

Reply to the manuscript review by Anonymous Referee #2

We thank Anonymous Referee #2 for their detailed review of our manuscript and for their constructive comments and suggestions. Below, the Referee's comments (in bold) are followed by our response (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 paper reports the results of a detailed intercomparison study on the performance of commercially available isotopic N₂O analyzers based on laser spectroscopic methods. Such analyzers allow for continuous measurement of absolute trace gas concentrations (here N₂O) and isotope ratios (here, $\delta^{15}\text{N}_{\text{alpha}}$, $\delta^{15}\text{N}_{\text{beta}}$, $\delta^{18}\text{O}$) under field conditions. Isotopic analysis of N₂O is challenging, but is of high interest for source and sink identification in the biogeochemical community.

The extensive study was very well planned and conducted and produced large amount of data. As a result, a very extensive paper has been compiled by the authors. The paper is clearly structured and well-written. However, in order to limit the length of the paper to a bearable level, I suggest to shorten the main part by moving part of the Figure content and some Tables into the Supplement.

The presented results underline the necessity to carefully check analyzer performance, even for such sophisticated instruments as the ones used in this study. Although absorption based techniques should be essentially calibration-free (as they are simply based on Beer-Lambert law), the measurement of isotope ratios is prone to even smallest inaccuracies of the analyzers. This becomes quite obvious in case of the presented large uncertainties in the Keeling type experiments for source identification.

The paper ends with a clear conclusion and recommendation for the use of laser-based isotopic N₂O analyzers in practical applications. This is very useful and helps to design reasonable calibration strategies for future experiments. The paper is very technical, and not too much effort was spent to elaborate physical/spectroscopic explanations for the worked-out gas matrix effects and cross sensitivity issues. This may be well considered outside the scope of this paper, however, at least some brief statements about possible explanations are desirable.

However, overall this very good-excellent paper is a pleasure to read and for sure it is very well suited for publication in AMT, subject to changes (sorry for the long list – but it is a long paper. . .) as outlined in the following:

Specific Comments:

Referee Comment 1 – Page 4 Line 16: There is no principle reason why laser spectroscopy should be limited to the MIR spectral range. Of course, isotope specific measurements can also be performed in the NIR, albeit the used instruments are based on strong rovibrational transitions of the asymmetric stretch vibrational band of N₂O. Detection in the NIR range, due to the fact that overtone or combination bands with lower line strengths must be probed, will be less sensitive, however, due to lower spectral congestion, interference issues may be less dramatic.

Authors' response: We thank the Referee for their comment. Indeed, isotope measurements can be performed in other spectral ranges, and thus is not limited to the MIR. In our study, we focussed on commercially available analyzers that all operate in the MIR to achieve highest sensitivity. There are research grade instruments operating in the NIR, as stated by the reviewer. Therefore, we will re-word this sentence to highlight that other spectral regions may be used:

P4 L16: "N₂O isotopocules can be analyzed by isotope-ratio mass spectrometry (IRMS) and laser spectroscopic techniques, with currently available commercial spectrometers operating in the mid-infrared (MIR) region to achieve highest sensitivities."

Referee Comment 2 – Page 5 Line 18: Whereas items (1), (2), and (4) seem to be clear to me, this is not the case for item (3). Is it possible to include a short explanation why changes in the total N₂O mole fraction also affect the determined delta values? Is this directly related to the "delta calibration approach" (what is this?)?

Authors' response: Please refer to our response to RC1 – Comment 4, where we address the delta calibration approach and N₂O mole fraction dependence.

Referee Comment 3 – Page 5 Line 21: While pressure broadening changes the absorption line shape of a specific rovibrational transition, the integral absorption should not be affected. As such, I would expect that instruments like the Picarro-CRDS that presumably measures peak absorption (at least this is the case for the corresponding isotopic CO₂ instrument) are more prone to gas matrix effects than instruments that are based on integral absorption (I think this is the case for the Los Gatos-OA-ICOS, for example). This should be explained at some point in the manuscript.

Authors' response: The authors agree that the specific detection scheme used by the analysers (CRDS, OA-ICOS, QCLAS), as well as the data acquisition and treatment, affect the analysers' response to changes in matrix gas composition (e.g. O₂). The importance of the data acquisition / treatment versus detection scheme can be seen by the different responses of CRDS I and II on changes in O₂ (Fig. 6). Because details on data acquisition / treatment are not accessible by users for all instruments, we prefer to provide readers with: 1) the observational data; 2) an explanation of the underlying fundamental causes; and 3) methods to correct these effects. For research grade instruments, with open-source data acquisition / treatment, it would be feasible to implement more sophisticated correction schemes, such as adapting pressure-broadening coefficients based on O₂ analysis. This, however, is beyond the scope of our study. To inform the reader that data acquisition / treatment can be advanced

for open-source analysers, particularly the QCLAS systems tested, we added some statements to the text:

P10 L24: "QCLAS instruments offer great liberty to the user as the system can also be operated with different parameter settings, such as the selection of spectral lines for quantification, wavenumber calibration, sample flow rate and pressure. Thereby different applications can be realized, from high flow eddy covariance studies or high mole fraction process studies to high-precision measurements coupled to a customized inlet system. In addition, spectral interferences and gas matrix effects can be taken into consideration by multi-line analysis, inclusion of the respective spectroscopic parameters in the spectral evaluation or adjustment of the pressure broadening coefficients. The spectrometers used in this study (QCLAS I – III) were tested under standard settings but were not optimized for the respective experiments. QCLAS I was operated as a single laser instrument using laser one, to optimize spectral resolution of the frequency sweeps".

In addition, the following section was added to the discussions (in addition to corrections implemented in Referee #1 Comment 22):

P P63 L23: "In-line with our results, we propose a step-by-step workflow that can be followed by researchers to acquire N₂O isotopocule measurements. 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 (e.g changes in [CH₄] at constant [N₂O]) and some bi-variant (e.g. changes in [CH₄] and [N₂O]) systems in our study, more complex systems (e.g. changes in [CH₄], [O₂] and [N₂O]) 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 4 – Table 1: From a spectroscopic point of view, it would be interesting to include the rotational quantum number and term energy (i.e. the energy of the lower state) of the probed transitions. On the one hand, pressure broadening and with it the gas matrix effect is known to sensitively depend on the rotational excitation of the probed molecules. On the other hand, the term energy largely determines the population of the lower state and with it is an important quantity to rationalize a potential temperature sensitivity of the instruments. According values can be taken from the HITRAN database.

Authors' response: We agree that rotational quantum numbers (J) and lower state energies (E") of probed transitions provide information on pressure broadening (gas matrix effects) and temperature sensitivity. Therefore, we will provide the respective numbers in a new Supplementary Material 11 and add the following statements and restructuring to the manuscript:

P60 Line 4: “Our results highlight that the precision at which laser-based analyzers acquire N₂O isotopocule measurements is a function of N₂O mole fraction, the selected measuring and averaging times and calibration frequency according to measurement stability. The degree of accuracy obtained using different laser spectrometers is ultimately a function of the robustness of corrections aimed at removing matrix and trace gas effects, and the selected calibration procedure aimed at standardizing the data to international scales.

New paragraph

All spectrometers tested displayed temperature effects on isotope measurements, which can be attributed to differences in the lower state energies of the probed N₂O isotopocule lines (Supplementary Material 11) (e.g. Wächter et al. 2008). The temperature sensitivities of all analyzers tested necessitates that, especially when deployed in the field, they be operated under temperature-controlled conditions (such as in maintained field stations), and/or their dependence adequately characterized and corrected.”

P60 Line 24: “[...] O₂ composition of the gas matrix. The underlying reason for this effect is differences in N₂ versus O₂ (and Ar) broadening parameters of the probed N₂O isotopocule lines. In short, the N₂, O₂ (and Ar) broadening parameters depend on rotational quantum numbers of the respective N₂O lines (Henry et al., 1985; Supplementary Material 11). Thus, differences in the rotational quantum numbers for a pair of isotopocules (e.g. ¹⁴N¹⁵N¹⁶O / ¹⁴N¹⁴N¹⁶O) relate to a difference in their N₂, O₂ and Ar broadening parameters. Consequently, differences in the O₂ or Ar content of the sample gas matrix and that of the reference gas affect measured isotope ratios and lead to changes in apparent delta values. Nonetheless, the magnitude of effects reported for the CRDS analyzers in this study varied [...]”

The following reference will be added to the updated manuscript:

Henry, A., Margottin-Maclou, M., and Lacombe, N.: N₂- and O₂-broadening parameters in the v₃ band of ¹⁴N₂¹⁶O, J. Mol. Spectrosc., 111, 291–300, doi:10.1016/0022-2852(85)90006-2, 1985.

Supplementary Material 11:

“Supplementary Material 11: Lower state energies of probed N₂O isotopocule lines

The lower state energies of probed N₂O isotopocule lines are provided in Table S11-1. Differences in the rotational quantum numbers for a pair of isotopocules (such as ¹⁴N¹⁵N¹⁶O / ¹⁴N¹⁴N¹⁶O) lead to changes in N₂, O₂ and Ar broadening parameters (Henry et al., 1985). If the sample gas matrix is different to that of the reference gas, deviations in the apparent delta values will arise.

Table S11-1. Wavenumber positions, line strength, branch / rotational quantum numbers and lower state energies of selected N₂O isotopocule lines applied for different laser spectrometers as retrieved from HITRAN2016 database.

	Line positions (cm ⁻¹)	Line strength (cm ⁻¹ /(molecule cm ⁻²))	Branch / rotational quantum number	Lower-state energy (cm ⁻¹)
OA-ICOS I				
¹⁴ N ¹⁴ N ¹⁶ O	2192.401	4.92E-20	P / 19	748.33
	2192.436	4.92E-20	P / 19	748.03
	2192.483	3.38E-19	P / 33	469.91
¹⁴ N ¹⁵ N ¹⁶ O	2192.309	3.31E-21	R / 18	143.27
¹⁵ N ¹⁴ N ¹⁶ O	2192.330	2.97E-21	P / 11	53.44
¹⁴ N ¹⁴ N ¹⁸ O	2192.133	1.11E-21	P / 28	321.10
CRDS I & II				
¹⁴ N ¹⁴ N ¹⁶ O	2196.21	5.16E-20	P / 15	689.55
	2196.24	5.16E-20	P / 15	689.36
¹⁴ N ¹⁵ N ¹⁶ O	2195.762	2.73E-21	R / 23	231.22
¹⁵ N ¹⁴ N ¹⁶ O	2195.796	2.20E-21	P / 7	22.67
¹⁴ N ¹⁴ N ¹⁸ O	2195.951	1.43E-21	P / 24	237.29
QCLAS I, II & III				
¹⁴ N ¹⁴ N ¹⁶ O	2188.045	2.60E-21	P / 9	1205.92
¹⁴ N ¹⁵ N ¹⁶ O	2187.943	3.29E-21	R / 12	65.36
¹⁵ N ¹⁴ N ¹⁶ O	2187.846	3.27E-21	P / 16	110.11
¹⁴ N ¹⁴ N ¹⁸ O	2203.281	1.79E-21	P / 16	107.59
TREX-QCLAS I				
¹⁴ N ¹⁴ N ¹⁶ O	2203.100	2.71E-21	R / 8	1198.37
	2203.114	1.44E-21	R / 8	1314.95
¹⁴ N ¹⁵ N ¹⁶ O	2203.359	9.80E-22	R / 35	527.64
¹⁵ N ¹⁴ N ¹⁶ O	2203.205	7.02E-22	R / 1	0.81
¹⁴ N ¹⁴ N ¹⁸ O	2203.281	1.79E-21	P / 16	107.59

Referee Comment 5 – Table 6 and Figure 3: How often these experiments have been repeated? How reproducible was the drift behavior of the QCLAS analyzers?

Authors' response: During reconnaissance testing in the ~two months prior to the final measurement campaign, we performed the Allan deviation testing on three separate occasions. These experiments yielded similar results (for both Allan "minimums", and 300s and 600s averaging times) for all analyzers. As further confirmation of the drift behavior in QCLAS I, the QCLAS II and QCLAS III analyzers were tested for their Allan deviation after the measurement campaign. As shown in Fig. 3, the drift behavior, albeit to different magnitudes, was evident. Moreover, a QCLAS system (CW-QC-TILDAS-SC-S-N₂OISO; Aerodyne Research Inc.) used by Yamamoto et al. (2014) showed similar drift (their Figure 2).

During our communications with Aerodyne Inc. technicians, we were made aware that they had developed an automatic spectral correction method to correct for data that was influenced by changing baseline structure. For this reason, we included a brief description of their methodology (courtesy of Aerodyne Inc.), and an example of the same Allan deviation

data for QCLAS I which had been re-processed by Aerodyne technicians using their correction methodology (see Table 6). This correction technique significantly decreased the magnitude of drift experienced by QCLAS I.

Accordingly, we will make the following additions to the updated manuscript:

Fig. 3 Caption: “[...] The dashed lines represent a slope of -0.5 (log-log scale) and indicate the expected behavior for Gaussian white noise in each analyzer. The Allan deviations of all analyzers tested were reproducible on three separate occasions prior to the test results presented here.”

Referee Comment 6 – Figure 4: I wonder how the cell temperatures have been measured? In the middle of the cell? one or two pint measurements? Is anything known about possible T-gradients across the measurement cells? It seems that the experiment has only been conducted once. Do the authors believe that the measured trends in the signals are robust? Actually, for practical applications it would also have been interesting to perform an experiment at static (but different) temperatures.

Authors’ response: The authors agree with Referee #2 that gas temperature measurements are delicate, as sensor temperature may deviate from the actual gas temperature due to inaccuracies and wall effects. Also, the gas temperature might not be homogeneous, calling for multiple temperature sensors. Nonetheless, plotting the cell temperature as additional supporting parameter, allows us to rationalize the observed T effects on N₂O mixing ratios and delta values. The temperature experiment was only conducted once to test and demonstrate the detrimental effects of lab temperature changes on analyzer performance and call for a air-condition lab environment. The authors do not claim or encourage to correct data based on the observed experiments, as the magnitude might depend on cooling / heating rate ($\Delta T / \Delta t$), starting / end temperature etc. As such, we will remove the following statement from P60 L6 in the Discussion:

P60 L6: “[...] The temperature sensitivities of all analyzers tested necessitates that, especially when such instruments are deployed in the field, laser spectrometers in general be operated under temperature-controlled conditions (such as in maintained field stations), and/or their dependence adequately characterized and corrected.”

Referee Comment 7 – Section 3.2: Please give some more information about possible reasons for the observed temperature effects.

Authors’ response: The authors agree and added lower state energies for the probed N₂O isotopocule lines to the supplementary information and a statement to the discussion section (see our response to Comment 4, above).

Referee Comment 8 – Page 33 Line 20: Again, the reason for the N₂O mole fraction dependence is not fully clear to me without further explanation. I am sure that this is explained in some detail in the cited Griffith et al. papers, however, is it possible to roughly outline the main reason for this in 1-2 sentences?

Authors' response: The authors agree, please refer to our response to RC1 – Comment 4, where we address the delta calibration approach and N₂O mole fraction dependence.

Referee Comment 9 – Figure 6: Actually, I am surprised to see the strong effect of O₂ content for the integrating OA-ICOS experiment as well, in particular for the total N₂O data (see also my comment above). Do the authors have a physical/spectroscopic explanation for this effect?

Authors' response: We will here refer to the same line of reasoning as given in response to Comments 3 and 4 (above).

Referee Comment 10 – Page 35 Line 6: The authors state that minor gas matrix effects have been observed for Ar (in comparison with O₂). Well, as the Ar content has been changed by only 1% in comparison to 21% for O₂. Therefore, I think, this statement is not fully valid. Overall, the effect (on a mole fraction basis) is not very much different. May be the authors allude to the maximum effect expected for real-world measurement conditions. Although the depicted trends seem to be instrument-specific in some cases (e.g., the different slopes of the gas matrix effects for variable N₂O content, which cannot be explained by a simple pressure broadening effect), I would appreciate to elaborate a little bit more on physical/spectroscopic reasons that may (at least partly) explain some of the observations.

Authors' response: The authors agree that the statement with respect to the limited effect of Ar on [N₂O] and delta values refers to the anticipated maximum changes in [Ar] of 1 %; i.e. the difference between a ambient air sample with argon and a calibration gas mixed in N₂/O₂. We do not foresee situations where measurements of N₂O isotopes would coincide with a gas matrix consisting higher than 1 % argon. Details on the underlying physical/spectroscopic causes are given in our response to RC2 – Comment 3 and 4. In addition, we added the following statements to the manuscript:

P35 L7: "The range investigated was between approximately 0 % and 0.95 % Ar, as anticipated for an N₂O in synthetic air (no Ar) reference gas versus a whole air (with Ar) sample gas. The effects observed for 0.95 % change in [Ar] were significantly smaller than that observed for O₂, but might extend to a similar range for sample and reference gases with higher differences in [Ar]. The interference effects were found to be best described by second-order polynomial functions, though we expect that a linear fit would serve equally well if a larger change in [Ar] was investigated. Although most functions to describe the dependence on Ar across all instruments were statistically significant ($p < 0.05$), maximum effects did not transgress the repeatability (1σ) of the Anchor gas measurements."

P39 L24: "Although we could have tested for effects for [Ar] changes greater than 0.95%, we limited our experiments to [Ar] expected in tropospheric samples."

P61 L5: "Although the Ar effects characterized in this study were not large (a maximum ~1 % change in [Ar]), it is nonetheless recommended as a precautionary measure that researchers ensure, where possible, the standard calibration gas Ar composition is similar to that of the sample gas."

Referee Comment 11 – In most Figures, the complete datasets for N₂O, delta 15N_{alpha}, delta15N_{beta} and deltaN18O are given for all five instruments. Even though it is interesting to see all these results, keeping in mind the length of the paper, the authors may consider to somewhat lower the total number of subplots in each Figure by showing only selected trends. This would also allow one to somewhat increase the font size of the captions that are often hard to read anyway. Of course, the complete dataset should be included in the Supplement.

Authors' response: In line with both Referee #1 and #2, we have increased the text size and lowered the number of subplots in Figs. 3 – 14 so that the data may be viewed more easily. We also agree that the overall number of figures should be reduced, so we have transferred the original Figs. 7, 10 and 11 (Ar, CO, H₂O effects) to the new Supplementary Material 4. Thus, no data for Ar, CO and H₂O will be depicted in the main manuscript. We will refer the reader at the beginning of Sect. 3 (Results) to a new Supplementary Material 4 which provides the complete datasets:

P26 L17: **“3. Results**

Note: due to the large number of results acquired in this Section, only selected results are shown in Figs. 3 to 14. The complete datasets (including [N₂O], $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ acquired by all instruments tested) are provided in Supplementary Material 4.

3.1 Allan precision

[...]”

The following figures will be added to Supplementary Material 4:

“Supplementary Material 4: Complete Results datasets

Allan deviation plots (Sect. 3.1)

Fig. S4-1: *Original Fig. 3 with original figure caption

Temperature dependence plots (Sect. 3.2)

Fig. S4-2: *Original Fig. 4 with original figure caption

Mole fraction dependence plots (Sect. 3.4)

Fig. S4-3: *Original Fig. 5 with original figure caption

O₂ dependence plots (Sect. 3.5)

Fig. S4-4: *Original Fig. 6 with original figure caption

Ar dependence plots (Sect. 3.5)

Fig. S4-5: *Original Fig. 7 with original figure caption

CO₂ dependence plots (Sect. 3.6)

Fig. S4-6: *Original Fig. 8 with original figure caption

CH₄ dependence plots (Sect. 3.6)

Fig. S4-7: *Original Fig. 9 with original figure caption

CO dependence plots (Sect. 3.6)

Fig. S4-8: *Original Fig. 10 with original figure caption

H₂O dependence plots (Sect. 3.6)

Fig. S4-9: *Original Fig. 11 with original figure caption

Two end-member mixing correlation diagrams for measured vs expected (Sect. 3.7)

Figs. S4-10 to S4-14: *Original Figs. 12 to 16 with original figure captions

Two end-member mixing source intercept comparison plots (Sect. 3.7)

Fig. S4-15: *Original Fig. 17 with original figure caption”.

In Figs. 3, 5, 6, 7 and 8 in the updated manuscript, we compare the response of the analyzers across one consistent isotope (e.g. comparing all $\delta^{15}\text{N}^\alpha$ measurements for all instruments). In the updated Fig. 4, not all analyzers were clearly and uniformly affected across equivalent measurements – therefore, we show examples of measurements that were clearly temperature-dependent for each instrument ($\delta^{18}\text{O}$ for OA-ICOS I, $\delta^{15}\text{N}^\alpha$ for CRDS I, $[\text{N}_2\text{O}]$ for CRDS II, and $\delta^{15}\text{N}^\beta$ for QCLAS I). In Figs. 9 to 14, we compare the measurements of the analyzers for $\delta^{15}\text{N}^{\text{Bulk}}$ and SP as examples.

The following figures and captions were added to the manuscript as follows:

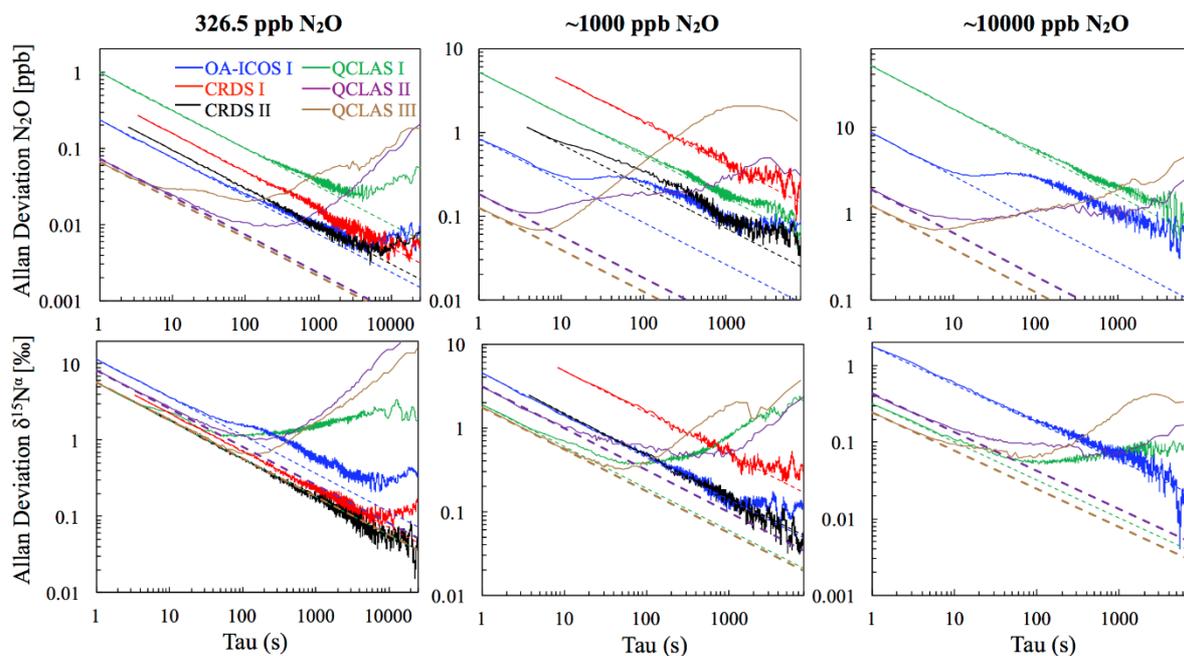


Fig. 3. Allan deviation (square root of Allan Variance) plots for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green), QCLAS II (purple) and QCLAS III (brown) at different N_2O mole fractions (326.5, 1000 and 10000 ppb). The dashed lines represent a slope of -0.5 (log-log scale) and indicate the expected behavior for Gaussian white noise in each analyzer. **The entire dataset is provided in Supplementary Material 4 (Fig. S4-1).**

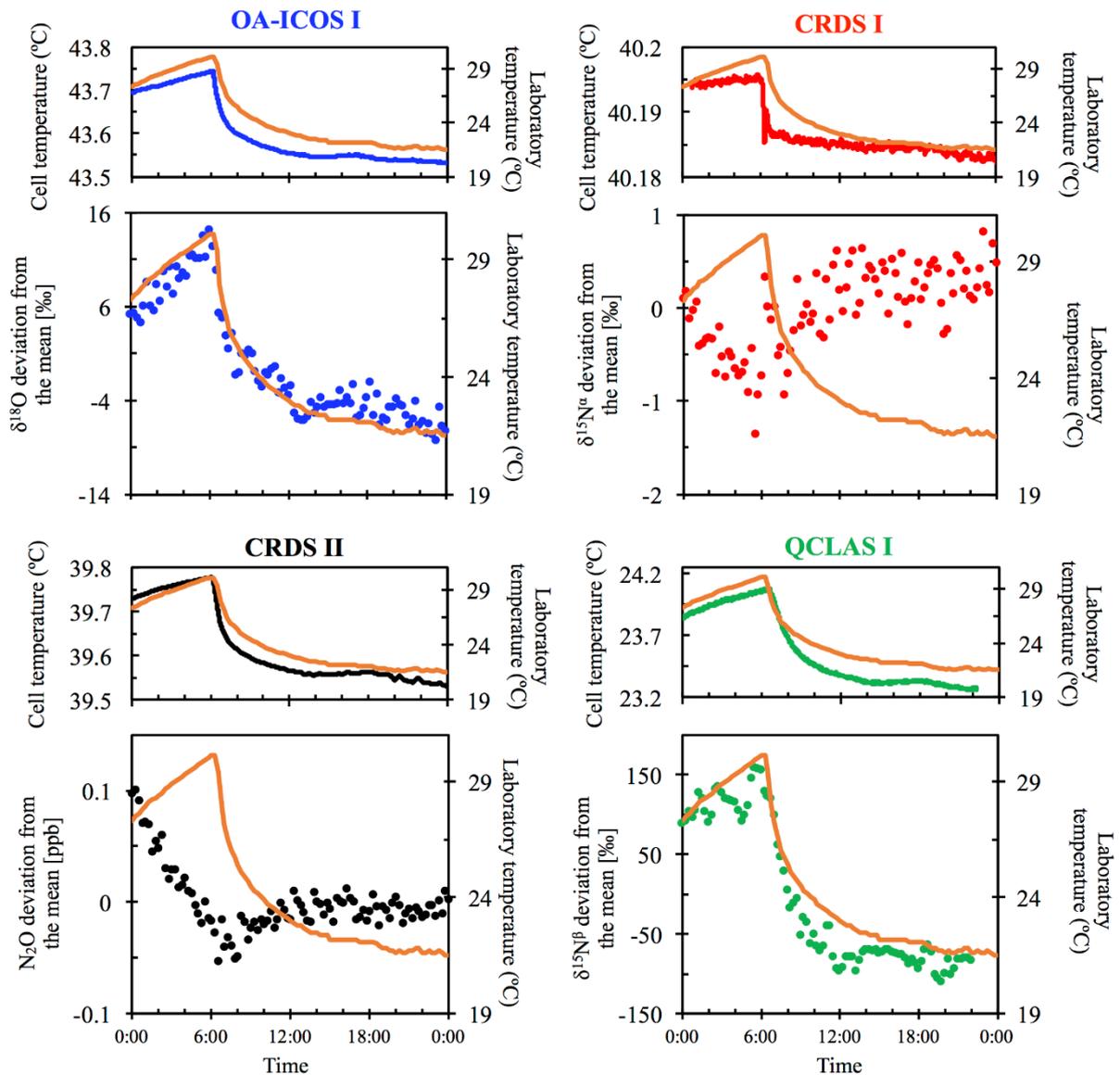


Fig. 4. Examples of the dependency of different measurements on laboratory temperature ($^{\circ}\text{C}$) for OA-ICOS I (blue), CRDS I (red), CRDS II (black) and QCLAS I (green). The complete dataset is provided in Supplementary Material 4 (Fig. S4-2). The laboratory temperature is indicated by a solid orange line and was allowed to vary over time. Cell temperatures for each instrument are also plotted for comparison. Results are plotted as the deviation from the mean, without any anchoring to reference gases.

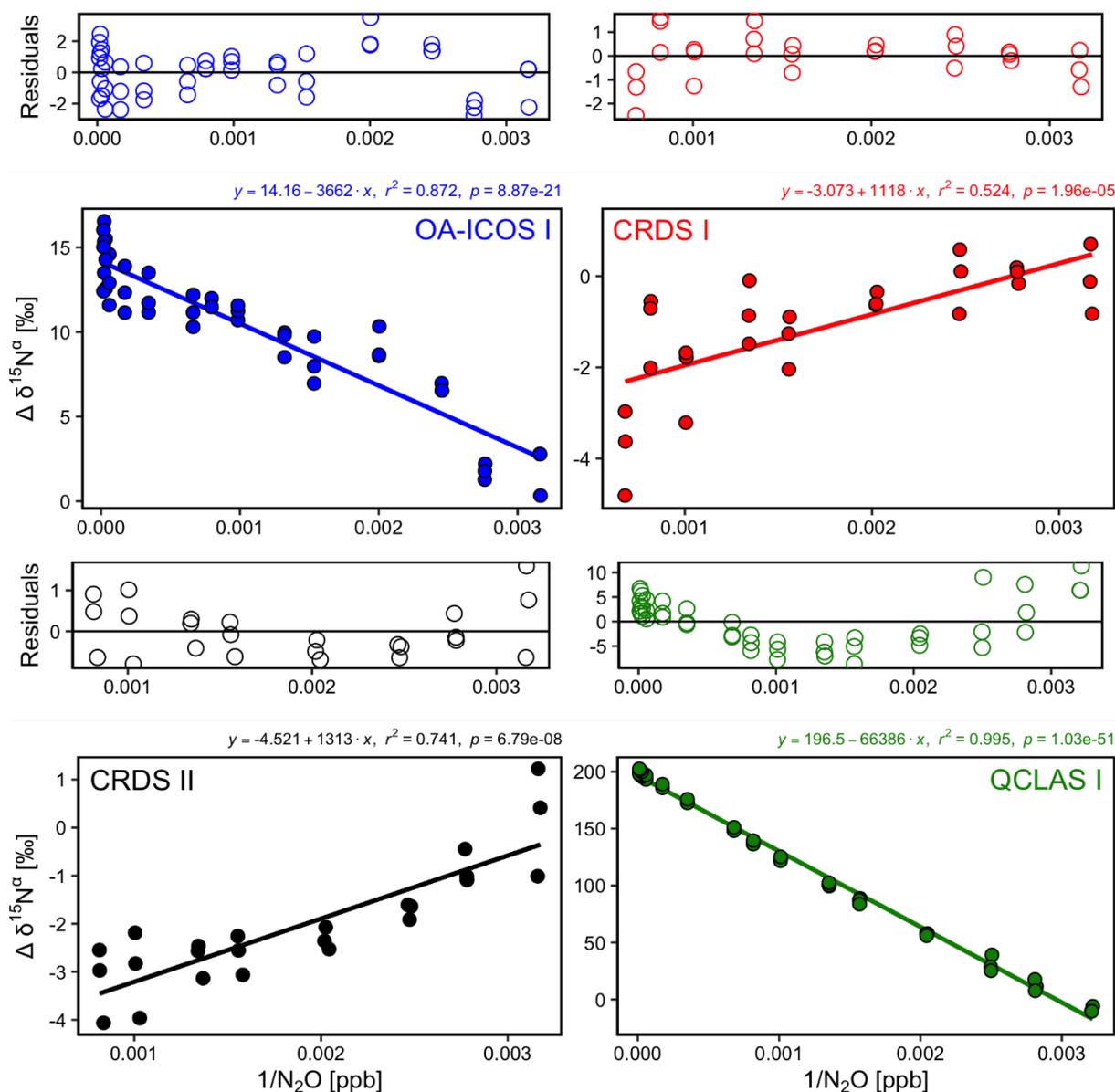


Fig. 5. Deviations of the measured $\delta^{15}\text{N}^{\alpha}$ values according to $1/[\text{N}_2\text{O}]$ for the OA-ICOS I (blue), CRDS I (red), CRDS II (black) and QCLAS I (green). Measurements span the manufacturer-specified operational ranges of the analyzers. The experiment was repeated on three separate days. A linear regression is indicated by the solid line, and a residual plot is provided above each plot. Individual linear equations, coefficients of determination (r^2) and p-values are indicated above each plot. **The entire dataset is provided in Supplementary Material 4 (Fig. S4-3).**

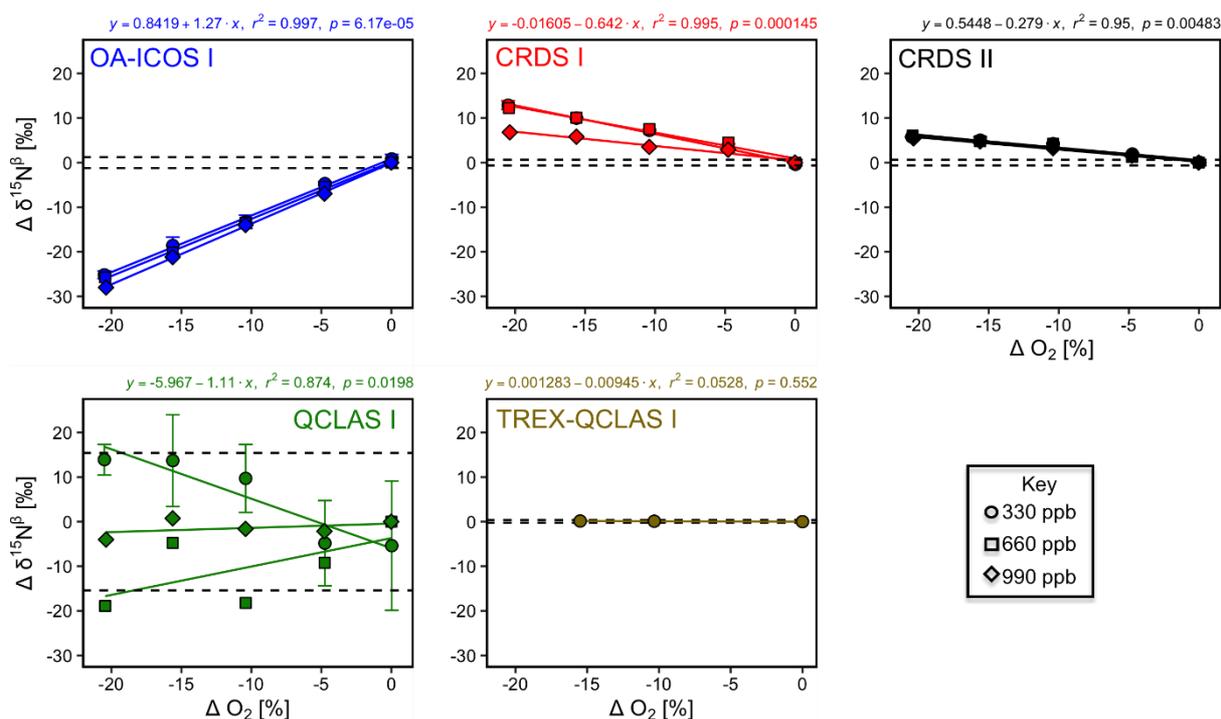


Fig. 6. Deviations of the measured $\delta^{15}\text{N}^\beta$ values according to ΔO_2 (%) at different N_2O mole fractions (330, 660 and 990 ppb) for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^\alpha$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-4). The standard deviation of the Anchor gas ($\pm 1\sigma$) is indicated by dashed lines. Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described using linear regression, which are indicated by a solid line. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot for the 330 ppb N_2O data only.

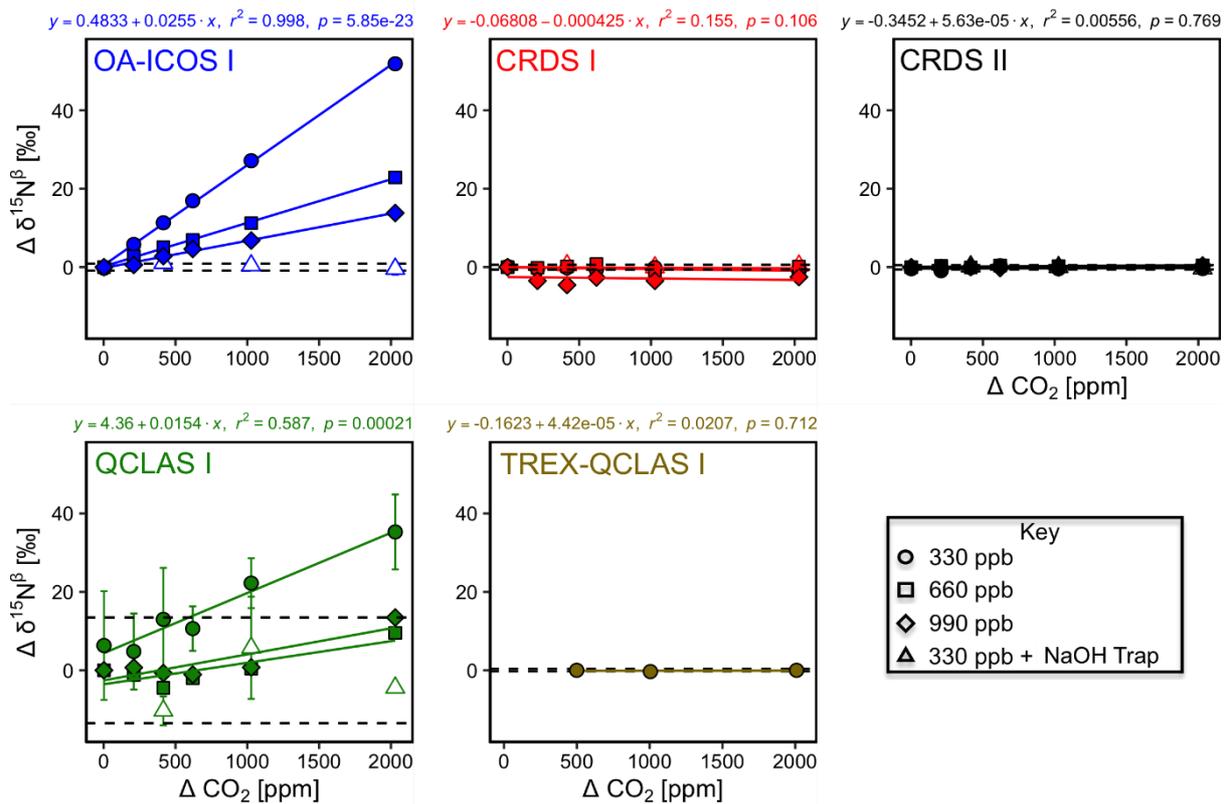


Fig. 7. Deviations of the measured $\delta^{15}\text{N}^\beta$ values according to ΔCO_2 (ppm) at different N_2O mole fractions (330, 660 and 990 ppb) for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^\alpha$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-6). The standard deviation of the Anchor gas ($\pm 1\sigma$) is indicated by dashed lines. Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described by linear fits, which are indicated by solid lines. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot for the 330 ppb N_2O data only.

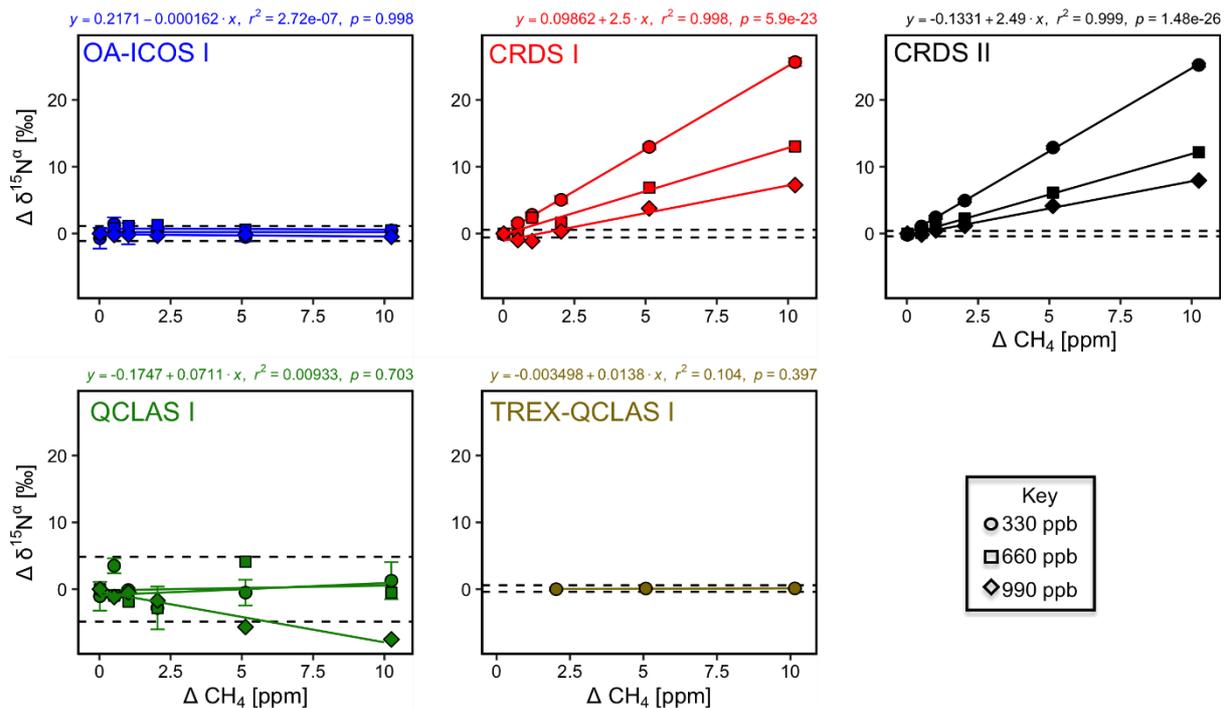


Fig. 8. Deviations of the measured $\delta^{15}\text{N}^{\alpha}$ values according to ΔCH_4 (ppm) at different N_2O mole fractions (330, 660 and 990 ppb) for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-7). Data points represent the mean and standard deviation (1σ) of triplicate measurements. Dependencies are best-described by linear fits, which are indicated by solid lines. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot for the 330 ppb N_2O data only.

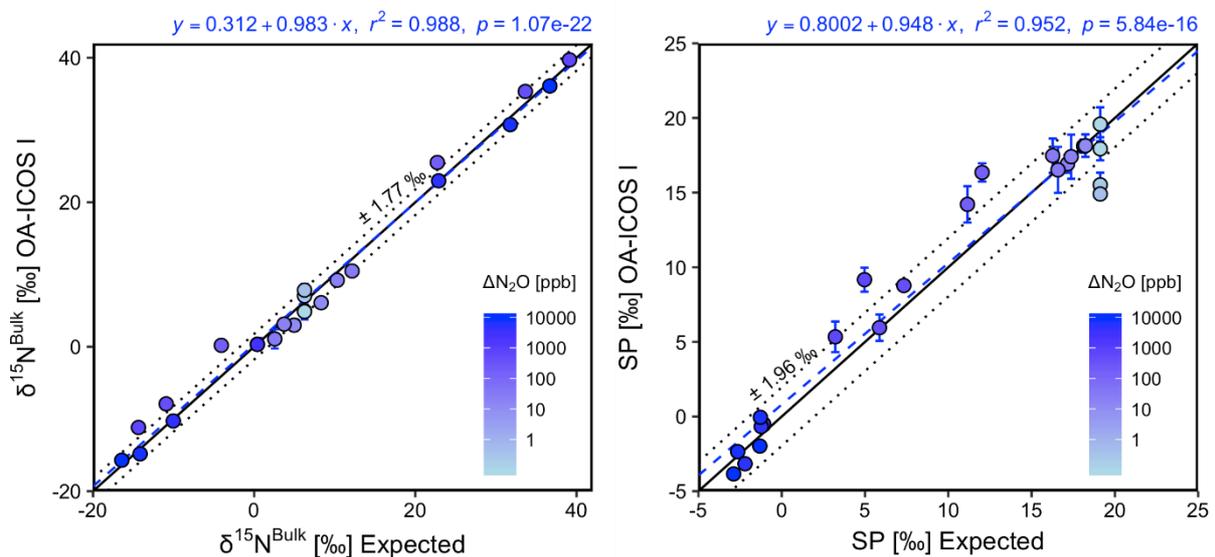


Fig. 9. Correlation diagrams for $\delta^{15}\text{N}^{\text{bulk}}$ and SP measurements at various $\Delta\text{N}_2\text{O}$ mole fractions analyzed by OA-ICOS I plotted against expected values. The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig S4-10). The solid black line denotes the 1:1 line, while the dotted line indicates $\pm 1\sigma$ of the residuals from the 1:1 line. The dashed blue line represents a linear fit to the data. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements.

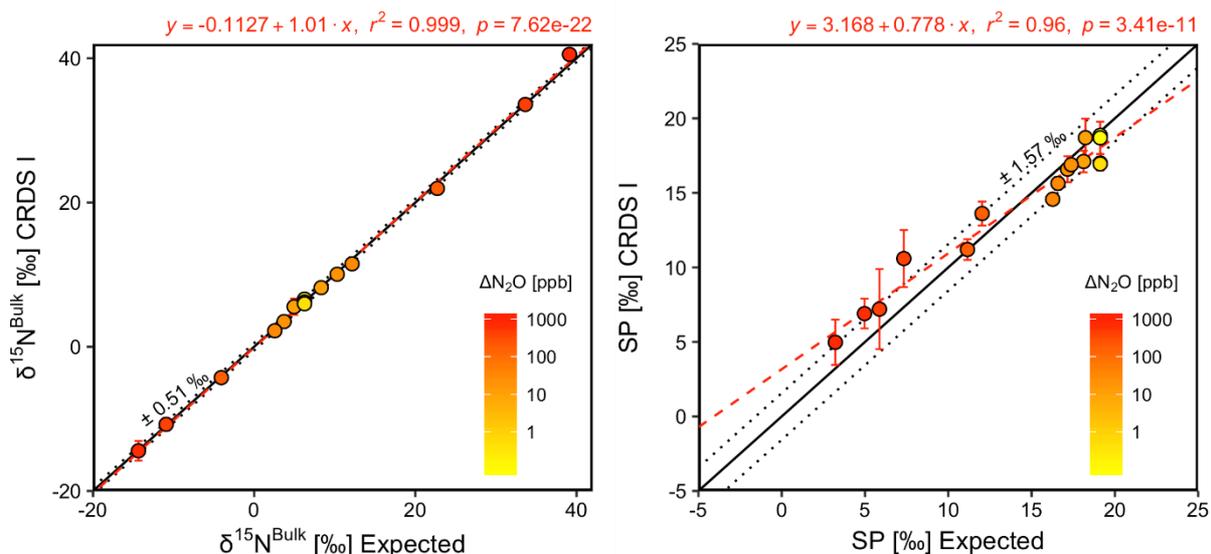


Fig. 10. Correlation diagrams for $\delta^{15}\text{N}^{\text{bulk}}$ and SP measurements at various $\Delta\text{N}_2\text{O}$ mole fractions analyzed by CRDS I plotted against expected values. The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-11). The solid black line denotes the 1:1 line, while the dotted line indicates $\pm 1\sigma$ of the residuals from the 1:1 line. The dashed blue line represents a linear fit to the data. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements.

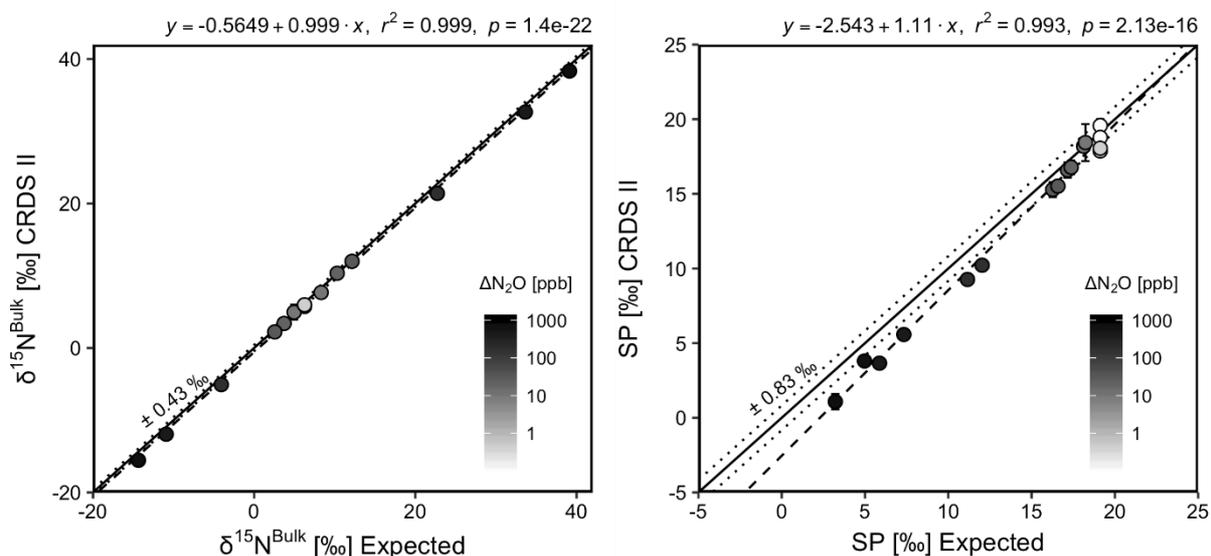


Fig. 11. Correlation diagrams for $\delta^{15}\text{N}^{\text{bulk}}$ and SP measurements at various $\Delta\text{N}_2\text{O}$ mole fractions analyzed by CRDS II plotted against expected values. The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-12). The solid black line denotes the 1:1 line, while the dotted line indicates $\pm 1\sigma$ of the residuals from the 1:1 line. The dashed blue line represents a linear fit to the data. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements.

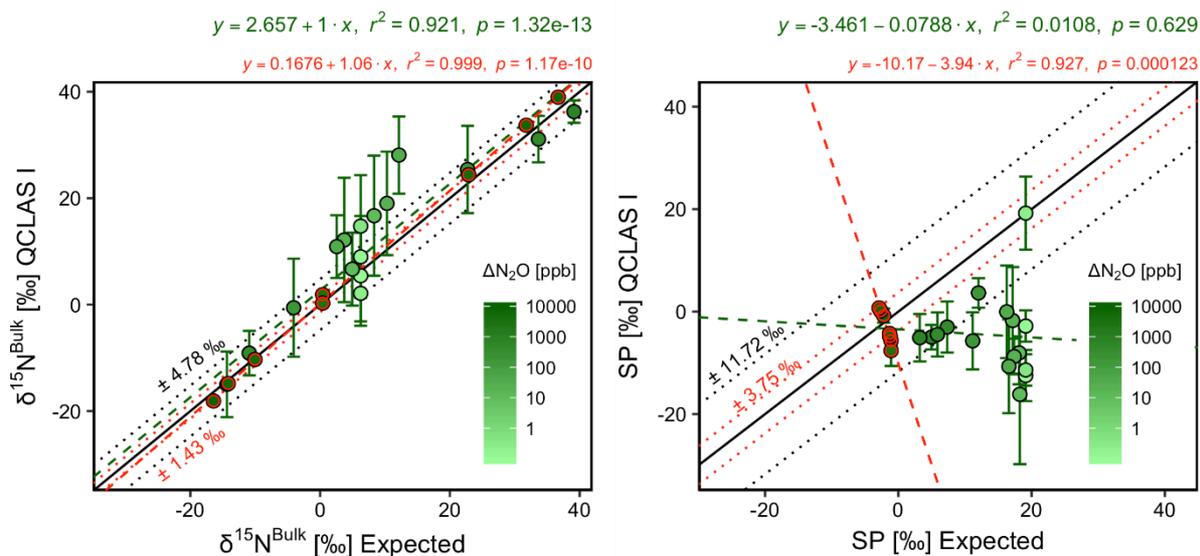


Fig. 12. Correlation diagrams for $\delta^{15}\text{N}^{\text{bulk}}$ and SP measurements at various $\Delta\text{N}_2\text{O}$ mole fractions analyzed by QCLAS I plotted against expected values. The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-13). The solid black line denotes the 1:1 line, while the dotted line indicates $\pm 1\sigma$ of the residuals from the 1:1 line. The dashed blue line represents a linear fit to the data. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements. Results for Exp. 5-6 are highlighted in red, with the dashed red line indicating a linear fit to this data.

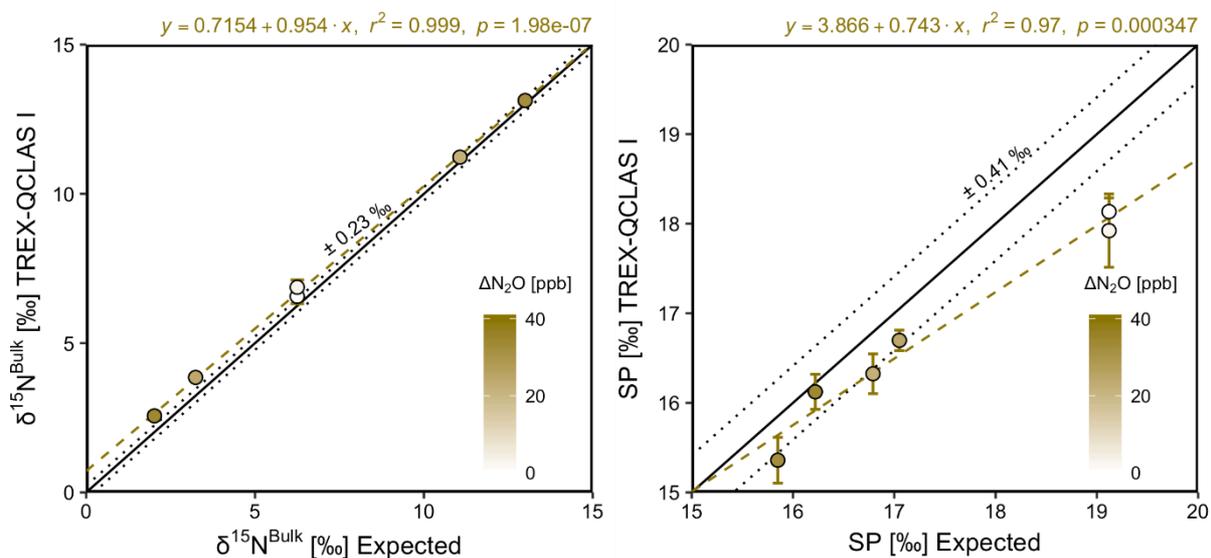


Fig. 13. Correlation diagrams for $\delta^{15}\text{N}^{\text{bulk}}$ and SP measurements at various $\Delta\text{N}_2\text{O}$ mole fractions analyzed by TREX-QCLAS I plotted against expected values. The remaining plots for $[\text{N}_2\text{O}]$, $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-14). The solid black line denotes the 1:1 line, while the dotted line indicates $\pm 1\sigma$ of the residuals from the 1:1 line. The dashed blue line represents a linear fit to the data. Individual equations, coefficients of determination (r^2) and p -values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements.

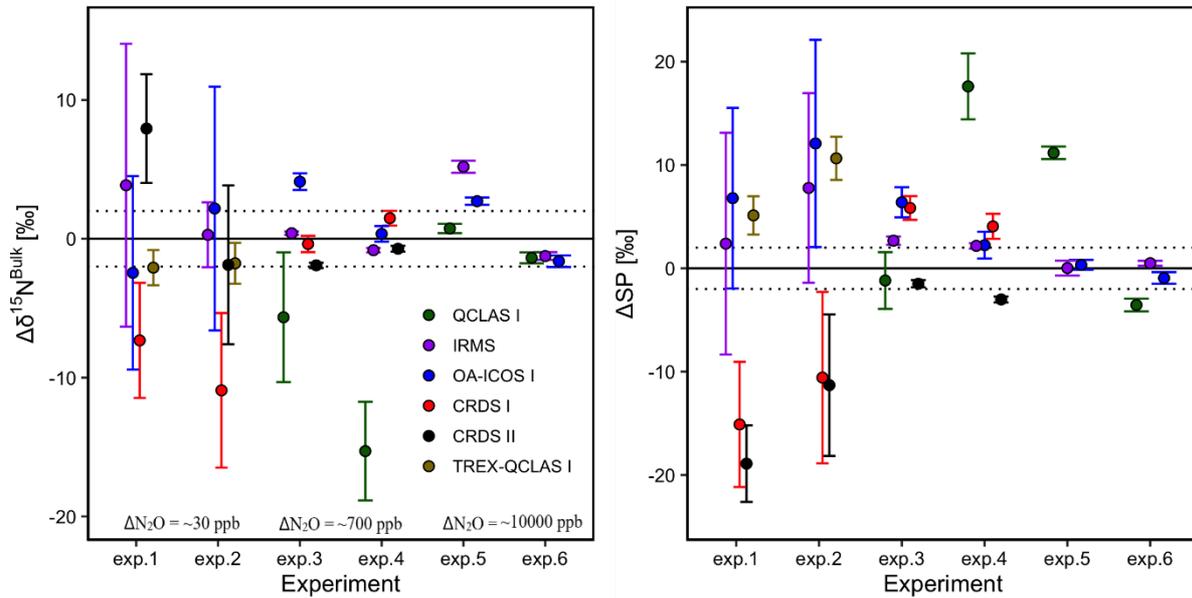


Fig. 14. $\Delta\delta^{15}\text{N}^{\text{bulk}}$ and ΔSP ($\text{Estimated}_{\text{Source}} - \text{True}_{\text{Source}}$) values derived from OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and IRMS (purple) via Keeling analysis of the two end-member mixing scenario. The remaining plots for $\delta^{15}\text{N}^{\alpha}$, $\delta^{15}\text{N}^{\beta}$ and $\delta^{18}\text{O}$ are provided in Supplementary Material 4 (Fig. S4-15). $\text{Estimated}_{\text{Source}} = \text{True}_{\text{Source}}$ is indicated by a solid black line at $y = 0$, and the dotted lines indicated $\pm 2\%$ deviation from $y = 0$. The change in concentration exceeding that of the background gas is indicated for experiments 1-2 ($\Delta\text{N}_2\text{O} = \sim 30$ ppb), 3-4 ($\Delta\text{N}_2\text{O} = \sim 700$ ppb) and 5-6 ($\Delta\text{N}_2\text{O} = \sim 10000$ ppb). Note: the QCLAS I results for experiments 1 and 2 are not depicted to maintain clarity, as they exceed the selected y-axis scale.

Furthermore, to limit the word count, in Sect. 4.3 we will replace the written *Measurement workflow* with Fig. 15, which closely parallels the workflow.

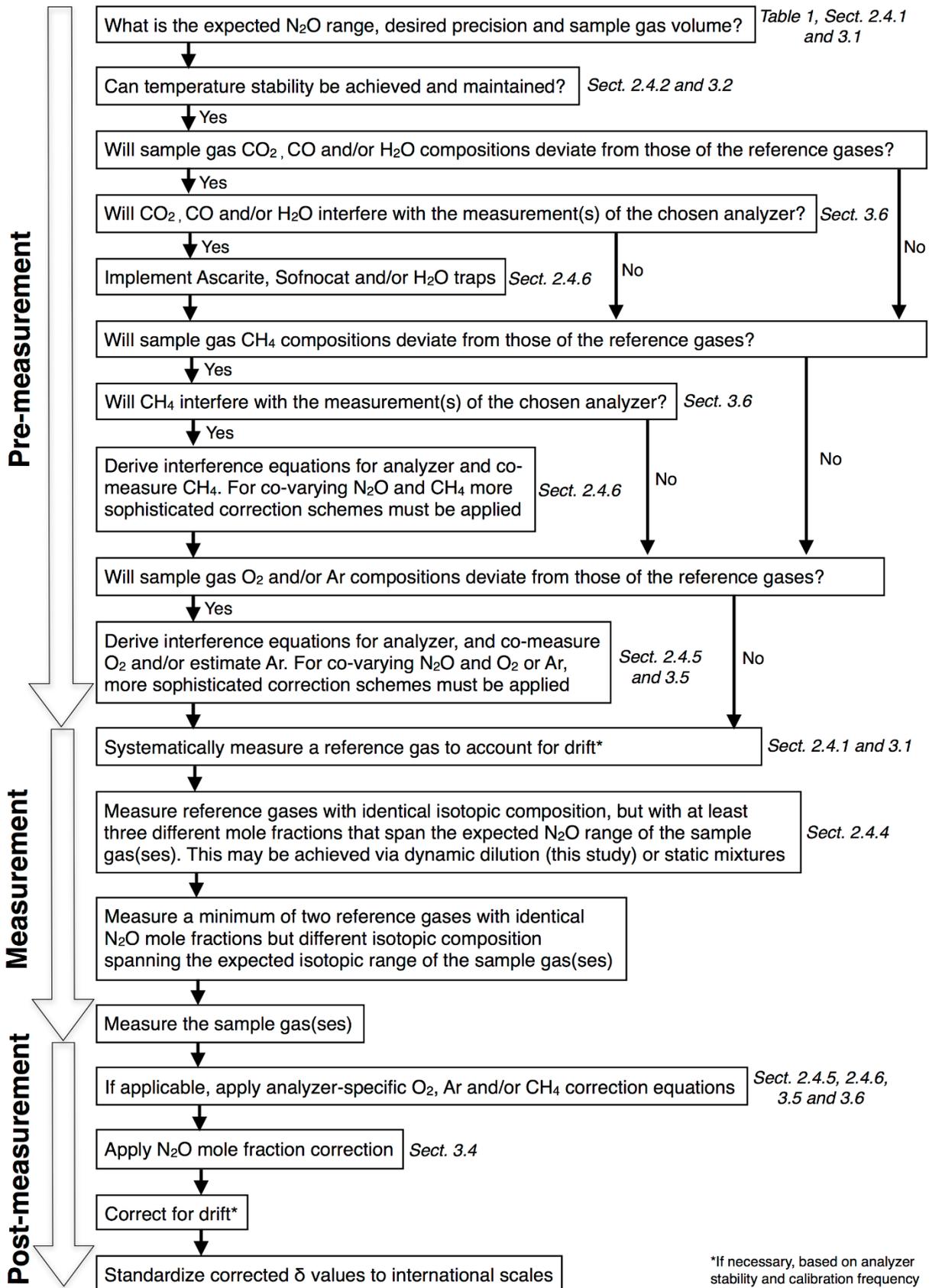


Fig. 15. Proposed measurement workflow for the operation of N₂O isotope laser spectrometers. Relevant sections of this study are shown next to each step.

Referee Comment 12 – I agree with the anonymous referee 1 that a summary table highlighting the particular advantages and limitations of each instrument would be very helpful. Such a Table should also include an item about the versatility of an instrument (how many parameters can be set/changed by the user to fit a particular experimental requirement) or the disclosure of details of the used data evaluation algorithms (for black box instruments, it may be hard to figure out the physical reason for a specific instrumental behavior).

Authors' response: Please refer to our response to Referee 1. A summary table (new Table 8) has been included in our reply, which addresses both Referee 1 and Referee 2 comments. Regarding the versatility of analysers, we agree there is basic difference between CRDS and OA-ICOS (Picarro Inc. and ABB LGR Inc.) and QCLAS (ARI) instruments, as the latter enables greater flexibility with respect to experimental parameters. Besides instrumental variables (flows, cell pressure, temperature, etc.), many spectroscopic parameters can also be set, including spectral line selection (multi-line analysis, inclusion of interferants, pressure broadening, etc.). This is already mentioned in the text on P10 L24, and the statement was extended as detailed in Comment 3 above.

Referee Comment 13 – I think, some of the reported interferences and shortcomings of the instruments could be (at least partly) overcome by multi-line analysis. So far, laser spectroscopic instruments typically use only one selected absorption line for analysis of one species. In particular cross-sensitivity issues could be identified easier and also be less pronounced for multi-line instruments.

Authors' response: We thank the reviewer for this comment. Indeed, multi-line analysis could overcome the spectral interference effects we have reported in our manuscript. This might be feasible given the availability of commercial multi-laser instruments or with new broadly tuneable light sources. However, this technology is only currently available for research grade instruments and not yet for commercial use.

Technical Corrections:

Referee Comment 14 – Page 5 Line 5: Please add an original reference for CRDS as well.

Authors' response: We assume that the Referee is referring to P4 L28. We will add the following reference to the updated manuscript, well as in Table 1:

P4 L28: "(QCLAS; Aerodyne Research Inc. [ARI]; Wächter et al., 2008), cavity ring-down spectroscopy (CRDS; Picarro Inc.; Berden et al., 2000) [...]"

Berden, G., Peeters, R. and Meijer, G.: Cavity ring-down spectroscopy: Experimental schemes and applications, *Int. Rev. Phys. Chem.*, 19, 565–607, doi: 10.1080/014423500750040627, 2000.

Referee Comment 15 – Page 9 Line 2 & Page 9 Line 19: I think that referring to the manufacturer website is OK. However, in addition an appropriate original reference should be included that explains details of the OA-ICOS and CRDS techniques.

Authors' response: Agreed. We have updated as follows:

P9 L2: “[...] reader is referred to the webpage of ABB-Los Gatos Research Inc. (ABB-Los Gatos Research Inc., 2019) and Baer et al. (2002).”

P9 L19: “[...] reader to the webpage of Picarro Inc. (Picarro Inc., 2019) and Berden et al. (2000).”

Referee Comment 16 – Page 8-Page 11: Next to the manufacturing date, the serial number of the used instruments should be included for future reference.

Authors' response: We will include serial numbers as follows:

P8 L6: “The N₂OIA-30e-EP (model 914-0027, serial number 15-830, ABB-Los Gatos Research Inc., USA) [...]”

P9 L12: “[...] a 2015 model (referred to as CRDS I, serial number 5001-PVU-JDD-S5001, delivered September 2015) provided by the Niels Bohr Institute, University of Copenhagen, Denmark; and a 2018 model (referred to as CRDS II, serial number 5070-DAS-JDD-S5079, delivered June 2018) provided by Karlsruhe Institute of Technology [...]”

P10 L9: “[...] Three QCLAS instruments (ARI, USA; CW-QC-TILDAS-SC-D) were used in this study. One instrument (QCLAS I, serial number 046), purchased in 2013, was provided by Karlsruhe Institute of Technology, Germany and two instruments, purchased in 2014 (QCLAS II, serial number 065) and 2016 (QCLAS III, serial number 077) [...]”

P11 L13: “A compact mini QCLAS device (CW-QC-TILDAS-76-CS; ARI, USA, serial number 074) coupled with a preconcentration system, called trace gas extractor (TREX) was provided by Empa, Switzerland.

Referee Comment 17 – Page 14 Line 3-6: The (more detailed) synthesis procedure could be moved to the Supplement.

Authors' response: In-line with Referee #1's comments, we will move a large portion of Sect. 2.2.2 into Supplementary Material 2. This includes P14 L3-6 as requested here by Referee #2.

Referee Comment 18 – Page 18 Line 15: The Picarro-CRDS analyzer really does not report any absolute numbers for the individual mole fractions? May be they are provided in some of the log files?

Authors' response: We verified that mole fractions of individual isotopocules are not available in the extended log files of our G5131-i, which was confirmed by Picarro technicians. Mole fractions are certainly generated during data processing; however, because post-processing might be conducted by internal software prior to data output, we did not extract them from the reported delta values.

Referee Comment 19 – Page 19 Line 16: While the meaning of the index “true” is clear in this context, I would prefer the index “reference” instead of “true”.

Authors’ response: We agree with the Referee’s suggestion and have made the following changes in Lines 14 to 16. We also have made minor changes to the equations to highlight what corrections were performed prior to executing Eq. 4:

P19 L14:

$$\delta_{Cal,G} = \frac{\delta_{ref,S1} - \delta_{ref,S2}}{\delta_{corr,S1} - \delta_{corr,S2}} * (\delta_{corr,G} - \delta_{corr,S1}) + \delta_{ref,S1} \quad (4)$$

where $\delta_{Cal,G}$ is the calibrated δ value for sample gas G normalized to international isotope ratio scales; $\delta_{ref,S1}$ and $\delta_{ref,S2}$ are the respective δ values assigned to reference gases S1-C_{330ppb} and S2-C_{330ppb}; $\delta_{corr,S1}$ and $\delta_{corr,S2}$ are the δ values measured for the reference gases S1-C_{330ppb} and S2-C_{330ppb} which, if required, were drift-corrected; and $\delta_{corr,G}$ is the trace gas-corrected, mole fraction-corrected (Sect.2.4.8 only) and drift-corrected (if required) δ value measured for the sample gas G.”

Referee Comment 20– Page 21 Line 15: Please refer the reader to Fig 4 , because the actual T versus t trend is given there.

Authors’ response: We believe that introducing Fig. 4 at this stage of the manuscript would disrupt the structure as the figure belongs to the results section, and therefore we would prefer not to introduce Fig. 4 here.

We refer Referee #2 to our response to Referee #1 Comment 11, as we identified some errors in the main text, which we have now rectified, as well as clarifying some details about the experiment.

Referee Comment 21 – Page 26 Line 21: Replace “greatest” by “best”?

Authors’ response: We agree with the Referee’s suggestion and have changed it to the following:

P26 L21: “[...] both CRDS analyzers showed the best precision and stability for the measurement [...]”

Referee Comment 22 – Figure 5: The text labels are too small to be readable. I suggest to leave out the residual plots to free some space.

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

Referee Comment 23 – Page 39 Line 25: Weird sentence.

Authors’ response: We have updated the sentence as detailed in Comment 10 above.

Referee Comment 24 – Table 9+10: These Tables could be moved to the Supplement.

Authors' response: We agree that these tables should be moved to the supplement to free up space in the manuscript. We note, however, that if we move Table 9 (trace gas interference slopes) to the supplement, then it is worthwhile also moving Table 8 (gas matrix interference slopes) to the supplement as well, seeing as they describe similar effects. We will therefore move Table 8 and 9 to the new Supplementary Material 8 and Table 10 to Supplementary Material 11 in keeping with the numbering for the revised Supplementary Material:

Supplementary Material 8:

“Supplementary Material 8 – Continuity of gas matrix and trace gas corrections at higher N₂O mole fractions

Gas matrix (O₂) and trace gas (CO₂, CH₄ and CO) experiments conducted at 660 and 990 ppb N₂O showed that the interference effects on N₂O mole fraction and delta values is also dependent on N₂O mole fraction (Tables S8-1 and S8-2). Figs. S8-1 to S8-4 show all data (330, 660 and 990 ppb N₂O) acquired during O₂, CO₂, CH₄ and CO dependence testing, and shows data corrected using Eqs. (7-8) for O₂ and Eq. (9) for CO₂, CH₄ and CO. [...] The O₂ constants A and B, and a, b and c estimated for each analyzer are provided in Table S8-3, while the approximated trace gas constant values of A_x , B_x , a_x and b_x for each analyzer are provided in Table S8-4.”

Supplementary Material 10:

“Supplementary Material 10: Extrapolated source intercept values

In Sect. 3.7.2, the extrapolated source intercept values acquired using Keeling analysis showed large standard errors, especially for Experiments 1 and 2 (Table S10-1). This was mostly due to the small mole fraction range (i.e. large inverse mole fraction range) over which the regression line was extrapolated in order to acquire the intercept value.”

*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 – O₂ effects (updated)
- 7 – CO₂ effects (updated)
- 8 – CH₄ 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 [N₂O] isotope reference gases, ambient reference gases, 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 N₂O mole fractions
- 9 – Comparison with GC-IRMS
- 10 – Extrapolated source intercept values (new)
- 11 – Lower state energies of probed N₂O isotopocule lines (new)