



Supplement of

N_2O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison

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Section S1 – IRMS Methodology

- 10 IRMS analyses were conducted at ETH Zürich using a gas preparation unit (Trace Gas, Elementar, Manchester, UK) coupled to an IsoPrime100 IRMS (Elementar, Manchester, UK). The gas preparation unit was modified with an additional chemical trap (0.5 in diameter stainless steel), located immediately downstream from the autosampler to pre-condition samples. This pre-trap was filled before each run with new NaOH, Mg(ClO₄)₂, and activated carbon in the direction of flow and was designed as a first step to
- 15 scrub CO₂ and H₂O. After pre-scrubbing, the samples were purged through a second set of chemical traps (NaOH, Mg(ClO₄)₂) before cryogenic trapping and focusing in liquid N₂. Before final injection into the IRMS, the purified gas sample was directed through a permeation drier and subsequently separated in a gas chromatograph column (5 Å molecular sieve). The IRMS is equipped with five Faraday cups with m/z of 30, 31, 44, 45, 46, measuring δ^{15} N^{bulk} and δ^{18} O of N₂O and δ^{15} N of the NO⁺ molecule dissociated
- from N₂O during ionization in the source. The ¹⁵N/¹⁴N ratio of the NO molecule reflects the α (central) position N of the initial N₂O, thus allowing the measurement of the site-specific isotopic composition of N₂O. During each run three sets of two working standards (~ 3 ppm N₂O mixed in synthetic air) with different isotopic composition ($\delta^{15}N^{\alpha} = 0.954 \pm 0.123$ ‰ and 34.446 ± 0.179 ‰; $\delta^{15}N^{\beta} = 2.574 \pm 0.086$ ‰ and 35.98 ± 0.221 ‰; $\delta^{18}O = 39.741 \pm 0.051$ ‰ and 38.527 ± 0.107 ‰) were included with a batch of
- 25 22 samples at the beginning, middle and end of each run. Sample peak ratios are initially reported against a N₂O reference gas peak (100% N₂O, Carbagas, Gümligen, Switzerland) and are subsequently corrected for drift and span using the working standards. Instrument linearity and stability was frequently checked by injection of 10 reference gas pulses of either varying or identical height respectively, with accepted levels of < 0.03 ‰ nA⁻¹. Since instrument linearity could only be achieved for either N₂O or NO, the
- 30 instrument was tuned for the former and $\delta^{15}N^{\alpha}$ non-linearity subsequently corrected using sample peak heights by determining non-linearity of $\delta^{15}N^{\alpha}$ with diluted working standards.

As detailed in Sect. 2.2.2, the isotopic composition of high [N2O] isotope reference gases in synthetic air (S1-a90ppm, S2-a90ppm) was analyzed in relation to N2O isotope standards (Call, 2 and 3) in the same gas

5 matrix (matrix a) using laser spectroscopy (CW-QC-TILDAS-200; ARI, Billerica, USA). Ambient mole fraction N₂O isotope reference gases (S1-c_{330ppb}, S2-c_{330ppb}) and PA1 and PA2 were analyzed by TREX-QCLAS (Sect. 2.1.4) using N₂O isotope standards (Cal1 – Cal5) shown in Table S2-1. Cal1 – Cal5 have been previously measured by Sakae Toyoda at Tokyo Institute of Technology."

Table S2-1. N₂O 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 ₂ O isotope standard used for calibration	δ ¹⁵ N ^α vs AIR-N ₂ [‰]	δ ¹⁵ N ^β vs AIR-N₂ [‰]	δ ¹⁸ O vs VSMOW [‰]	S1- a90ppm	S2- a90ppm	S1- c330ppb	S2- сззоррь	PA1	PA2
Call 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					✓	✓

Figs. S3-1 to S3-10 depict the setup for the gas matrix, trace gas and two end-member mixing experiments undertaken in this study. Experiments were performed simultaneously for all analyzers, with the exception of the TREX-QCLAS, which requires an extensive measurement protocol to trap and measure N₂O (Ibraim et al. 2018) and thus could not be integrated concurrently with the other englyzers.

5 N_2O (Ibraim et al., 2018) and thus could not be integrated concurrently with the other analyzers.



Fig. S3-1. Experimental setup for the O₂ dependence testing performed in Section 2.4.5.



10 Fig. S3-2. Experimental setup for the Ar dependence testing performed in Section 2.4.5.



Fig. S3-3. Experimental setup for the H₂O dependence testing performed in Section 2.4.6.



Fig. S3-4. Experimental setup for the CO₂ dependence testing performed in Section 2.4.6.



Fig. S3-5. Experimental setup for the CH₄ dependence testing performed in Section 2.4.6.



5 Fig. S3-6. Experimental setup for the CO dependence testing performed in Section 2.4.6.



Fig. S3-7. Experimental setup for the Ascarite and Sofnocat trap testing performed in Section 2.4.7.



Fig. S3-8. Experimental setup for Experiments 1 and 2 performed in Section 2.4.8.



Fig. S3-9. Experimental setup for Experiments 3 and 4 performed in Section 2.4.8.



5 Fig. S3-10. Experimental setup for Experiments 5 and 6 performed in Section 2.4.8.

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], $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ acquired by all instruments tested) are shown below.



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Fig. S4-1. 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 N₂O mole fractions (~327, 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 Allan deviations of all analyzers tested were reproducible on three separate occasions prior to the test results presented here.



Fig. S4-2. Dependency of the measured $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values on laboratory temperature (°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. The analyzers began acquiring measurements at 00:00 on 8/07/2018, capturing the end of the rising limb of the laboratory temperature. Results are plotted as the deviation from the mean, without any anchoring to reference gases.



Fig. S4-3. Deviations of the measured δ¹⁵N^α, δ¹⁵N^β and δ¹⁸O values according to 1/[N₂O] 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 (r²) and p-values are indicated above each plot.



Fig. S4-4. Deviations of the measured [N₂O], $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and δ^{18} O values according to ΔO_2 (%) at different N₂O 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 standard deviation of the Anchor gas (±1 σ) is indicated by dashed lines. Data points represent the

5 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 N₂O data only.



Fig. S4-5. Deviations of the measured [N₂O], $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and δ^{18} O values according to ΔAr (%) for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). Data points represent the mean and standard deviation (1 σ) of triplicate measurements. Dependencies are best-described by polynomial fits, which are indicated by solid lines. Individual equations, coefficients of determination (r^2) and p-values are indicated above each plot.



Fig. S4-6. Deviations of the measured $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values according to ΔCO_2 (ppm) at different N₂O 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 standard deviation of the Anchor gas ($\pm 1\sigma$) is indicated by dashed lines. Data points represent the

5 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 N₂O data only.



Fig. S4-7. Deviations of the measured [N₂O], $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and δ^{18} O values according to Δ CH₄ (ppm) at different N₂O 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). Data points represent the mean and standard deviation (1 σ) of triplicate measurements. Dependencies are heat described by linear fits, which are indicated by solid lines. Individual equations, accelerations (r^2)

5 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 N₂O data only.



Fig. S4-8. Deviations of the measured $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values according to ΔCO (ppm) at different N₂O mole fractions (330, 660 and 990 ppb) for OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green) and TREX-QCLAS I (brown). The standard deviation of the Anchor gas ($\pm 1\sigma$) is indicated by dashed lines. Data points represent the

5 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 N₂O data only.



Fig. S4-9. Deviations of the measured $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values according to ΔH_2O (ppm) for OA-ICOS I (blue), CRDS I (red), CRDS II (black) and QCLAS I (green). The standard deviation of the Anchor gas (±1 σ) is indicated by dashed lines. Data points represent the mean and standard deviation (1 σ) of triplicate measurements. Dependencies are best-described by either linear or polynomial fits, which are indicated by solid lines. Individual equations, coefficients of

5 best-described by either linear or polynomial fits, which are indicated by solid lines. Individual equations, coefficients of determination (r^2) and *p*-values are indicated above each plot.



Fig. S4-10. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O mole fractions analyzed by the OA-ICOS I plotted against expected values. 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

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different $\Delta N_2 O$ mole fractions, and the 1:1 line is similarly a solid line.



Fig. S4-11. Correlation diagrams for [N₂O], δ¹⁵N^α, δ¹⁵N^β, δ¹⁵N^β, δ¹⁵N^{bulk}, SP and δ¹⁸O measurements at various ΔN₂O mole fractions analyzed by the CRDS I plotted against expected values. The solid black line denotes the 1:1 line, while the dotted line indicates ±1σ of the residuals from the 1:1 line. The dashed red line represents a linear fit to the data. Individual equations, coefficients of determination (r²) and p-values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements. The inset plots indicate the standard deviation (1σ) of the triplicate measurements and the 1:1 line is similarly a solid line.



Fig. S4-12. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O mole fractions analyzed by the CRDS II plotted against expected values. 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 black 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

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different $\Delta N_2 O$ mole fractions, and the 1:1 line is similarly a solid line.



Fig. S4-13. Correlation diagrams for N₂O mole fractions, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$ and SP measurements at various ΔN_2O mole fractions analyzed by the QCLAS I plotted against expected values. 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 green line represents a linear fit to the data.

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O mole fractions, and the 1:1 line is similarly a solid line. Results for Exp. 5-6 are highlighted in red, with the dashed red line indicating a linear fit to this data.



Fig. S4-14. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O mole fractions analyzed by the TREX-QCLAS I plotted against expected values. 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 green 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O mole fractions, and the 1:1 line is similarly a solid line.



Fig. S4-15. Δδ¹⁵N^α, Δδ¹⁵N^β, Δδ¹⁵N^{bulk}, ΔSP and Δδ¹⁸O (Estimated_{Source} – True_{Source}) values derived from the 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. Estimated_{Source} = True_{Source} is indicated by a solid black line at y = 0, and the dotted lines indicated ± 2‰ deviation from y = 0. The change in concentration exceeding that of the background gas is indicated for experiments 1-2 (ΔN₂O = ~30 ppb), 3-4 (ΔN₂O = ~700 ppb) and 5-6 (ΔN₂O = ~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.

The primary cause of the observed excess drift in QCLAS I isotopocule measurements was fluctuating spectral baseline structure. That baseline structure, at an absorbance level of $\sim 5 \times 10^{-5}$, was likely due to

- 5 interference fringes that were enhanced by somewhat dirty absorption cell mirrors (pers. comm. Aerodyne Research Inc.). One way to reduce the effects of excess baseline structure is to employ the instrument operation mode "Automatic Background", wherein a spectrum is recorded while zero-air is injected, and subsequent spectra are divided by the recorded background spectrum. Periodic zero-air injections with refreshed background spectra can reduce the effect of changing baseline structure. Aerodyne recommends
- 10 that "Automatic Background" be used in measurements with very weak absorptions, such as in the measurements reported in this paper. However, Aerodyne Research Inc. recognizes that frequent backgrounds may not be convenient or practical in all circumstances. Also, instrument operators may not observe a gradual increase in baseline structure over time.
- 15 Recently, Aerodyne has been developing a new method of correcting data that is influenced by changing baseline structure. In this new method, injections of zero air and calibrations may be less frequent than would otherwise be necessary. An outline of the correction method provided by Aerodyne Research Inc. is as follows. Mixing ratio (MR) and spectral data are grouped according to type: background gas, calibration gas (Cal), and air sample measurements. Averages for the MR's and spectra for the groups are
- 20 subtracted. An aggregate subtracted spectrum array is smoothed to the absorption linewidth. A principal component analysis [PCA] is performed, so that spectral fluctuations are represented as a sum of vectors, $V_i(x)$, times amplitude histories, $A_i(t)$. For the "Cal" segments, we fit the recorded MR's with a sub-set of $\{A_i(t)\}$. If the specific linear combination of $\{A_i(t)\}$ from the MR fit well-represent the "Cal" segments, we apply that linear combination of $\{A_i(t)\}$ to the full measured data-set to determine MR adjustments.

25

In the Allan variance experiments performed on QCLAS I in this study (Sect. 3.1), the instruments were continuously sampling from a tank, so fictive hourly calibration periods (5 m duration) were created and used to generate mixing-ratio corrections. This method is computationally rapid, as ~8 hr of MR data can

be adjusted in seconds. A summary of the corrected data is provided in Table S5-1. This new method is not yet published or broadly verified, but Aerodyne Research Inc. intends, after further validation, to share the methodology with the measurement community.

5	Table S5-1. Summary of the corrected QCLAS I Allan variance data acquired in Sect. 3.1. 10 data refers
	to Allan deviation (square root of Allan variance).

		N ₂ O [ppb]			$\delta^{15} N^{lpha}$ [‰]		$\delta^{15} N^{\beta}$ [‰]			
N ₂ O [ppb]	1σ (1s)	1σ (300s)	1σ (600s)	1σ (1s)	1σ (300s)	1σ (600s)	lσ (1s)	1σ (300s)	1σ (600s)	
326.5	0.062	0.021	0.024	1.2	0.39	0.37	1.7	0.42	0.55	
1000	0.165	0.14	0.10	1.4	0.19	0.23	1.4	0.20	0.22	
10000	2.9	0.46	0.38	0.33	0.027	0.029	0.25	0.024	0.028	

Section S6 – Short-term repeatability

To test the short-term repeatability of the instruments, sample gas at different at different [N₂O]: ambient (PA1), 1 ppm , 10 ppm N₂O was repeatedly analyzed 10 times for 15 min, intercepted by dry ambient air for 5 min. Gas mixtures with 1 and 10 ppm N₂O were prepared by dynamically diluting S1- c_{90ppm} with matrix gas c. All data were corrected for drift using a linear interpolation of two bracketing anchor gas

measurements (cf. Lebegue et al., 2016).

5

In Table S6-1 and S6-2 the short-term repeatability is expressed as standard deviation (1 σ) of 10 repeated measurements using averaging times of 300 s and 600 s, respectively. At ~327 ppb N₂O, the best repeatability for δ values was achieved by TREX-QCLAS I, with around 0.3 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, and $\delta^{18}O$ at 300 s averaging. The CRDS analyzers showed a similar repeatability level of 0.25–0.40 ‰ for all δ values, at 600 s averaging, somewhat worse 0.35–0.6 ‰ at 300 s, but without the requirement for preconcentration. OA-ICOS I achieved a repeatability of 0.75 ‰ (1.1 ‰) for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$, and 1.3 ‰ (2.4‰) for $\delta^{18}O$ at 600 s (300 s) averaging. QCLAS analyzers without preconcentration (QCLAS I)

- 15 showed poor repeatability for δ values regardless of averaging time, in-line with results acquired in Sect.
 3.1. In contrast to δ values, the best [N₂O] repeatability was achieved by both the OA-ICOS I and QCLAS I (0.02 ppb), while the repeatability was worst for TREX–QCLAS I (0.48 ppb), due to the multiple parameters involved in [N₂O] analysis.
- At 1 ppm N₂O, the repeatability of δ -measurements improved for all instruments, with the exception of CRDS I, compared to ~327 ppb N₂O. CRDS II achieved the best repeatability of 0.15 0.24 ‰ (0.20 0.26 ‰) for δ values at 600 s (300 s) averaging, while the repeatability for CRDS I did not profit from an increase in [N₂O] but degraded to 0.39 0.49 ‰ (0.65 0.91 ‰). OA-ICOS I achieved a repeatability of 0.28–0.37 ‰ (0.21–0.27 ‰) for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ and 0.69 ‰ (0.54 ‰) for $\delta^{18}O$ at 300 s (600 s) averaging.
- 25 QCLAS I showed again the weakest repeatability for δ values of 2–7 ‰, irrespective of the averaging time. Again the best repeatability for [N₂O] was achieved by OA-ICOS I and QCLAS I but worsened for all instruments compared to ~327 ppb N₂O.

At 10 ppm N₂O, δ -measurement repeatability improved further compared to both near-atmospheric and 1 ppm measurements. The best repeatability was demonstrated by OA-ICOS I with 0.09‰, 0.16‰ and 0.20‰ at 300 s averaging, and 0.06‰, 0.13‰ and 16‰ at 600 s averaging for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$, respectively. The repeatability of QCLAS I was also largely improved to 0.3–0.45 ‰ for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$. In contrast, QCLAS I achieved the best [N₂O] repeatability of 1.05 ppb (1.45 ppb) at 600 s (300 s) averaging.

Table S6-1. Repeatability acquired for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ as standard deviation (1 σ) for 10 repeated measurements at 300 s averaging time. Measurements were made at 326.5 ppb (PA1), 1000 ppb and 10000 ppb N₂O.

		1σ	N ₂ O	1σ	$\delta^{15} N^{\alpha}$	1σ	$\delta^{15}N^{\beta}$	1σ	$\delta^{18}O$
Instrument	n	N_2O	range	$\delta^{15}N^{\alpha}$	range	$\delta^{15}N^{\beta}$	range	$\delta^{18}O$	range
		[ppb]	[ppb]	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]
			320	5.5 ppb N ₂	0				
CRDS I	10	0.17	0.50	0.48	1.82	0.38	1.07	0.59	2.03
CRDS II	10	0.05	0.13	0.58	1.64	0.37	1.14	0.35	0.94
OA-ICOS I	10	0.02	0.06	1.12	3.32	1.14	3.26	2.40	7.06
QCLAS I	10	0.02	0.05	6.60	19.19	9.84	31.35	-	-
TREX-QCLAS I	10	0.48	1.36	0.27	0.68	0.31	0.97	0.29	0.73
			10	00 ppb N ₂	0				
CRDS I	10	0.87	2.78	0.75	2.37	0.91	2.82	0.65	1.95
CRDS II	10	0.45	1.15	0.20	0.70	0.26	0.91	0.23	0.61
OA-ICOS I	10	0.24	0.88	0.37	1.40	0.28	0.83	0.69	2.28
QCLAS I	10	0.31	0.87	2.38	7.47	6.62	16.75	-	-
			100	000 ppb N	$_{2}O$				
OA-ICOS I	10	2.13	6.65	0.09	0.26	0.16	0.49	0.20	0.64
QCLAS I	10	1.45	4.77	0.28	0.99	0.43	1.54	-	-

10

Table S6-2. Repeatability acquired for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ as standard deviation (1 σ) for 10 repeated measurements at 600s averaging time. Measurements were made at 326.5 ppb (PA1), 1000 ppb and 10000 ppb N₂O.

		1σ	N ₂ O	1σ	$\delta^{15} N^{\alpha}$	1σ	$\delta^{15}N^{\beta}$	1σ	$\delta^{18}O$
Instrument	n	N_2O	range	$\delta^{15} N^{\alpha}$	range	$\delta^{15}N^{\beta}$	range	$\delta^{18}O$	range
		[ppb]	[ppb]	[‰]	[‰]	[‰]	[‰]	[‰]	[‰]
			32	26.5 ppb N	2O				
CRDS I	10	0.17	0.48	0.39	1.12	0.23	0.84	0.37	1.43
CRDS II	10	0.05	0.13	0.34	1.04	0.29	1.04	0.30	1.07
OA-ICOS I	10	0.01	0.04	0.77	2.33	0.75	2.05	1.29	3.45
QCLAS I	10	0.02	0.06	6.99	17.63	11.66	32.97	-	-
			1	000 ppb N	2O				
CRDS I	10	0.66	2.05	0.49	1.72	0.48	1.47	0.39	1.15
CRDS II	10	0.39	1.15	0.24	0.70	0.15	0.46	0.16	0.50
OA-ICOS I	10	0.23	0.69	0.27	0.88	0.21	0.61	0.54	1.84
QCLAS I	10	0.21	0.62	2.21	7.19	6.34	16.30	-	-
			10	0000 ppb N	[₂ O				
OA-ICOS I	10	1.61	4.79	6.3·10 ⁻²	0.17	0.13	0.47	0.16	0.56
QCLAS I	10	1.05	3.09	0.28	0.89	0.46	1.64	-	-

Section S7 – Scaling of the signal-to-noise ratio

Expanding on the N_2O mole fraction dependence testing performed in Sect. 2.4.4, we plotted the uncertainty (1 σ) of the single 5 min-averaged measurements performed across the three days of mole fraction dependence experimentation acquired by each analyzer, as shown in Fig. S7-1. Because the 5-

- 5 min averaged data is acquired at the frequency rates as outlined in Table 1, individual points in Fig. S7-1 broadly correspond to the initial *starting point* of each Allan deviation plot (1s for OA-ICOS I, QCLAS I, II and III; 3.41s for CRDS I; 2.54s for CRDS II) for each analyzer measuring at a given N₂O mole fraction. Fig. S7-1 is therefore a useful guide for determining the theoretical optimum measurement precision range for each analyzer. The behavior of this δ-measurement uncertainty as a function of N₂O
- 10 mole fraction is also of great interest, as this will have important implications for situations where measurements cannot be repeated in order to increase certainty in the measurement (e.g. low sample volume or soil flux chamber measurements). For δ measurements, the greatest precision is likely to achieved by OA-ICOS I between ~6000–20000 ppb N₂O, CRDS I and II between ~500–1000 ppb N₂O, and QCLAS I between ~30000–90000 ppb.



Fig. S7-1. Scaling of single measurement standard deviation (1σ ; 300 second averaging time) as a function of N₂O mole fraction for the OA-ICOS I (blue), CRDS I (red), CRDS II (black) and QCLAS I (green). Data was acquired during the mole fraction dependence testing depicted in Fig. 5.

Gas matrix (O_2) and trace gas $(CO_2, CH_4 \text{ and } CO)$ 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

- 5 (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. Corrected data is provided if the linear regression conducted at 330 ppb N₂O for the interference effect was statistically significant at p < 0.05. The similarity between the CH₄ and CO dependencies for N₂O mole fraction measurements across all instruments suggests that the apparent
- 10 effects may be due to the dynamic dilution process, rather than a discrete spectral interference effect. Therefore, data has not been corrected for these effects. Correction using Eqs. (7-8) and Eqs. (11-12) removes the matrix and trace gas effects to the extent that corrected measurements are typically within the uncertainty bounds of the anchor. 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
- 15 each analyzer are provided in Table S8-4.



Fig. S8-1. Dependency of the measured [N₂O], δ¹⁵N^α, δ¹⁵N^β and δ¹⁸O values on changing O₂ content (%) for OA-ICOS I, CRDS I, CRDS II, and QCLAS I. Non-corrected data is shown in red for various N₂O
5 mole fraction testing (circle = 330 ppb; square = 660 ppb; diamond = 990 ppb). Corrected data using Eqs. (7-8) is shown in blue. The standard deviation of the Anchor gas (±1σ) is indicated by dashed lines.



Fig. S8-2. Dependency of the measured $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values on CO₂ (ppm) for OA-ICOS I, CRDS I, CRDS II, and QCLAS I. Non-corrected data is shown in red for various N₂O mole fraction testing (circle = 330 ppb; square = 660 ppb; diamond = 990 ppb). Corrected data using Eqs. (11-12) is shown in blue. The standard deviation of the Anchor gas (±1 σ) is indicated by dashed lines.



Fig. S8-3. Dependency of the measured N₂O mole fraction, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and δ^{18} O values on CH₄ (ppm) for OA-ICOS I, CRDS I, CRDS II, and QCLAS I. Non-corrected data is shown in red for various N₂O mole fractions tested (circle = 330 ppb; square = 660 ppb; diamond = 990 ppb). Corrected data using Eqs. (11-12) is shown in blue. The standard deviation of the Anchor gas (±1 σ) is indicated by dashed lines.



Fig. S8-4. Dependency of the measured N₂O mole fraction, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ values on CO (ppm) for OA-ICOS I, CRDS I, CRDS II, and QCLAS I. Non-corrected data is shown in red for various N2O mole fractions tested (circle = 330 ppb; square = 660 ppb; diamond = 990 ppb). Corrected data using Eqs.

5 (11-12) is shown in blue. The standard deviation of the Anchor gas $(\pm 1\sigma)$ is indicated by dashed lines.

		OA-IO	COS I	CRE	DS I	CRD	S II	QCL	AS I
ΔΟ ₂ [%]	Co- measured N ₂ O [ppb]	Slope	r^2	Slope	r ²	Slope	r ²	Slope	r ²
	330	-0.044	0.84	0.24	1.00	0.305	1.00	0.351	1.00
N ₂ O [ppb]	660	-0.273	0.98	0.478	0.99	0.608	1.00	0.690	1.00
	990	-0.570	0.99	0.61	0.99	0.859	1.00	0.979	1.00
	330	1.146	0.99	-1.364	1.00	-0.888	0.99	n.s.	n.s.
$\delta^{15} N^{lpha}$ [‰]	660	1.116	1.00	-1.387	1.00	-0.874	0.99	n.s.	n.s.
	990	1.204	1.00	-1.326	1.00	-0.891	0.99	0.374	0.90
	330	1.270	1.00	-0.642	1.00	-0.279	0.95	-1.111	0.87
$\delta^{15}N^{\beta}[\%]$	660	1.282	1.00	-0.580	0.98	-0.303	0.96	n.s.	n.s.
	990	1.361	1.00	-0.319	0.96	-0.273	0.99	n.s.	n.s.
	330	0.874	0.97	-0.577	0.98	-0.304	0.99	n.d.	n.d.
δ ¹⁸ Ο [‰]	660	1.419	0.99	-0.621	0.98	-0.267	0.94	n.d.	n.d.
	990	1.446	1.00	-0.507	0.97	-0.256	0.98	n.d.	n.d.

Table S8-1. Summary of regression slopes and coefficients of determination (r^2) for O₂ interferences performed at different N₂O mole fractions (330, 660 and 990 ppb) for OA-ICOS I, CRDS I and II, and QCLAS I.

n.d. not determined

5 n.s. not statistically significant at p < 0.05

		OA-ICO	S I	CRDS	Ι	CRDS	II	QCLAS	Ι
ΔCO ₂ [ppm]	Co- measured N ₂ O [ppb]	Slope	r^2	Slope	r ²	Slope	r^2	Slope	r^2
	330	1.12.10-3	0.96	4.90·10 ⁻⁴	0.88	4.94·10 ⁻⁴	0.83	n.s.	n.s.
N ₂ O [ppb]	660	1.50.10-3	0.99	6.57·10 ⁻⁴	0.75	6.45·10 ⁻⁴	0.73	-1.64.10-4	0.70
	990	1.92.10-3	0.99	n.s.	n.s.	1.37.10-3	0.87	n.s.	n.s.
	330	-8.70·10 ⁻³	0.95	-1.58.10-3	0.88	-6.83.10-4	0.66	n.s.	n.s.
$\delta^{15}N^{\alpha}[\%]$	660	-5.01·10 ⁻³	0.99	-6.95·10 ⁻⁴	0.76	n.s.	n.s.	n.s.	n.s.
	990	-3.80.10-3	1.00	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	330	2.55.10-2	1.00	n.s.	n.s.	n.s.	n.s.	1.54.10-2	0.59
$\delta^{15}N^{\beta}[\%]$	660	1.11.10-2	1.00	n.s.	n.s.	n.s.	n.s.	5.50·10 ⁻³	0.70
	990	6.94·10 ⁻³	0.99	n.s.	n.s.	n.s.	n.s.	6.64·10 ⁻³	0.76
	330	-2.65.10-2	0.99	-1.88.10-3	0.86	-1.20.10-3	0.72	n.d.	n.d.
δ ¹⁸ Ο [‰]	660	-1.66.10-2	1.00	n.s.	n.s.	n.s.	n.s.	n.d.	n.d.
	990	-1.18.10-2	1.00	n.s.	n.s.	5.09.10-4	0.72	n.d.	n.d.
ΔCH_4 [ppm]									
N-O [nnh]	330	-4.86.10-2	0.67	-3.91.10-2	0.48	-5.56·10 ⁻²	0.57	-4.15·10 ⁻²	0.45
	660	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Table S8-2. Summary of regression slopes and coefficients of determination (r^2) for trace gas interferences (CO₂, CH₄ and CO) performed at different N₂O mole fractions (330, 660 and 990 ppb) for OA-ICOS I, CRDS I and II, and QCLAS I.

	990	-1.28.10-1	0.92	n.s.	n.s.	-1.06·10 ⁻¹	0.69	-1.14·10 ⁻¹	0.88
	330	n.s.	n.s.	$2.50 \cdot 10^{0}$	1.00	$2.49 \cdot 10^{0}$	1.00	n.s.	n.s.
$\delta^{15}N^{lpha}$ [‰]	660	n.s.	n.s.	$1.29 \cdot 10^{0}$	0.98	$1.22 \cdot 10^{0}$	1.00	n.s.	n.s.
	990	n.s.	n.s.	8.26·10 ⁻¹	0.95	8.13·10 ⁻¹	0.99	-7.59·10 ⁻¹	0.93
	330	1.73.10-1	0.29	n.s.	n.s.	8.47.10-2	0.23	n.s.	n.s.
$\delta^{15}N^{\beta}$ [‰]	660	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	990	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	330	n.s.	n.s.	$1.14 \cdot 10^{0}$	0.98	1.29.10-1	0.97	n.d.	n.d.
δ ¹⁸ Ο [‰]	660	-2.21.10-1	0.74	7.34.10-1	0.99	6.36·10 ⁻¹	0.99	n.d.	n.d.
	990	n.s.	n.s.	3.76.10-1	0.79	3.55.10-1	0.98	n.d.	n.d.
ΔCO [ppm]									
	330	-2.90.10-1	0.72	-1.49.10-1	0.30	-2.39.10-1	0.59	-1.90·10 ⁻¹	0.51
N ₂ O [ppb]	660	-5.29.10-1	0.76	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	990	-7.72·10 ⁻¹	0.76	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
	330	n.s.	n.s.	$-1.50 \cdot 10^{0}$	0.82	$-1.64 \cdot 10^{0}$	0.77	$-4.04 \cdot 10^{0}$	0.76
$\delta^{15} N^{lpha}$ [‰]	660	n.s.	n.s.	n.s.	n.s.	-6.49·10 ⁻¹	0.81	n.s.	n.s.
	990	n.s.	n.s.	n.s.	n.s.	-4.16·10 ⁻¹	0.98	$-4.17 \cdot 10^{0}$	0.73
	330	n.s.	n.s.	$-2.19 \cdot 10^{0}$	0.95	$-2.41 \cdot 10^{0}$	0.92	-4.26·10 ⁰	0.29
$\delta^{15}N^{\beta}$ [‰]	660	n.s.	n.s.	$-1.31 \cdot 10^{0}$	0.67	$-1.44 \cdot 10^{0}$	0.89	n.s.	n.s.
	990	n.s.	n.s.	n.s.	n.s.	-7.86·10 ⁻¹	0.95	n.s.	n.s.
δ ¹⁸ Ο [‰]	330	n.s.	n.s.	-5.31·10 ⁻¹	0.32		n.s.	n.d.	n.d.

660	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.d.	n.d.
990	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.d.	n.d.

n.d. not determined

n.s. not statistically significant at $p \le 0.05$

Table S8-3. The fitted constants A, B, and a, b and c for OA-ICOS I, CRDS I, CRDS II and QCLAS I, derived using Eqs. 5 and 6. For values of 0, there was either no apparent trend or the fitted values fell
within the uncertainty of the measurements. The units for each constant are A: 1/(ppb_{N20}·%₀₂), B: 1/%₀₂, a: ‰/(ppb_{N20}²·%₀₂), b: ‰/(ppb_{N20}·%₀₂), and c: ‰/%₀₂.

	N ₂ O [ppb]	$\delta^{15} N^{lpha}$ [‰]	$\delta^{15} N^{eta}$ [‰]	δ ¹⁸ Ο [‰]	
		OA	A-ICOS I		
А	-5.97·10 ⁻⁷	n.a.	n.a.	n.a.	
a	n.a.	-1.37·10 ⁻⁸	-2.57·10 ⁻⁷	-2.93·10 ⁻⁶	
В	7.09.10-5	n.a.	n.a.	n.a.	
b	n.a.	2.07.10-4	5.39.10-4	4.82·10 ⁻³	
с	n.a.	$1.00 \cdot 10^{0}$	$1.07 \cdot 10^{0}$	-4.40.10-1	
		(CRDS I		
А	-2.40.10-7	n.a.	n.a.	n.a.	
a	n.a.	7.74.10-7	7.71.10-7	7.55.10-7	
В	8.67.10-4	n.a.	n.a.	n.a.	
b	n.a.	-9.55·10 ⁻⁴	-4.71.10-4	-8.51.10-4	
c	n.a.	$-1.18 \cdot 10^{0}$	-6.70·10 ⁻¹	-4.40.10-1	
		C	RDS II		
А	-2.38.10-7	n.a.	n.a.	n.a.	
a	n.a.	-3.11.10-8	-7.71.10-8	-8.34·10 ⁻⁸	
В	1.08.10-3	n.a.	n.a.	n.a.	
b	n.a.	6.71.10-7	1.93.10-4	2.03.10-4	
c	n.a.	-9.09·10 ⁻¹	-4.06.10-1	-3.92.10-1	

	QCLAS I									
А	-2.20.10-7	n.a.	n.a.	n.a.						
а	n.a.	0	0	n.d.						
В	1.21.10-3	n.a.	n.a.	n.a.						
b	n.a.	0	0	n.d.						
c	n.a.	0	0	n.d.						

n.a. not applicable

n.d. not determined

Table S8-4. The fitted constants Ax, Bx, ax and bx, for OA-ICOS I, CRDS I, CRDS II and QCLAS I, derived using Eqs. 9 and 10. For values of 0, there was either no apparent trend or the fitted values fell within the uncertainty of the measurements. The unit for A_x and a_x is $ppm_{N2O}/ppm_{trace gas}$, and the unit for

5 B_x and b_x is $1/ppm_{trace gas}$.

	[N;	2O]	δ ¹⁵	N ^α	δ^{15}	N ^β	δ^1	⁸ O
	А	В	α δ15Να	$b_{\delta 15N\alpha}$	a δ15Nβ	$b_{\delta 15N\beta}$	a 8180	b δ180
				OA-ICOS I				
CO ₂	-3.35.10-4	2.181.10-3	-1.50.10-3	-2.49.10-3	8.91·10 ⁻³	-1.86.10-3	-6.53.10-3	-6.25·10 ⁻³
CH4	0	0	0	0	5.71.10-2	0	0	0
СО	0	0	0	0	0	0	0	0
				CRDS I				
CO ₂	9.44·10 ⁻⁵	2.63.10-4	-7.780.10-4	-8.35·10 ⁻⁴	0	0	-1.32.10-3	-1.84·10 ⁻³
CH ₄	0	0	8.42.10-1	0	2.651.10-2	0	3.99.10-1	0
СО	0	0	-4.05.10-1	0	-7.88·10 ⁻¹	0	-1.34.10-1	0
				CRDS II				
CO ₂	-5.04.10-4	2.07.10-3	3.20.10-4	2.30.10-4	0	0	-1.06.10-3	1.59·10 ⁻³

CH ₄	0	0	7.94.10-1	0	3.71.10-2	0	4.27·10 ⁻¹	0
СО	0	0	-4.66.10-1	0	-7.83.10-1	0	-2.03.10-1	0
			QC	LAS I				
CO ₂	0	0	-8.56·10 ⁻⁶	0	-5.73·10 ⁻⁶	0	n.d.	n.d.
CH ₄	0	0	0	0	0	0	n.d.	n.d.
СО	0	0	$-1.41 \cdot 10^{0}$	0	$-1.57 \cdot 10^{0}$	0	n.d.	n.d.

n.d. not determined

Section S9 – Comparison with GC-IRMS

Fig. S9-1 shows the triplicate measurements (mean $\pm 1\sigma$) obtained using the GC-IRMS plotted against 5 expected mixing values calculated using MFC flow rates and the mole fraction and isotopic composition of *background* and *source*. A comparison between laser spectrometer and GC-IRMS measurements are presented in Figs. S9-2 to S9-5 using the mean $\pm 1\sigma$ of triplicate measurements. TREX-QCLAS I measurements were undertaken separately, and therefore were not directly compared to IRMS measurements.

10

There was excellent agreement between the IRMS and calculated expected isotope values (all r² > 0.99). Measurements for δ¹⁵N^α, δ¹⁵N^β and δ¹⁵N^{bulk} were all typically within ± 1 ‰ of expected values, while SP was within ± 0.7 ‰ of expected values. δ¹⁸O measurements were the poorest performing and were typically within ± 3 ‰ of expected values. The standard deviations of triplicate isotope measurements
15 were typically between 0.1 – 1 ‰.

Generally, there is good agreement between the laser spectrometers and GC measurements, but disagreement between the two techniques becomes pronounced at higher ΔN_2O for OA-ICOS I and QCLAS I during experiments 5 and 6. All analyzers, with the exception of one triplicated measurement

20 taken from CRDS I, showed better 1σ repeatability than those acquired using GC. There was excellent

agreement for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{15}N^{bulk}$ between the IRMS and both CRDS I and II at all concentrations tested. $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{15}N^{bulk}$ measurements for these analyzers were typically within ± 1 ‰ of those acquired from IRMS, while SP measurements were typically within ± 1.3 ‰. OA-ICOS I $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{15}N^{bulk}$ measurements were typically within ± 2.5 ‰ of IRMS, while SP were in slightly better

- 5 agreement (± 1.7 ‰). Conversely, QCLAS I showed good agreement with IRMS only at higher ΔN_2O (> 1,000 ppb), presumably due to less precise measurements that are expected (based on results acquired in Section 3) to be acquired at the lower concentrations tested. For OA-ICOS I, the repeatability of the triplicate $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$ and SP measurements was typically better than the IRMS exclusively at higher ΔN_2O (>1,000 ppb). CRDS I and II had comparable repeatability to the IRMS, and there was no
- 10 clear distinction based on ΔN_2O . QCLAS I showed comparable or better repeatability to IRMS only at higher ΔN_2O (>1,000 ppb).

 δ^{18} O measurements from OA-ICOS I, and CRDS I and II showed good agreement with IRMS results (all $r^2 > 0.98$), with the vast majority of measurements similarly within $\pm 2\%$. OA-ICOS I δ^{18} O measurements

15 had typically better repeatability compared to IRMS at higher ΔN_2O , while both CRDS analyzers showed varied repeatability regardless of ΔN_2O .



Fig. S9-1. Correlation diagrams for [N₂O], δ¹⁵N^α, δ¹⁵N^β, δ¹⁵N^{bulk}, SP and δ¹⁸O measurements at various ΔN₂O mole fractions analyzed by GC-IRMS plotted against expected values. The solid black line denotes the 1:1 line, while the dotted line indicates ±1σ of the residuals from the 1:1 line. The dashed black line represents a linear fit to the data. Individual equations, coefficients of determination (r²) and p-values are indicated above each plot. Each data point represents the mean and standard deviation (1σ) of triplicate measurements. The inset plots indicate the standard deviation (1σ) of the triplicate measurements and the 1:1 line.



Fig. S9-2. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O concentrations analyzed by both OA-ICOS I and GC-IRMS. 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

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O concentrations, and the 1:1 line is similarly a solid line.



Fig. S9-3. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O concentrations analyzed by both CRDS I and GC-IRMS. 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 red 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

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O concentrations, and the 1:1 line is similarly a solid line.



Fig. S9-4. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$, SP and $\delta^{18}O$ measurements at various ΔN_2O concentrations analyzed by both CRDS II and GC-IRMS. 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 black 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

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O concentrations, and the 1:1 line is similarly a solid line.



Fig. S9-5. Correlation diagrams for $[N_2O]$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N^{bulk}$ and SP measurements at various ΔN_2O concentrations analyzed by both QCLAS I and GC-IRMS. 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 green line represents a linear fit to the data. Individual equations, coefficients

5 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. The inset plots indicate the standard deviation (1σ) of the triplicate measurements achieved at different ΔN_2O concentrations, and the 1:1 line is similarly a solid line.

Section S10: Extrapolated *source* intercept values

5

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.

Table 10. Intercept values obtained by the four analyzers from the Keeling analysis. The error reported is 1 standard error. A 3-point concentration correction was applied to the data. Error (Source_{Estimated} – Source_{True}) represents the error (‰) between the *estimated* source values and the *true* source values. ΔN_2O represents the average concentration difference (ppb) between the highest concentration in each experiment and the *background* based on the measurements recorded by each analyzer.

Experiment	$\Delta N_2 O$	Instrument				Error (Sources , Sources)					
sequence	[ppb]			OA-ICOS I			-	Ellor (Sol	ITCEEstimated -	Source _{True})	
		S15NTG F0/ 1	S15N18 F0/ 1	SISN Thulk FO/ 1			$\delta^{15} N^{\alpha}$	$\delta^{15}N^{\beta}$	$\delta^{15}N^{bulk}$	SP	$\delta^{18}O$
	$0^{10} N^{\alpha} [\%_0] = 0^{10} N^{\alpha} [\%_0] = 0^{10} N^{\alpha} M [\%_0] = SP [\%_0] = 0^{10} O [\%_0]$	ð ¹⁸ U [‰]	[‰]	[‰]	[‰]	[‰]	[‰]				
1 – Enriched	31.42	$71.15\ \pm 8.44$	$80.04\ \pm 7.93$	$75.62 \ \pm 6.97$	-8.84 ± 8.74	$131.2 \ \pm 16.16$	0.89	-5.84	-2.45	6.79	2.35
2-Depleted	31.26	$-37.4\ \pm 10.91$	$-37.19 \ \pm 9.34$	$-36.59\ \pm 8.78$	$0.28 \ \pm 10.02$	$58.65\ \pm 8.78$	7.27	-4.32	2.18	12.08	33.40
3-Depleted	694.22	$-18.53 \ \pm 1.19$	$-22.7\ \pm 0.56$	$-20.56 \ \pm 0.60$	$4.27\ \pm 1.46$	$26.49 \ \pm 1.41$	7.21	0.92	4.12	6.39	-4.85
4-Enriched	701.46	$54.64 \ \pm 1.03$	$57.21 \ \pm 0.63$	$55.94 \ \pm 0.56$	$-2.51 \ \pm 1.30$	$107.3 \ \pm 2.06$	1.43	-0.75	0.35	2.24	4.75
5-Enriched	9831.51	$53.3\ \pm 0.07$	$56.62 \ \pm 0.49$	$54.96 \ \pm 0.26$	$\textbf{-3.33} \hspace{0.1in} \pm \hspace{0.1in} \textbf{0.48}$	$105.1 \ \pm 1.17$	2.88	2.54	2.71	0.33	5.88
6 – Depleted	9933.59	$-26.46 \ \pm 0.16$	$-24.02 \ \pm 0.70$	$-25.26 \ \pm 0.42$	$\textbf{-2.35}\ \pm 0.56$	$31.49 \ \pm 1.21$	-2.11	-1.08	-1.62	-0.94	-0.30
				CRDS I							
1 – Enriched	29.37	55.66 ± 4.27	86.39 ± 5.76	70.75 ± 4.15	$\textbf{-30.73} \pm 6.05$	134.5 ± 3.81	-14.60	0.51	-7.32	-15.10	5.65
2 - Depleted	29.21	$\textbf{-61.43} \pm 8.86$	$\textbf{-40.32} \pm 5.10$	$\textbf{-49.69} \pm 5.57$	$\textbf{-22.37} \pm 8.29$	22.32 ± 6.54	-16.76	-7.45	-10.92	-10.57	-2.93
3-Depleted	646.99	$\textbf{-23.14} \pm 0.86$	$\textbf{-26.89} \pm 0.73$	$\textbf{-25.05} \pm 0.59$	3.72 ± 1.15	26.89 ± 0.78	2.60	-3.27	-0.37	5.84	-4.45
4-Enriched	651.93	56.83 ± 0.74	57.41 ± 0.8	57.07 ± 0.53	$\textbf{-0.69} \pm 1.21$	103.8 ± 0.95	3.62	-0.55	1.48	4.06	1.27
				CRDS II							
1 - Enriched	29.55	68.45 ± 3.15	103.53 ± 5.16	86.01 ± 3.92	-34.52 ± 3.7	140.05 ± 3.52	-1.81	17.65	7.94	-18.89	11.21
2-Depleted	29.41	$\textbf{-52.51} \pm 7.94$	$\textbf{-29.32} \pm 5.47$	$\textbf{-40.65} \pm 5.72$	$\textbf{-23.1}\pm6.84$	25.76 ± 7.31	-7.84	3.55	-1.88	-11.30	0.51
3-Depleted	620.28	$\textbf{-28.49} \pm 0.30$	$\textbf{-24.8} \pm 0.22$	$\textbf{-26.59} \pm 0.19$	$\textbf{-3.61} \pm 0.35$	28.23 ± 0.24	-2.76	-1.18	-1.91	-1.49	-3.11
4-Enriched	626.24	50.94 ± 0.30	58.78 ± 0.21	54.87 ± 0.21	$\textbf{-7.76} \pm 0.29$	104.75 ± 0.25	-2.27	0.82	-0.72	-3.01	2.25
				QCLAS I							
1 - Enriched	30.52	185.3 ± 84.81	157.7 ± 74.91	172.3 ± 68.04	26.11 ± 59.38	-	115.0	71.81	94.27	41.74	-
2-Depleted	30.48	106.5 ± 68.41	103.3 ± 111.5	102.7 ± 82.67	2.23 ± 76.5	-	151.1	136.2	141.5	14.03	-
3-Depleted	648.35	$\textbf{-32.8} \pm \textbf{4.83}$	$\textbf{-27.92} \pm 5.12$	$\textbf{-30.33} \pm \textbf{4.67}$	$\textbf{-3.3}\pm2.74$	-	-7.07	-4.30	-5.65	-1.18	-
4-Enriched	654.63	46.36 ± 5.03	34.08 ± 2.84	40.29 ± 3.55	12.85 ± 3.19	-	-6.85	-23.88	-15.30	17.60	-
5-Enriched	9231.17	56.8 ± 0.17	49.17 ± 0.63	52.99 ± 0.33	7.51 ± 0.61	-	6.38	-4.91	0.74	11.17	-
6 - Depleted	9323.02	-27.44 ± 0.48	-22.49 ± 0.53	-25.02 ± 0.39	$\textbf{-4.96} \pm \textbf{0.61}$	-	-3.09	0.45	-1.38	-3.55	-

				TREX-QCLAS I							
1 – Enriched	32.38	73.95 ± 1.71	86.49 ± 1.80	80.20 ± 1.27	-12.54 ± 1.85	134.3 ± 1.81	0.48	-4.64	-2.10	5.12	0.55
2 - Depleted	34.14	-44.84 ± 0.83	-41.78 ± 1.83	-43.31 ± 1.47	-3.02 ± 2.08	25.96 ± 1.33	3.55	-7.09	-1.79	10.64	1.90
				GC-IRMS							
1 – Enriched	30.14	75.31 ± 8.78	88.49 ± 13.71	81.93 ± 10.19	-13.24 ± 10.73	144.2 ± 12.88	5.06	2.61	3.86	2.39	15.35
2 - Depleted	30.43	-40.50 ± 4.63	-36.49 ± 5.61	-38.48 ± 2.34	-4.02 ± 9.17	24.12 ± 3.46	4.17	-3.62	0.27	7.77	-1.13
3-Depleted	668.62	-24.00 ± 0.23	$\textbf{-24.55} \pm 0.25$	-24.28 ± 0.12	0.55 ± 0.40	29.77 ± 0.27	1.74	-0.93	0.40	2.67	-1.57
4-Enriched	674.33	53.48 ± 0.19	56.05 ± 0.23	54.76 ± 0.16	-2.57 ± 0.27	106.7 ± 0.26	0.26	-1.91	-0.82	2.17	4.24
5-Enriched	8540.91	55.62 ± 0.33	59.25 ± 0.73	57.44 ± 0.44	-3.63 ± 0.72	111.5 ± 0.51	5.20	5.17	5.19	0.03	12.37
6 – Depleted	8958.53	$\textbf{-25.35} \pm 0.29$	$\textbf{-24.43} \pm 0.32$	$\textbf{-24.89} \pm 0.28$	$\textbf{-0.92} \pm 0.24$	31.38 ± 0.39	-1.00	-1.49	-1.24	0.49	-0.41

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 ${}^{14}N^{15}N^{16}O / {}^{14}N^{14}N^{16}O$) 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.

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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	Line strength	Branch / rotational	Lower-state	
	(cm^{-1})	(cm ⁻¹ /(molecule cm ⁻	quantum number	energy (cm ⁻¹)	
		²))			
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			