s.

a) Includes QCLAS I, II and III
b) Likely due to inaccuracies during dynamic dilution (see text for details)
n.d. not determined
n.s. not statistically significant at $p < 0.05$ and/or $r^2 < 0.5$

Referee comment 1 - Page 4 Line 25: Start a new paragraph here.

Authors' response: Agreed and revised.

Referee comment 2 - Page 5 Line 9: Readers could potentially benefit from a brief explanation of the principles of the spectroscopic approach compared to IRMS. This would provide some context for the trace gas effects described later.

Authors' response: We agree with this suggestion. In keeping with Referee #1 and Referee #2's comments regarding the length of our manuscript, we have opted to only briefly explain the spectroscopic approach in comparison to IRMS to limit the length of the manuscript. This paragraph (with minor re-structuring) now reads:

(New Paragraph) P4 L27: "The advancement of mid-infrared laser spectroscopic techniques was enabled by the invention and availability of non-cryogenic light sources which have been coupled with different detection schemes, such as direct absorption quantum cascade laser absorption spectroscopy (QCLAS; Aerodyne Research Inc. [ARI]; Wächter et al., 2008), cavity ring-down spectroscopy (CRDS; Picarro Inc.) and off-axis integrated-cavity-output spectroscopy (OA-ICOS; ABB Los Gatos Research Inc.; Baer et al., 2002) to realize compact

field-deployable analyzers. In short, the emission wavelength of a laser light source is rapidly and repetitively scanned through a spectral region containing the spectral lines of the target N_2O isotopocules. The laser light is coupled into a multi-path cell filled with the sample gas, and the mixing ratios of individual isotopic species are determined from the detected absorption using Beer's Law. The wavelengths of spectral lines of N_2O isotopocules with distinct ^{17}O, ^{18}O or position-specific ^{15}N substitution are unique due to the existence of characteristic rotational-vibrational spectra (Rothman et al., 2005). Thus, unlike IRMS, laser spectroscopy does not require mass-overlap correction. However, the spectral lines may have varying degrees of overlap with those of other gaseous species, which, if unaccounted for, may produce erroneous apparent absorption intensities. One advantage of laser spectroscopy is that instruments can analyze the N_2O isotopic composition in gaseous mixtures (e.g. ambient air) in a flow-through mode, providing real-time data with minimal or no sample pretreatment, which is highly attractive to better resolve the temporal complexity of N_2O production and consumption processes (Decock and Six, 2013; Heil et al., 2014; Köster et al., 2013; Winther et al., 2018).

Referee comment 3 - Page 5 Line 16: Temperature? Humidity? Expand on this a little more for the uninitiated.

Authors' response: We apologise for the unclear explanation. Our intention was to highlight that fluctuations in ambient temperature may cause drift effects due to moving interference fringes when using these instruments (see Werle et al., 1993). We did not intend to highlight the effects of humidity in point (3), because fluctuations in humidity would cause spectral interferences due to overlapping water vapor spectral peaks that are mentioned in point (4), rather than causing drift effects. The following changes have been made to the manuscript:

 "(3) laser spectrometers are subject to drift effects (e.g. due to moving interference fringes), particularly under fluctuating laboratory temperatures, which limits their performance (Werle et al., 1993)."

Referee comment 4 - Page 5 Line 18: This approach needs to be defined, especially if the purpose of this paper is to educate people new to this field.

Authors' response: This was also a concern of Referee #2, and therefore we reply to all concerns here. We agree that this approach should be defined. However, because this topic has been discussed to great lengths elsewhere (Sturm, 2013; Wen et al., 2013; Griffith et al. 2012; Flores et al., 2017; Griffith, 2018), and to limit manuscript length, we will refrain from providing too much information in our manuscript.

As outlined in Griffith (2018), calibration of spectrometers can be achieved two ways: calibrating on derived isotopologue/isotopocule ratios or delta values (Approach A; what we referred to as a "δ-calibration approach"), or calibrating on derived individual isotopocule amount fractions (Approach B). In Approach A, raw measured delta values are calculated from measured uncalibrated isotopologue/isotopocule amount fractions, and then calibrated against the delta values of the reference gases. In Approach B, raw measured amount fractions of isotopocules are calibrated against a set of reference gases with known isotopocule amount fractions, prior to deriving ratio or delta values.

In our manuscript, we applied Approach A for three reasons: 1) N_2O isotope reference materials provide delta values but not amount fractions (Ostrom et al., 2018); 2) to remain consistent with the IRMS community, who calibrate results using Approach A; and 3) not all laser spectrometers tested (such as G5131-I and II, CRDS, Picarro Inc.) make the amount fraction data available to the user. It is therefore reasonable to assume that most users of these instruments will undertake Approach A.

However, as discussed in Sturm (2013; Atmos. Meas. Tech. Discuss., 6, C170–C176) and Wen et al. (2013), Approach A introduces a concentration dependence to delta values in potentially two ways: 1) if the analyzer measurements of isotopologue/isotopocule mole fractions are linear, yet the relationship between measured and true mole fractions have a non-zero intercept (Eq. 14 in Griffith et al., 2012); and/or 2) if the instrument response has non-zero offsets in integrated peak area due to baseline structures (such as fringe effects). This effect was observed in several studies in our laboratory, e.g. Tuzson et al. (2008), Wächter et al. (2008) and Eyer et al. (2016). The effect is dominant at low amount fractions, but less prominent at higher amount fractions, as shown in the Eq. below:

$$\delta a_{eff} = \left(\frac{\frac{[^{15}N^{14}N^{16}O] - [A]}{[^{14}N^{14}N^{16}O]}}{r_A} - 1 \right) = \left(\frac{\frac{[^{15}N^{14}N^{16}O]}{[^{14}N^{14}N^{16}O]}}{r_A} - 1 \right) - \frac{\frac{[A]}{[^{14}N^{14}N^{16}O]}}{r_A}$$

$$\delta a_{eff} = \delta a - \frac{[A]}{r_A} \cdot \frac{1}{[^{14}N^{14}N^{16}O]}$$

where δa_{eff} is the apparent delta value including the baseline effect; δa is the true delta value; $[^{15}N^{14}N^{16}O]$ refers to the amount fraction for the isotopocule $^{15}N^{14}N^{16}O$ (used here as an example) derived from its integrated peak area; $[^{14}N^{14}N^{16}O]$ refers to the amount fraction of the isotopocule $^{14}N^{14}N^{16}O$; r_A is the isotopocule amount fraction in the standard gas; and the offset caused by base-line structure is expressed as amount fraction [A]. Transformation provides $\frac{[A]}{r_A}$, which is a constant that scales linearly with the variable $\frac{1}{[^{14}N^{14}N^{16}O]}$.

Accordingly, we observed an inverse concentration dependence in all spectrometers, as shown in Fig. 5. In contrast, as outlined by Griffith (2018), Approach B removes this concentration dependence, removing the need for correction. Although this could potentially simplify the workflow procedure, we did not test nor compare approaches for the reasons given above.

We have therefore made the following changes to the manuscript:

P5 L18: "(3) if apparent delta values retrieved from a spectrometer are calculated from raw uncalibrated isotopocule mole fractions, referred to here as a δ-calibration approach, an inverse concentration dependence may be introduced. This can arise if the analyzer measurements of isotopocule mole fractions are linear, yet the relationship between measured and true mole fractions have a non-zero intercept (e.g. Griffith et al., 2012; Griffith, 2018), such as due to baseline structures (e.g. interfering fringes; Tuzson et al. 2008);"

We have omitted the following because it is discussed in the Discussion on P60:

P33 L16: "[…] analyzers tested~~, which is characteristic of optical analyzers calibrated using a δ-calibration scheme (Griffith et al., 2012; Griffith, 2018).~~ However, examination of the residuals from the linear regression revealed varying degrees of residual curvature, highlighting that further non-linear terms would be required to adequately describe, and correct for, this mole fraction dependence ~~(see Griffith et al., 2012)~~."

P60 L14: "The experiments performed in this study were undertaken using a standardized protocol. Calibration was performed on isotope δ values derived from raw uncalibrated isotopocule amount fractions, thus requiring [N_2O] dependence corrections. Alternative approaches aimed at calibrating isotopocule amount fractions prior to deriving δ values were not included in our study, but have the potential to remove the need for this correction (e.g. Wen et al., 2013; Flores et al., 2017; Griffith, 2018) if appropriate reference materials become available."

P66 L16: "[…] (if calibration relies on raw δ values derived from uncalibrated isotopocule amount fractions; i.e. a δ-calibration approach)."

We have added the following reference:
Tuzson, B., Mohn, J., Zeeman, M.J., Werner, R.A., Eugster, W., Zahniser, M.S., Nelson, D.D., McManus, J.B., and Emmenegger, L.: High precision and continuous field measurements of $\delta13C$ and $\delta18O$ in carbon dioxide with a cryogen-free QCLAS, Appl. Phys. B, 92, 451, doi:10.1007/s00340-008-3085-4, 2008.

Referee comment 5 - Page 10 Line 14: What does cw mean?

Authors' response: The term "cw" stands for continuous wave. This was first abbreviated on P9 L16.

Referee comment 6 - Page 11 Line 10: This is a weird place to stick this sentence. Unclear if this is describing one of the studies mentioned in the previous sentence.

Authors' response: We agree that this sentence may be ambiguous in whether it is referring to Yamamoto et al. (2014) or not. Our intention was to highlight the data treatment required by Yamamoto et al. (2014) in order to obtain the precision levels achieved with their QCLAS system. These included correcting for mole fraction dependence and drift. These authors also highlighted the necessity to carefully control the operating temperature of their instrument. We have subsequently made the following changes to the manuscript:

P11 L10:"[…] with a closed chamber system. To achieve the precision and accuracy levels reported in their study, Yamamoto et al. (2014) corrected their measurements for mixing ratio dependence and minimized instrumental drift by measuring N_2 gas every 1 hr for background-correction. These authors also showed that careful temperature control of their instrument in an air-conditioned cabinet was necessary for achieving optimal results."

Referee comment 7 - Page 15 Line 1: This would be easier to digest in a table.

Authors' response: We agree that this would be much better suited to a table. Again, because of the length of our report, we have opted to include the following table and accompanying text as Supplementary Material 2. Changes are as follows:

P14 L25: "The isotopic composition of high [N_2O] isotope reference gases in synthetic air (S1-a_{90ppm}, S2-a_{90ppm}) was analyzed in relation to N_2O isotope standards (Cal1 – Cal3) in an identical matrix gas (matrix a) using laser spectroscopy (CW-QC-TILDAS-200; ARI, Billerica, USA). The composition of Cal1 – Cal3 are outlined in Supplementary Material 2."

Supplementary Material 2:
"Supplementary Material 2: Analysis of high [N_2O] isotope reference gases, ambient reference gasses, PA1 and PA2

As detailed in Sect. 2.2.2, the isotopic composition of high [N_2O] isotope reference gases in synthetic air (S1-a_{90ppm}, S2-a_{90ppm}) was analyzed in relation to N_2O isotope standards (Cal1, 2 and 3) in the same gas matrix (matrix a) using laser spectroscopy (CW-QC-TILDAS-200; ARI, Billerica, USA). Ambient mole fraction N_2O isotope reference gases (S1-c_{330ppb}, S2-c_{330ppb}) and PA1 and PA2 were analyzed by TREX-QCLAS (Sect. 2.1.4) using N_2O isotope standards (Cal1 to 5) shown in Table S2-1. Cal1 – Cal5 have been previously measured by Sakae Toyoda at Tokyo Institute of Technology."

Table S2-1. N_2O isotope standards (Cal1 – Cal5) used for the analysis of reference gases (S1, S2) and pressurized air (PA1, PA2). The standards (Cal1 – Cal5) used for analysis of the respective gases are indicated by a tick (✓)

N_2O isotope standard used for calibration	$\delta^{15}N^\alpha$ vs AIR-N_2 [‰]	$\delta^{15}N^\beta$ vs AIR-N_2 [‰]	$\delta^{18}O$ vs VSMOW [‰]	S1-a_{90ppm}	S2-a_{90ppm}	S1-c_{330ppb}	S2-c_{330ppb}	PA1	PA2
Cal1 in matrix a	2.06±0.05	1.98±0.20	36.12±0.32	✓		✓			
Cal2 in matrix a	-48.59±0.25	-46.11±0.43	27.37±0.11	✓	✓	✓	✓		
Cal3 in matrix a	25.73±0.24	25.44±0.36	35.86±0.22		✓		✓		
Cal4 in matrix a	16.29±0.07	-2.59±0.06	39.37±0.04					✓	✓
Cal5 in matrix a	-51.09±0.07	-48.12±0.04	30.81±0.03					✓	✓

Referee comment 8 - Page 15 Line 15: Some more context about why this was done would help orient the reader.

Authors' response: Due to differences in the gas matrix, S1-b_{90ppm}, S1-c_{90ppm} and S2-c_{90ppm} cannot be analysed directly by QCLAS, but only after dilution to ambient mixing ratios by TREX-QCLAS. To avoid higher uncertainty levels, the delta values of S1-a_{90ppm} and S2-a_{90ppm} were assigned to S1-b_{90ppm}, S1-c_{90ppm} and S2-c_{90ppm} since all 90 ppm mixtures were generated from the same source of pure N_2O diluted with the different gas matrices a, b and c. We would therefore not expect any deviation in delta values during this dilution process. The absence of significant deviations was assured by analysis of all reference gases as described in the manuscript. To help the reader to understand this issue, a short sub-sentence was added to Page 15 Line 15:

P15 L15:"[...] acquired for S1-a_{90ppm} and S2-a_{90ppm} were assigned, since all S1 and S2 reference gases (irrespective of gas matrix) were generated from the same source of pure N_2O gas.

Direct analysis of S1-b$_{90ppm}$, S1-c$_{90ppm}$ and S2-c$_{90ppm}$ by QCLAS was not feasible as no N$_2$O isotope standards in matrix b and c were available. The absence of significant difference […]"

Referee comment 9 - Page 16 Line 6: This would be easier to digest in a table.

Authors' response: Please refer to our response for Comment 7. Changes to the main text and Supplementary Material 2 are as follows:

P16 L4: "Ambient mole fraction N$_2$O isotope reference gases (S1-c$_{330ppb}$, S2-c$_{330ppb}$) and PA1 and PA2 were analyzed by TREX-QCLAS (Sect. 2.1.4) using N$_2$O isotope standards (Cal1 – Cal5) as outlined in Supplementary Material 2."

Supplementary Material 2: Comment 7 addresses this.

*Note: While addressing these Referee comments, we also noticed that on P16 L6, reference gases S1-c$_{330ppb}$ and S2-c$_{330ppb}$ were incorrectly written as S1-c$_{330ppm}$ and S2-c$_{330ppm}$. We have rectified this mistake in the Supplementary Material.

Referee comment 10 - Page 20 Table 4: Why were three QCLAS mentioned earlier in the text if only one tested?

Authors' response: To clarify – we conducted all experiments on QCLAS I, but only conducted the Allan Variance experiments at ambient concentrations for QCLAS II and III, as stated in Table 4. The reason for doing this was so that we could test whether the drift experienced by QCLAS I (a 2012 model) was reproducible using newer models of QCLAS (2014 and 2016 models). In hindsight, all experiments should have been performed on either QCLAS II or III given that they achieved greater precision than QCLAS I. One advantage of our experimental setup was that the experiments were performed simultaneously for OA-ICOS I, CRDS I, CRDS II and QCLAS I, and thus all these instruments measured the same gas mixtures allowing for direct comparison of results. The testing for reproducibility of drift in the QCLAS systems was conducted on QCLAS II and III after the initial experimental period had finished and instruments had been returned to their respective labs. Thus, we could not re-run our experiments.

We acknowledge that by mentioning QCLAS II and III in the main text, and then not showing any results for the instruments, that this may cause confusion. Therefore, we agree that clarification is warranted. We have therefore added the following sentences to the updated manuscript:

Starting P10 L9: "Three QCLAS instruments (ARI, USA; CW-QC-TILDAS-SC-D) were used in this study. One instrument (QCLAS I), purchased in 2013, was provided by Karlsruhe Institute of Technology, Germany and two instruments, purchased in 2014 (QCLAS II) and 2016 (QCLAS III), were supplied by ETH Zürich, Switzerland (Table 1). QCLAS I was used in all experiments presented in this study, while QCLAS II and III were only used to assess the reproducibility of drift reported in Sect. 3.1."

Referee comment 11 - Page 21 Line 16: How quickly did the temperature change?

Authors' response: We thank the Referee for making this comment, as it allowed us to review the data more closely and identify an error in P21 L 15: <u>the laboratory temperature was turned off for 10hrs, not 30hrs as stated.</u>

The initial rise in temperature of the laboratory from 21℃ to 30℃ occurred over a 10 hr period while the air-conditioning was turned off at ~22:00 on 7/07/2018. This equates to an increase of roughly 0.9℃ per hour. Detectable increases in the laboratory temperature occurred within 15 minutes of turning off the air conditioning due to the simultaneous operation of over 6 laser spectrometers and auxiliary devices in the laboratory releasing significant amounts of heat to the room. Once the air conditioning in the laboratory was turned back on at ~08:00 on 8/07/2018, the temperature returned to 21℃ over a period of 16 hrs, equating to a decrease of roughly 0.6℃ per hour. Unfortunately, due to unforeseeable delays in operating the instruments, we were only able to start the 24 hr analyser measurement period shortly before 00:00 on 8/07/2018 as shown in Fig. 4. Thus, we only captured the last stages of the rising limb of the temperature change in the laboratory, which should be clarified to the reader.

In light of this, we have made the following changes to the updated manuscript:

P21 L15: "[…] conditioning of the laboratory was turned off for ==10 h. This== led to a rise in temperature from 21℃ to 30==℃, equating to an increase in temperature of approximately 0.9℃ per hour. The increase in laboratory room temperature was detectable shortly after the air conditioning was turned off due to considerable heat being released from several other instruments located in the laboratory.== Thereafter, the air conditioning was restarted and the laboratory temperature returned to 21℃ ==over the course of 16 h, equating to a decrease of roughly 0.6℃ per hour, with most pronounced effects observable shortly after restart of air conditioning when temperature changes were highest.=="

Fig. 4. Caption: "[…] ==Cell temperatures for each instrument are also plotted for comparison. The analyzers began acquiring measurements at 00:00 on 8/07/2018, capturing the end of the rising limb of the laboratory temperature.=="

Referee comment 12 - Page 27 Line 7: Suggest starting a new paragraph here since the rest of this paragraph focuses on the QCLAS only. This will help make the information more digestible as well since this is otherwise a long paragraph.

Authors' response: We agree with this suggestion and will start a new paragraph here.

Referee comment 13 - Page 32 Fig. 4: Text too microscopic to read. should use landscape format.

Authors' response: Please refer to Referee #2 Comment 11.

Referee comment 14 - Page 34 Fig. 5: The text in the figure is too microscopic to read.

Authors' response: We agree. Please refer to Referee #2 Comment 11.

Referee comment 15 - Page 36 Fig. 6: Should use landscape format to show this figure because text too microscopic.

Authors' response: Please refer to Referee #2 Comment 11.

Referee comment 16 - Page 42 Fig. 8: Cannot read the microscopic text. Use landscape format.

Authors' response: Please refer to Referee #2 Comment 11.

Referee comment 17 - Page 43 Fig. 9: Cannot read the microscopic text. Use landscape format. This same comment applies for the following figures as well.

Authors' response: Please refer to Referee #2 Comment 11.

Referee comment 18 - Page 57 Line 3: This is a really important result to highlight.

Authors' response: We agree that this is an important result to highlight, and, as such, had re-emphasised this in the Discussion (Sect. 4.4) on P65 L16: "Our results show that large uncertainties exist for N_2O source apportionment using Keeling analysis performed at near-ambient N_2O mole fractions.". In keeping with all Referee's comments to limit the size of the manuscript, we wish to refrain from adding any further text highlighting this point.

Referee comment 19 - Page 60 Line 23: On the order of? It would be helpful to give some numbers here to remind the readers of the order of magnitude.

Authors' response: While we agree with the Referee's comment, we would prefer not to go into excessive detail regarding the magnitude of numbers here, because there are many numbers that could be quoted (5 analyzers were tested at 5 different O_2 compositions, and at 3 different N_2O concentrations). Thus, we would prefer to leave this as a general statement regarding the magnitude of the effect, as follows:

P60 L24: "[…] matrix. Although the magnitude of this effect ultimately varied across the analysers and was dependent on N_2O mixing ratios, the effect of a change in O_2 composition of 20.5 % was typically on the order of 10 to 30 ‰ for δ values."

Referee comment 20 - Page 63 Line 16: But this depends on the absorbance cell size. Supercells will require more flushing. And also depends on the pressures operated at.

Authors' response: That is correct. The volumes reported do reflect these different operating pressures, as well as the different flows, as mentioned in the text starting from P63 L14. To clarify this, we re-wrote parts of this paragraph:

*Please note that the following includes corrections implemented as part of our Reply to RC3 Comment 1.

P63 L11: "Researchers should also consider the sample gas volume required for a given measurement application using a specific laser spectrometer. In our experience, ensuring that five laser cavity cell volumes have been flushed prior to measurement is *best practice* to negate any memory effects when these instruments are operated using continuous flow-through configurations (as opposed to discrete sample measurements in a closed laser cavity). By following this procedure and using the operating parameters selected in this study (Table 1), the sample gas volume required for a single 300 s measurement is approximately 80 mL for CRDS II, 150 mL for CRDS I, 600 mL for OA-ICOS I and 1200 mL for QCLAS I. ~~The different sample volumes required for CRDS I and CRDS II is due to the different selected flow rates.~~ By comparison, TREX-QCLAS I requires approximately 5 L of sample gas to allow for N_2O preconcentration. These sample gas volumes represent typical numbers for atmospheric applications; however, instrument parameter settings such as flow rate and cell pressure, which ultimately change the required sample volume, can be optimized depending on the measurement application. This is particularly the case for QCLAS instruments, which can be operated with different user-adjustable settings. For applications requiring discrete sample analysis (e.g. the headspace analysis of $\delta^{15}N$ and $\delta^{18}O$ in N_2O derived from dissolved NO_3^-), high N_2O concentration gas samples with lower volumes can be introduced to these instruments using injection ports and dilution gases (e.g. Soto et al., 2015; Wassenaar et al., 2018); however we did not test these capabilities in our study. ~~Thus, users should carefully consider the available volume of the sample gas, although the possibility exists to dilute high concentration samples to increase gas volume. Researchers should also ensure that gas samples contain N_2O within the operational ranges of the different laser spectrometers (Table 1).~~"

Referee comment 21 - Page 64 Line 5: differ from

Authors' response: This sentence has been deleted and replaced with Fig. 15.

Referee comment 22 - Page 64 Line 8: But CH₄ is issue for only ICOS and CRDS?

Authors' response: Correct. The workflow seeks to cover all possible sources of measurement error tested in our study. CH_4 co-measurement is only relevant if the user is using a spectrometer employing a spectral range where N_2O isotopocule lines overlap with those of CH_4. This also applies for other substances. To clarify this, a general statement was added at the beginning of Section 4.3 P63 L25. Please note that we have included a new Fig. 15 to depict this workflow (see RC2 Comment 11):

P63 L23: "In-line with our results, we propose a step-by-step workflow that can be followed by researchers to acquire N_2O isotopocule measurements (Fig. 15). This workflow seeks to cover all sources of potential error tested in our study. Not all steps will be applicable because interference effects vary across analyzers. For QCLAS analyzers, which offer high versatility, interference effects can also be approached by multi-line analysis, inclusion of interfering spectral lines or adaption of pressure broadening parameters in the spectral fitting algorithm.

For specific applications, such as incubation experiments with He, accessory injection units and setups using TREX, related actions have to be taken. While we tested several mono-variant and some bi-variant (e.g. changes in [CH$_4$] and [N$_2$O]) systems in our study, more complex systems (e.g. [CH$_4$] and [O$_2$], or even [CH$_4$], [O$_2$] and [N$_2$O]) were not tested, and deviations from additive behavior are to be expected. Depending on the desired precision, users may vary the measurement and averaging times, and calibration frequency.

Referee comment 23 - Page 66 Line 26: Perhaps this point can be moved elsewhere because the placement here undercuts the final message of the paper.

Authors' response: We agree and will move this point to P65 L12. We shall also rephrase it so that it does not undercut our findings so much:

P65 L12: "[…] performance, as shown in Supplementary Material 3. It is worth noting that, although the results of our study are representative of the performance of the instruments tested, the magnitude of reported effects and performances are likely to vary within the same analyser models."

The original paragraph has been deleted in line with Comment 24 below:
"~~It is important to note that the results of this study should be interpreted for these analyzer models only, and results are likely to vary slightly across the same make. Newer analyzers and models may yield better performance than reported here. As illustrated by the noticeable improvement between the CRDS I (2015 model) and CRDS II (2018 model), it is foreseeable that the performance of N2O isotope laser spectrometers will continue to improve into the future. Future studies should focus on quantifying the error contributions to N2O isotopocule analysis using laser spectroscopy.~~"

Referee comment 24 - Page 67 Line 3: This last sentence doesn't seem to fit the rest of this paragraph and is a weak ending. Suggest just deleting this last sentence.

Authors' response: We have deleted this sentence.

*Updated Figure numbering:
1 – Isotopocule line positions and interferants
2 – Generalized experimental setup (updated)
3 – Allan deviation plots (updated)
4 – Temperature dependence plots (updated)
5 – Mole fraction dependence plots (updated)
6 – O$_2$ effects (updated)
7 – CO$_2$ effects (updated)
8 – CH$_4$ effects (updated)
9 – OA-ICOS I measured vs expected (updated)
10 – CRDS I measured vs expected (updated)
11 – CRDS II measured vs expected (updated)
12 – QCLAS I measured vs expected (updated)
13 – TREX-QCLAS I measured vs expected (updated)

14 – Source intercepts (updated)
15 – Measurement workflow (new)

*Updated Table numbering:
1 – Instrument overview
2 – Matrix gases and interference test gases
3 – Reference gas compositions
4 – Overview of experiments
5 – Gas mixtures introduced for gas matrix and trace gas experiments
6 – Allan deviation
7 – Long-term repeatability
8 – Results summary (new)

*Updated Supplementary Materials numbering:

1 – IRMS methodology
2 – Analysis of high [N_2O] isotope reference gases, ambient reference gasses, PA1 and PA2 (new)
3 – Experimental setups
4 – Complete datasets (new)
5 – Application of an automatic spectral correction method for QCLAS measurements
6 – Short-term repeatability
7 – Scaling of the signal-to-noise ratio
8 – Continuity of gas matrix and trace gas corrections at higher N_2O mole fractions
9 – Comparison with GC-IRMS
10 – Extrapolated source intercept values (new)
11 – Lower state energies of probed N_2O isotopocule lines (new)