Isotopically characterised N\textsubscript{2}O reference materials for use as community standards

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Funding information 
EMPIR program co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation program, Grant/Award Number: 16ENV06 Metrology for Stable Isotope Reference Standards (SIRS); H2020 Marie Skłodowska-Curie Actions, Grant/Award Number: EMPAPOSTDOCS-II; 754364; Japanese Swiss Science and Technology Program (JSPS International Fellowship for Research in Japan), Grant/Award Number: GR18108; Swiss National Science Foundation, Grant/Award Numbers: 200021_163075, 200021_166255 

Rationale: Information on the isotopic composition of nitrous oxide (N\textsubscript{2}O) at natural abundance supports the identification of its source and sink processes. In recent years, a number of mass spectrometric and laser spectroscopic techniques have been developed and are increasingly used by the research community. Advances in this active research area, however, critically depend on the availability of suitable N\textsubscript{2}O isotope Reference Materials (RMs). 

Methods: Within the project Metrology for Stable Isotope Reference Standards (SIRS), seven pure N\textsubscript{2}O isotope RMs have been developed and their $^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O, $^{17}$O/$^{16}$O ratios and $^{15}$N site preference (SP) have been analysed by specialised laboratories against isotope reference materials. A particular focus was on the $^{15}$N site-specific isotopic composition, as this measurand is both highly diagnostic for source appointment and challenging to analyse and link to existing scales.
Results: The established N$_2$O isotope RMs offer a wide spread in delta ($\delta$) values: $\delta^{15}$N: 0 to +104‰, $\delta^{18}$O: +39 to +155‰, and $\delta^{15}$NSP: –4 to +20‰. Conversion and uncertainty propagation of $\delta^{15}$N and $\delta^{18}$O to the Air-N$_2$ and VSMOW scales, respectively, provides robust estimates for $\delta^{15}$N(N$_2$O) and $\delta^{18}$O(N$_2$O), with overall uncertainties of about 0.05‰ and 0.15‰, respectively. For $\delta^{15}$NSP, an offset of >1.5‰ compared with earlier calibration approaches was detected, which should be revisited in the future.

Conclusions: A set of seven N$_2$O isotope RMs anchored to the international isotope-ratio scales was developed that will promote the implementation of the recommended two-point calibration approach. Particularly, the availability of $\delta^{17}$O data for N$_2$O RMs is expected to improve data quality/correction algorithms with respect to $\delta^{15}$NSP and $\delta^{15}$N analysis by mass spectrometry. We anticipate that the N$_2$O isotope RMs will enhance compatibility between laboratories and accelerate research progress in this emerging field.

1 | INTRODUCTION

Since its first application by Sakae Toyoda and Naohiro Yoshida in 1999,$^3$ site-specific N$_2$O isotope analysis has been applied by many research groups to differentiate N$_2$O source and sink processes at different spatio-temporal scales (see reviews by Toyoda et al.$^2$ Ostrom et al.$^3$ Decock et al.$^4$ Denk et al.$^5$ and Yu et al.$^6$). Likewise, dual-isotope plots (e.g. $\delta^{15}$NSP/$\delta^{15}$N) or so-called “isotope mapping” approaches have been used to constrain the contributions of specific pathways, and the effect of isotope fractionation during N$_2$O reduction.$^7,8$ The informative value of N$_2$O isotope data has been markedly increased by using the data to inform biogeochemical models, providing regional and global patterns of N$_2$O losses and independent process information.$^9$–$^{12}$ Advances in applications have been accompanied and accelerated by progress in analytics, complementing the traditional high-precision isotope-ratio mass-spectrometry (IRMS)$^1,13$ by laser spectroscopic techniques, with the potential for field applicability and real-time data coverage.$^{14}$–$^{19}$

The isotopic composition of a sample is reported using the delta ($\delta$) notation, which is the relative difference in isotope ratio ($\Delta$) between a sample P and a reference material, i.e. $\delta(P/ref) = R_P/R_{ref} - 1$. For nitrogen, the $^{15}$N/$^{14}$N isotope ratio is used, $R(\text{N}^{15})/R(\text{N}^{14}) = x(\text{N}^{15})/x(\text{N}^{14})$, where x is the isotopic abundance and tropospheric N$_2$ is the international reference material for the Air-N$_2$ scale. For oxygen, the $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O ratios are used, which are related to the Vienna Standard Mean Ocean Water (VSMOW) scale. In addition, we adopt the following notation conventions: $\delta^{15}$N = $\delta^{15}$N/$^{15}$N, P/Air-N$_2$) (average of both nitrogen atoms) and $\delta^{18}$O = $\delta^{18}$O/$^{16}$O, P/VSMOW). The $^{15}$N site preference (SP) is defined by the predominance of $^{15}$N substitution in the central (a) position as compared to the terminal (b) position, and calculated accordingly as $\delta^{15}$NSP = $\delta^{15}$N$^a$ – $\delta^{15}$N$^b$. All $\delta$ values in this paper are reported against Air-N$_2$ (for $^{15}$N/$^{14}$N ratios) and against VSMOW (for $^{18}$O/$^{16}$O and $^{17}$O/$^{16}$O ratios).

Further progress in N$_2$O isotope research critically depends on the compatibility of laboratory results.$^{20}$ To achieve this, individual laboratories have to implement a traceability chain, i.e. a hierarchy of reference materials which descends with increasing uncertainty, linking the isotopic composition of primary RMs used to realise the respective scale, through secondary standards and working laboratory standards to a sample.$^{21}$ Generally, two RMs with distinct $\delta$ values should be used for calibration purposes, following the two-point data normalisation requirement. However, primary RMs and secondary scale anchors for $\delta^{15}$N (ammonium sulfate, potassium nitrate) as well as $\delta^{17}$O and $\delta^{18}$O (water) have a different chemical identity than N$_2$O sample gas. Thus, a chemical conversion reaction$^{20}$ has to be implemented prior to analysis, which requires specialised laboratories.

The synthesis of N$_2$O by thermal decomposition of isotopically characterised ammonium nitrate (NH$_4$NO$_3$) has been suggested as an approach to link the position-dependent nitrogen isotopic composition of N$_2$O to the Air-N$_2$ scale.$^1$ The basic concept of this technique is that the nitrogen atom at the α-position of of the formed N$_2$O originates from NO$_3^-$, while the β-nitrogen comes from NH$_4^+$. The validity of the NH$_4$NO$_3$ decomposition technique has been confirmed$^{23,24}$ but its accuracy for the calibration of $\delta^{15}$N$^\alpha$ and $\delta^{15}$N$^\beta$ was found to be limited by non-quantitative NH$_4$NO$_3$ decomposition in combination with substantially different isotope enrichment factors of $\sim$4 or $\sim$19‰ for the conversion of the NO$_3^-$ or NH$_4^+$ nitrogen atom into the α- or β-position of the N$_2$O molecule.$^{25}$ To overcome such difficulties, two new N$_2$O reference gases, USGS51 and USGS52, recently became available with assigned $\delta$ values based on a preliminary assessment by Naohiro Yoshida and Sakae Toyoda (Tokyo Institute of Technology).$^{26,27}$ However, the two standards offer only a small range of $\delta^{15}$N and $\delta^{18}$O values (< 1%), which is not suitable for a two-point calibration approach.
In the present study, we report the development of additional N₂O RMs within the framework of the European Metrology Programme for Innovation and Research (EMPIR) 16ENV06 project ‘Metrology for Stable Isotope Reference Standards (SIRS)’. The target isotopic composition of N₂O RMs was selected according to discussions at a stakeholder workshop at the 19th GGMT conference at Empa (29 August 2017). The focus of this study is to extend the range of isotopic composition of N₂O RMs compared to RMs presented in Ostrom et al. and to provide additional δ¹⁷O data in order to improve data quality/correction algorithms with respect to δ¹⁵NSP and δ¹⁵N analysis by mass spectrometry. In addition, the link of δ values to the international isotope-ratio scales was revisited.

2 | EXPERIMENTAL

The main purpose of this study is the provision of isotopically characterised N₂O RMs, covering an extended range of delta values as compared to existing gases. Figure 1 provides a schematic overview on the links established within this study between existing international RMs and the novel gaseous N₂O RMs.

In section 2.1 (‘left branch’ of Figure 1), ¹⁵N/¹⁴N isotope ratios on the Air-N₂ scale were propagated from NH₄⁺ and NO₃⁻ salts supplied by IAEA/USGS, through isotopic analysis of gravimetrically prepared NH₄NO₃ salts (section 2.1.2) and their thermal decomposition (section 2.1.3), to δ¹⁵N(N₂O) / δ¹⁵N(N₂O) in the novel gases.

Table 1: International RMs applied in this study for the analysis of δ¹⁵N(NH₄NO₃), δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) in NH₄NO₃ salts (section 2.1.2) and δ¹⁵N as well as δ¹⁸O in N₂O RMs (section 2.2). Values are taken from Brand et al. and Ostrom et al. and reported in ‰.

| RMs         | δ¹⁵NAir-N₂ | σ | δ¹⁸OVSMOW | σ |
|-------------|------------|---|-----------|---|
| IAEA-N-1    | NH₄SO₄    | +0.43 | 0.07 | - | - |
| IAEA-N-2    | NH₄SO₄    | +20.41 | 0.12 | - | - |
| USGS25      | NH₄SO₄    | -30.41 | 0.27 | - | - |
| USGS26      | NH₄SO₄    | +53.75 | 0.24 | - | - |
| IAEA-NO-3   | KNO₃      | +4.72  | 0.13 | +13.2 | - |
| USGS32      | KNO₃      | +180   | 0 | +25.4 | 0.2 |
| USGS34      | KNO₃      | -1.8   | 0.1 | -27.78 | 0.37 |
| USGS35      | NaNO₃     | +2.7   | 0.1 | +56.81 | 0.31 |
| USGS40      | L-glutamic acid | -4.52 | 0.06 | - | - |
| USGS51      | N₂O       | +1.21  | 0.21 | +41.45 | 0.34 |
| USGS52      | N₂O       | +0.29  | 0.25 | +40.80 | 0.40 |
N₂O RMs. The international RMs applied in this study are listed in Table 1. To provide a reliable link between the Air-N₂ scale and the N₂O site-specific isotopic composition, the NH₄NO₃ decomposition reaction was optimised for high yield, reproducibility, and N₂O purity (see section 2.1.3). Following the recommended two-point calibration approach, a number of NH₄NO₃ salts, ranging from ¹⁵N-depleted to ¹⁵N-enriched, were prepared (see section 2.1.1), decomposed, and analysed.

In section 2.2 (“right branch” of Figure 1), preparation of N₂O RMs and analysis by expert laboratories for δ¹⁵N(N₂O), δ¹⁸O(N₂O), δ¹⁵O(N₂O) and δ¹⁸O(N₂O) is described. In one laboratory (Empa), δ¹⁵N(N₂O) in the N₂O RMs was linked to the Air-N₂ scale making use of the traceability chain established in section 2.1. Links to scale applied in the other laboratories are independent and are described in detail in the respective experimental sections.

2.1 | Re-evaluation of NH₄NO₃ thermal decomposition technique to propagate δ¹⁵N(NO₃⁻)/δ¹⁵N(NH₄⁺) to δ¹⁵N(N₂O)/δ¹⁵N(N₂O)

2.1.1 | Preparation of NH₄NO₃ salts

Six NH₄NO₃ salts (S1–S6), covering a wide range of δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) values, were produced by gravimetric mixing of five commercially available NH₄NO₃ salts (A–E): A: unlabelled NH₄NO₃ (purity >98%, K299.1, Carl Roth GmbH, Karlsruhe, Germany), B: ¹⁵N-enriched, were prepared (see section 2.1.1), decomposed, and analysed. Six NH₄NO₃ salts (S1–S6) were sent together with international reference materials ((NH₄)₂SO₄, NaNO₃, KNO₃) provided by the IAEA (International Atomic Energy Agency, Vienna, Austria) and by USGS (U.S. Geological Survey, Reston, USA) (Table 1) to eight isotope laboratories. Table 3 provides basic information on the analytical techniques applied by the laboratories. Details on the analytics are given in the supporting information (Supplementary Method 1).

2.1.2 | Analysis of NH₄NO₃ salts for δ¹⁵N(NH₄NO₃), δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) against IAEA and USGS RMs

Subsamples of the prepared NH₄NO₃ salts (S1–S6) were sent to eight isotope laboratories (Table 3) or around 100 g (S1–S5) or around 40 g (S6) were gravimetrically mixed with appropriate amounts of salts B, C, D, and E to obtain the desired isotopic composition. The salt mixtures were dissolved in deionised water (Milli-Q Advantage A10, Millipore AG, Switzerland), recrystallised, dried, and then stored in air-tight sample containers. The isotopic homogeneity of S1–S6 was confirmed by repeated IRMS analysis (MPI-BGC), demonstrating δ¹⁵N(NH₄NO₃) values within ±0.2‰ (n = 10).

δ¹⁵N(NH₄NO₃), δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) results from all laboratories were calibrated using the provided international IAEA and USGS reference materials, with δ¹⁵N values and uncertainties according to Brand et al.²⁹ and references cited therein. The uncertainty of laboratory results (σ_cal) was estimated from the uncertainty (σ_i) in the linear calibration function (Equation 1), considering the uncertainty in IAEA and USGS standards and their analyses, as well as the uncertainty (σ_meas) in δ¹⁵N_meas, following the law of error propagation (Equation 2).³⁹⁻⁴¹

\[
\delta^{15}N_{\text{meas}} = (\delta^{15}N_{\text{cal}} \pm \sigma_{\text{cal}}) \pm \sigma_{\text{meas}}
\]

\[
\sigma_{\text{cal}} = \sqrt{(\sigma_{\text{meas}})^2 + (\sigma_{\text{meas}})^2 + \sigma_{\text{meas}}^2}
\]

Results (δ¹⁵N_cal, σ_cal) from individual laboratories i were combined to a weighted mean value (δ¹⁵N_weighted, Equation 3) with an uncertainty (σ_weighted, Equation 4)²²:

\[
\delta^{15}N_{\text{weighted}} = \left( \frac{\delta^{15}N_{\text{cal,1}}}{\sigma_{\text{cal,1}}^2} + \frac{\delta^{15}N_{\text{cal,2}}}{\sigma_{\text{cal,2}}^2} + \cdots \right) \times \sigma_{\text{weighted}}^2
\]
\[ \sigma_{\text{weighted}} = \sqrt{\left( \frac{1}{\sigma_{\text{cal},1}} \right)^2 + \left( \frac{1}{\sigma_{\text{cal},2}} \right)^2 + \ldots} \] (4)

2.1.3 | NH₄NO₃ (S1–S6) thermal decomposition to N₂O (S1-N₂O–S6-N₂O)

Aliquots of approximately 1.0 g (12.5 mmol) of NH₄NO₃ salts (S1–S6) were weighed into round-bottomed glass flasks with a break-seal (150 mL, borosilicate glass, Willi Möller AG, Zürich, Switzerland). In a variant of the NH₄NO₃ decomposition reaction according to Szabò et al., 43 1.4 g NH₄HSO₄ (>99.99%, Art. No. 455849-100G, Sigma Aldrich GmbH, Buchs, Switzerland) and 0.2 g (NH₄)₂SO₄ (>99.5%, Art. No. 09978-500G, Sigma Aldrich GmbH, Buchs, Switzerland) were added. Adding surplus NH₄⁺ salt will lead to a loss in δ¹⁵N information but was included to test if very high reaction yields can be achieved, which might still be attractive. Therefore, for S1, both variants (with/without NH₄HSO₄/(NH₄)₂SO₄) were tested, while for S2–S6 only decomposition without NH₄⁺ addition was performed. Thereafter, the flasks were evacuated (<10⁻¹ mbar) and flame-sealed. The sealed flasks were placed in a circulating-air oven (model TSW 120 ED, Salvis AG, Reussbühl Switzerland) and heated to 270°C for 24 h.38

After the decomposition reaction, the N₂O product gas, e.g. S1-derived-N₂O (here: S1-N₂O) or S6-derived-N₂O (S6-N₂O), was purified on a vacuum manifold by cryogenic distillation. Reaction by- and side-products (e.g. H₂O, HNO₃, NH₃) were trapped at 78°C.

Table 3 Analytical techniques applied by the involved isotope laboratories for the analysis of δ¹⁵N(NH₄NO₃), δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) in NH₄NO₃ salts (S1–S6). Details on the analytics are given in the supporting information (Supplementary Method 1).

| Laboratory                  | Measurand                          | Technique                                                                                      |
|-----------------------------|------------------------------------|-----------------------------------------------------------------------------------------------|
| MPI-BGCLab (1)             | δ¹⁵N(NH₄NO₃)                       | NH₄NO₃ analysis by elemental analyser (EA)/IRMS                                               |
| UC DavisLab (2)            | δ¹⁵N(NH₄NO₃)                       | NH₄NO₃ analysis by EA/IRMS                                                                   |
| University of GhentLab (3) | δ¹⁵N(NH₄NO₃) δ¹⁵N(NH₄⁺)            | NH₄NO₃ analysis by EA/IRMS30 NH₄⁺ oxidation with BrO⁻ to nitrite (NO₂⁻), reaction with hydroxylamine (NH₂OH) to N₂O; purge-and-trap (PT)-IRMS analysis31 |
| University of PittsburghLab (4) | δ¹⁵N(NH₄NO₃) δ¹⁵N(NO₃⁻)            | NO₃⁻ conversion into N₂O by denitrifier method; PT-IRMS analysis32,33                           |
| UEF-BGCLab (5)             | δ¹⁵N(NH₄⁺)δ¹⁵N(NO₃⁻)               | NH₃ microdiffusion on acid-impregnated glass fibre filter, followed by EA/IRMS analysis35     |
| University of ViennaLab (6) | δ¹⁵N(NH₄⁺)δ¹⁵N(NO₃⁻)               | NH₃ microdiffusion on acid-impregnated glass fibre filters, followed by EA/IRMS analysis35   |
| Tokyo Institute of TechnologyLab (7) | δ¹⁵N(NH₄⁺)δ¹⁵N(NO₃⁻)            | NO₃⁻ reaction with VCl₃ and NaN₃ under acidic conditions to N₂O; PT-IRMS analysis35          |
| HydroisotopeLab (8)        | δ¹⁵N(NH₄⁺) δ¹⁵N(NO₃⁻)              | NH₄⁺ oxidation with LiBrO to N₂; IRMS analysis                                                 |

No. 09978-500G, Sigma Aldrich GmbH, Buchs, Switzerland) were added. Adding surplus NH₄⁺ salt will lead to a loss in δ¹⁵N information but was included to test if very high reaction yields might be achieved, which might still be attractive. Therefore, for S1, both variants (with/without NH₄HSO₄/(NH₄)₂SO₄) were tested, while for S2–S6 only decomposition without NH₄⁺ addition was performed. Thereafter, the flasks were evacuated (<10⁻¹ mbar) and flame-sealed. The sealed flasks were placed in a circulating-air oven (model TSW 120 ED, Salvis AG, Reussbühl Switzerland) and heated to 270°C for 24 h.38 After the decomposition reaction, the N₂O product gas, e.g. S1-derived-N₂O (here: S1-N₂O) or S6-derived-N₂O (S6-N₂O), was purified on a vacuum manifold by cryogenic distillation. Reaction by- and side-products (e.g. H₂O, HNO₃, NH₃) were trapped at −78°C.
(dry ice/ethanol bath); N₂O was trapped at –196°C (liquid N₂) in a coiled stainless-steel tube, while N₂ and O₂ (side products) were removed by evaporation with an oil-sealed rotary vane pump (RV3, Edwards Ltd, Crawley, UK). Thereafter, the N₂O product was condensed into 10 mL stainless-steel flasks (CS-20181323-ARBOR, ARBOR Fluidtec AG, Wohlen, Switzerland) under liquid-nitrogen cooling. The cryogenic extraction was repeated five times to fully capture the produced N₂O. Finally, the N₂O yield was determined gravimetrically (XP205 analytical balance, Mettler Toledo AG, Greifensee, Switzerland). The N₂O purity, i.e. the absence of IR-active impurities (<5 μmol mol⁻¹ NO, <1 μmol mol⁻¹ NO₂, and <0.5 μmol mol⁻¹ NH₃), was confirmed by FTIR spectroscopy (Gasmet CX4000 FTIR gas analyser, Temet Instruments Oy, Helsinki, Finland). The distillation procedure (e.g. the trap size and the timing) was optimised for quantitative removal of N₂ (<0.01%) and N₂O recovery (>99.4%), using different gravimetric mixtures of high-purity N₂O and N₂ (Messer Schweiz, Lenzburg, Switzerland).

Test for consistency of NH₄NO₃ decomposition reaction

First, the consistency of the NH₄NO₃ decomposition reaction across the large range of δ values (15N-depleted to highly 15N-enriched in S1–S6 for both salts and N₂O) was tested. In detail, such tests were made by comparing δ¹⁵N of NH₄NO₃-derived N₂O gases (S1-N₂O–S6-N₂O) with the δ¹⁵N(NO₃⁻) of substrate NH₄NO₃ salts (S1–S6) and δ¹⁵N with δ¹⁵N(NH₄⁺), respectively. While the link provided by the NH₄NO₃ decomposition reaction was assumed to be valid across a wide range of δ values, the analytics involved in δ¹⁵N(NO₃⁻) or δ¹⁵N(NO₃⁻) analysis might display non-linearities.

For this consistency test, the N₂O gases S2-N₂O, S3-N₂O, S5-N₂O and S6-N₂O were analysed together with S1-N₂O and S4-N₂O using the QCLAS analyser (section 2.2.2). S1-N₂O and S4-N₂O were selected as calibration gases, as they differ substantially in delta values (>50‰ in δ¹⁵N) and in preliminary experiments displayed a consistent offset between δ¹⁵N(N₂O), δ¹⁵N(N₂O) and δ¹⁵N(NH₄⁺) values (data not shown). For actual δ¹⁵N and δ¹⁵N of S1-N₂O and S4-N₂O, known δ¹⁵N(NO₃⁻) and δ¹⁵N(NH₄⁺) values of the respective NH₄NO₃ salts were adopted and no correction for fractionation effects due to incomplete decomposition or branching isotope effects due to N₂ production was applied. The uncertainty of actual δ¹⁵N and δ¹⁵N for S1-N₂O and S4-N₂O was estimated from the uncertainty of weighted mean δ¹⁵N(NO₃⁻) and δ¹⁵N(NH₄⁺) values (Table S5) and the standard deviation of δ¹⁵N and δ¹⁵N analysis for repeated decomposition experiments using the law of error propagation.

Measured δ¹⁵N values of S1-N₂O and S4-N₂O and actual values, i.e. δ¹⁵N(NO₃⁻) of the educt NH₄NO₃ salts S1/S4, were used to define a linear calibration function (Equation 1). Then, δ¹⁵Ncal values were calculated from measured δ¹⁵N values of S2–N₂O, S3–N₂O, S5–N₂O and S6–N₂O using this correction function. The combined uncertainty in δ¹⁵Ncal values was calculated from the uncertainty in the actual δ¹⁵N values and the analyses of S1–N₂O and S4–N₂O, as well as the uncertainty in the measured δ¹⁵Nα of the N₂O gases S2–N₂O, S3–N₂O, S5–N₂O and S6–N₂O, in accordance with Equation 2. Finally, the agreement of δ¹⁵Ncal values (Equation 1) of the individual N₂O gases (S1-N₂O–S6-N₂O) was tested against the actual δ¹⁵Nα values, i.e. the δ¹⁵N(NO₃⁻) of the respective NH₄NO₃ salts (S1–S6). The same procedure was applied to δ¹⁵N₀ and δ¹⁵N₁.

2.2 | Preparation of N₂O RMs and analysis for δ¹⁵N(N₂O), δ¹⁸O(N₂O), δ¹⁷O(N₂O) and δ¹⁵NSP(N₂O)

2.2.1 | Preparation of N₂O RMs

Currently available commercial N₂O gases offer only limited isotopic variability. Therefore, high-purity N₂O (99.999%, Linde, Germany) was supplemented with defined amounts of ¹⁵N-enriched/¹⁵N-depleted and ¹⁸O-enriched N₂O dopant gas using a ten-port two-position valve (EH2C10WEPH, Valco Instruments Inc., Schenkon, Switzerland) with sample loops of different volumes (Table 4). The gas was transferred into evacuated Luxfer aluminium cylinders (3 L, 10 L, 20 L) with ROTAREX valves (Matar, Mazzano, Italy) to a final filling pressure below 45 bar to avoid condensation, given that the cylinder temperature remains above 15°C.

The dopant gases were commercial ¹⁵N¹⁴NO and ¹⁴N¹⁵NO (isotopic purity >98%, Cambridge Isotope Laboratories Inc., Tewksbury, USA), as well as ¹⁸O-enriched N₂O (93.25 ± 0.10‰ NN¹⁶O, 63.75 ± 0.76‰ NN¹⁸O) and ¹⁵N-depleted N₂O (δ¹⁵N = (−2.54 ± 0.005)‰, δ¹⁵N₀ = (−162.21 ± 0.03)‰, δ¹⁸O = (−38.92 ± 0.03)‰), both produced and characterised at Empa. Details on the production and analysis of ¹⁸O-enriched N₂O and ¹⁵N-depleted N₂O are provided in the supporting information (Supplementary Method 2). N₂O RMs were provided to laboratories in 50 mL (Lab TT, Lab UEA) or 150 mL (Lab MPI) stainless-steel flasks (CS-07291113-ARBOR, Arbor Fluidtec AG, Wohlen, Switzerland) for isotopic analysis.

2.2.2 | Analysis of N₂O RMs for δ¹⁵Nα and δ¹⁵N₀ by QCLAS at Empa (Lab Empa)

For analysis of δ¹⁵Nα, δ¹⁵N₀ and δ¹⁸O in the N₂O gases, a QCLAS spectrometer (Aerodyne Research Inc., Billerica, MA, USA) equipped with a continuous-wave quantum cascade laser (cw-QCL) with spectral emission at 2203 cm⁻¹ and an astigmatic Herriott multi-pass absorption cell (204 m path length) was applied. Prior to analysis, pure N₂O gases (e.g. RM1–RM6, S1-N₂O–S6-N₂O) were diluted to around 50 μmol mol⁻¹ using one cylinder of synthetic air (20.5 ± 0.5)% O₂ in N₂, Messer Schweiz AG, Switzerland) into 2 L high-pressure stainless-steel cylinders (Luxfer, Messer Schweiz AG, Switzerland) using a ten-port two-position valve (EH2C10WEPH with a 1 mL sample loop, Valco Instruments Inc., Schenkon, Switzerland). A singular cylinder of synthetic air was used for all experiments to minimise differences in the oxygen content, which would otherwise affect pressure broadening of absorption lines, result in differences in apparent
Overview of N₂O RMs produced from high-purity N₂O supplemented with ¹⁵N-enriched/¹⁵N-depleted and ¹⁸O-enriched N₂O

| Characteristic | High-purity N₂O | ¹⁵N¹⁴NO | ¹⁴N¹⁵NO | NN¹⁸O | ¹⁵N¹⁰-depl. N₂O |
|----------------|------------------|---------|---------|-------|-----------------|
| RM1A/RM1B      | High-purity N₂O  | X       |         |       |                 |
| RM2            | Ambient isotopic composition | X |         | X     |                 |
| RM3A/RM3B      | ¹⁵N⁻¹⁸O-enriched; no SP | X |         | X     |                 |
| RM4            | ¹⁵N⁻¹⁸O-highly enriched; no SP | X |         | X     |                 |
| RM5            | ¹⁵N-enriched; SP | X       |         | X     |                 |

Isotopologue mole fractions and increase uncertainties. The selection of synthetic air as diluent is somewhat arbitrary and not meant to represent an alternative for a full-air matrix for high-accuracy ambient N₂O isotope analysis, which would enclose noble and trace gases depending on the analytics and accuracy requirements.

The spectroscopically determined isotope ratios were related to the isotope-ratio scales realised by Toyoda et al.² through the analysis of calibration gases CG1 (δ¹⁵N₀ = (+25.73 ± 0.24)‰, δ¹⁵N₀ = (+25.44 ± 0.36)‰, δ¹⁸O₀ = (+35.86 ± 0.22)%o) and CG2 (δ¹⁵N₀ = (−84.59 ± 0.25)%o, δ¹⁵N₀ = (−46.11 ± 0.43)%o, δ¹⁸O₀ = (+27.37 ± 0.11)%o). The isotopic composition of the calibration gases had been previously analysed by Sakae Toyoda at the Tokyo Institute of Technology using their analytical technique as a link to the international scales.

For the analysis of N₂O RMs by QCLAS, the site-specific isotopic information provided by NH₄NO₃-derived N₂O gases S1-N₂O (δ¹⁵N₀ = (−1.41 ± 0.21)%o, δ¹⁵N₀ = (+0.33 ± 0.12)%o) and S4-N₂O (δ¹⁵N₀ = (+52.36 ± 0.15)%o, δ¹⁵N₀ = (+53.06 ± 0.16)%o) was propagated to the N₂O RMs (RM1–RM5). For this, the N₂O RMs were analysed together with S1-N₂O and S4-N₂O, as described in the preceding section, to propagate the moiety-specific isotopic composition defined by S1 and S4 to the novel RMs (Equation 1). An uncertainty assessment was conducted according to Equation 2 including uncertainties of S1-N₂O and S4-N₂O, as discussed above, their analyses, and the analyses of RMs.

### 2.2.4 Analysis of N₂O RMs for δ¹⁵N and δ¹⁸O by EA/IRMS and DI-IRMS at MPI-BGC (Lab MPI)

**Analysis for δ¹⁵N by EA/IRMS (MPI-I)**

δ¹⁵N values of the N₂O RMs were determined using a modified EA/IRMS system (EA 1110 CHN combustion analyzer, CE Instruments Ltd, Wigan, UK; Delta plus isotope ratio mass spectrometer, Thermo Fisher Scientific, Bremen, Germany). The system and the method used have been described by Sperlich et al.⁴⁶ The δ¹⁵N values of the sample N₂O were scaled to IAEA-N-1 and USGS32. In addition to the sample gases, an in-house standard N₂O gas NINO was analysed in each sample run, which was used as an anchor for δ¹⁵N measurements by DI-IRMS. USGS40, and the in-house standards Ali-j3 (δ¹⁵N = (−1.51 ± 0.1)%o; acetic anilide) and Caf-j3 (δ¹⁵N = (−15.46 ± 0.1)%o; caffeine), were analysed in each daily run as quality controls, but not used for data correction.

**Analysis for δ¹⁵N and δ¹⁸O by dual-inlet IRMS (MPI-II)**

The N₂O RMs were analysed twice (September 2019, February 2021) on a DI-IRMS system (MAT253, Thermo Fisher Scientific, Bremen,
In addition, USGS52 was calculated using the values reported by Ostrom et al.47 Thus, we scaled the results of laboratories. Therefore, we scaled the N 2O RM samples and a N 2O-MG-6.0 working reference using separately subsampled flasks. We note that the δ15N and δ18O measurements of the sample gas (N2O RM) and the N2O standards, gases (NINO, USGS51) and from the standard deviation for repeated measurements of the sample gas (N2O RM) and the N2O standards, following the law of error propagation.

2.2.5 Analysis of N2O RMs for δ15N, δ18O and δ17O by IRMS at UEAB (Lab UEAB)

Analysis for δ15N, δ18O and δ17O by GC/IRMS (UEA-I)

The N2O RM samples and a N2O-MG-6.0 working reference (99.9999% chemical purity, N2O-MG-6.0, Messer-Griesheim, Krefeld, Germany) were diluted to 0.09 mmol mol\(^{-1}\) in N2 (zero grade, BOC, UK), filled into 20 mL serum vials (Wheaton, Fisher Scientific, Loughborough, UK) and analysed for 45δ(N2O) and 46δ(N2O) on a custom-built automated cryogenic extraction and purification system comprised of an autosampler, a valve system, and PoraPLOT Q pre- and main columns (Agilent Technologies, Santa Clara, USA), coupled to a GEO 20-20 isotope ratio mass spectrometer (Sercon Ltd, Crewe, UK).

Using the same mass spectrometer, these samples were also analysed for 33δ(O2) = δ17O, 34δ(O2) = δ18O (the error of this approximation is <0.01‰) and 29δ(N2) = δ15N after cryogenic N2 extraction and decomposition to N2 and O2 with a 500 mm long pure gold tube (1.6 mm OD, 0.6 mm ID; Heimerle & Meule, Pforzheim, Germany) held at 854°C. N2 and O2 were separated directly (without further cryofocusing) on a molecular-sieve 5-Å PLOT main column (Restek, Bellefonte, USA, 30 m × 0.32 mm, 30 μm, 30°C, 1.3 mL min\(^{-1}\) (at 20°C and 1 bar, standard temperature and pressure)). The quantitative conversion of N2O was verified by swapping the molecular-sieve main column for the PoraPLOT Q main column and testing for residual N2O with the mass spectrometer. The raw δ17O and δ18O measurements were affected by scale compression. To correct for this, a logarithmic scale normalisation was applied using the δ18O value of +112.4‰ (relative to N2O-MG-6.0) derived from the 46δ(N2O) measurements of the diluted RM4 sample measured on the GEO 20-20 mass spectrometer. The same normalisation was used for δ17O as for δ18O because no N2O reference material with a calibrated δ17O value was available. No scale-normalisation was applied to the δ15N measurements.

Uncertainties were calculated using the law of error propagation from the standard deviations of replicate measurements against the working reference gas and the calibration uncertainties of the working reference gas against Air-N2 and VSMOW.42

Analysis for δ15N, δ18O and δ17O by dual-inlet IRMS (UEA-II)

The N2O RM samples were analysed for 45δ(N2O) and 46δ(N2O) with respect to the N2O working reference N2O-MG-6.0 using the dual-inlet system of a Finnigan MAT 253 isotope ratio mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The N2O-MG-6.0 working reference has been calibrated by Kaiser et al.,50 who reported values of δ15N = (+1.01 ± 0.06‰) with respect to Air-N2, as well as δ18O = (+38.45 ± 0.22‰) and δ17O = (+19.66 ± 0.11‰) with respect to VSMOW.51 Actual δ17O values of N2O RMs analysed with the Sercon GEO 20-20 were used for the data correction according to Kaiser et al.47 Uncertainties were calculated using the law of error propagation from the standard deviations of replicate measurements against the working reference gas and the calibration uncertainties of the working reference gas against Air-N2 and VSMOW.42

3 RESULTS AND DISCUSSION

3.1 Re-evaluation of the NH4NO3 thermal decomposition technique to propagate δ15N(N(OH)3)\(^-\) to δ15N(NH4\(^+\))

In the following sections, the main procedures for anchoring of δ15N\(^+\) and δ17N\(^+\) in N2O to the Air-N2 scale and calculating uncertainties are described. Section 3.1.1 details results of δ15N(NH4\(^+\)) and δ15N(NO3\(^-\)) analyses in NH4NO3 salts (S1–S6) by eight isotope laboratories against international IAEA and USGS standards. Section 3.1.2 informs about optimal conditions for NH4NO3 decomposition at high yield, repeatability, and N2O purity. To enable the two-point calibration, a number of NH4NO3 salts with different isotopic composition were produced and decomposed and the consistency of δ15N\(^+\) and δ15N\(^-\) of the N2O gases (S1-N2O–S6-N2O) and the δ15N(NH4\(^+\)) and δ15N(NO3\(^-\)) of NH4NO3 salts (S1–S6) was tested (section 3.1.3).

3.1.1 Isotopic composition of NH4NO3 salts for δ15N(NH4NO3), δ15N(NO3\(^-\)) and δ15N(NH4\(^+\))

The isotopic composition of the prepared NH4NO3 salts (S1–S6), as analysed by the eight isotope laboratories and calibrated to Air-N2 by analysis of IAEA and USGS standards, is indicated in Table 5.
In contrast, microdiffusion methods tend to underestimate $\delta^{15}$N values of both NO$_3^-$ and NH$_4^+$, which may be reflected in the $\delta^{15}$N(NH$_4^+$) values of Lab 6 but not those of Lab 5, where a similar technique was used. Conversely, systematic fractionation effects by preparation techniques should be accounted for by identical treatment (IT) of the provided IAEA and USGS standards for data correction. In summary, analysis of $\delta^{15}$N (NH$_4^+$) and $\delta^{15}$N(NO$_3^-$) is still challenging; however, the ensemble of techniques applied in this study provides good agreement with $\delta^{15}$N (NH$_4$NO$_3$) values.

### 3.1.2 Optimal reaction conditions for NH$_4$NO$_3$ thermal decomposition to N$_2$O

Under optimised reaction conditions (270°C, 24 h) and distillation procedure, an average N$_2$O yield of 93–95% was achieved for the decomposition of NH$_4$NO$_3$ salts S1–S6 (Table S1, supporting information). The yield and repeatability of the decomposition reaction are somewhat better than reported in our earlier study (91.2–93.5%) and published by Toyoda et al (90.1 ± 3.7%), n = 3; (65.6 ± 5.1%), n = 20. A further increase in the yield of the NH$_4$NO$_3$ decomposition was achieved by

#### TABLE 5 $\delta^{15}$N(NH$_4$NO$_3$) (top), $\delta^{15}$N(NO$_3^-$) (middle), and $\delta^{15}$N(NH$_4^+$) (bottom) of prepared NH$_4$NO$_3$ salts (S1–S6) analysed by different laboratories using techniques described in Table 3 and the supporting information (Supplementary Method 1). Results from individual laboratories were calibrated using international (IAEA, USGS) standards 29 and their uncertainties ($\sigma$) calculated following the law of error propagation. Laboratories: (1) MPI-BGC, (2) UC Davis, (3) University of Ghent, (4) University of Pittsburgh, (5) UEF-BGC, (6) University of Vienna, (7) Tokyo Tech, (8) Hydroisotop techniques applied in this study provides good agreement with a higher uncertainty.

| Laboratory | $\delta^{15}$N(NH$_4$NO$_3$)/‰ | $\delta^{15}$N(NO$_3^-$)/‰ | $\delta^{15}$N(NH$_4^+$)/‰ |
|------------|-------------------------------|-----------------------------|-----------------------------|
|            | S1                            | S2                          | S3                          |
|            | Lab (1)                       | Lab (2)                     | Lab (3)                     |
|            | +2.07                         | +12.95                      | +13.41                      |
|            | Lab (4)                       | Lab (5)                     | Lab (6)                     |
|            | +13.80                        | +13.47                      | +13.75                      |
|            | Lab (7)                       | Lab (8)                     | Lab (9)                     |
|            | +14.48                        | +15.73                      | +51.60                      |
|            | Lab (10)                      | Lab (11)                    | Lab (12)                    |
|            | +117.50                       | +114.33                     | +100.35                     |
|            | Lab (13)                      | Lab (14)                    | Lab (15)                    |
|            | +101.22                       | +101.08                     | +101.22                     |
|            | Lab (16)                      | Lab (17)                    | Lab (18)                    |
|            | +100.08                       | +101.08                     | +101.22                     |
|            | Lab (19)                      | Lab (20)                    | Lab (21)                    |
|            | +50.47                        | +50.47                      | +50.47                      |

*Results were not considered for calculation of weighted mean values as the applied technique is associated with a higher uncertainty.
conducting the reaction in a NH₄HSO₄–(NH₄)₂SO₄ melt (around 2%), as suggested for industrial applications by Szabó et al. This variant displayed comparable δ¹⁵N⁰ values but a loss in the δ¹⁵N⁰ information due to NH₄⁺ salt addition, and was thus not continued.

No correction was applied to δ¹⁵N⁰ and δ¹⁵N⁰ for the loss in N₂O (around 5–7%), mainly due to uncertainties in the reaction mechanisms (incomplete decomposition or side-reaction), which makes it difficult to estimate the effect on δ values. Assuming incomplete reaction accompanied by fractionation effects, according to our earlier study, a 5% reduction in yield for S1–S6 should result in 0.7/3.0/1.8‰ lower δ¹⁵N⁰/δ¹⁵N⁰/δ¹⁵N⁰ values, respectively. However, a much smaller difference in δ¹⁵N was observed when comparing results of N₂O RMs analysed by QCLAS (calibrated by NH₄NO₃ decomposition) with IRMS analyses. Therefore, our assumption is that the decrease in yield is at least partly caused by a “branching” side reaction, e.g. nitrogen gas (N₂) production, which was observed to display higher δ¹⁵N(N₂) values. We speculate that N₂ production has a minor effect on δ¹⁵N⁰, δ¹⁵N⁰ and δ¹⁵N⁰, but the effect is expected to depend on the timing of N₂ generation, which is not known.

3.1.3 | Consistency of isotopic composition of S1-N₂O–S6-N₂O

A general goal of the current project was to provide a link to the Air-N₂ scale and to determine the N₂O site-specific isotopic composition across a wide range of δ values. Therefore, the consistency of the isotopic composition of the N₂O gases (δ¹⁵N⁰, δ¹⁵N⁰, S1-N₂O–S6-N₂O) and the NH₄NO₃ salts (δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻), S1–S6) was tested. The detailed procedure is described in section 2.1.3. In short, assuming the validity of the NH₄NO₃ decomposition reaction, measured δ¹⁵N⁰ values of S1-N₂O/S4-N₂O and actual δ¹⁵N⁰ values, i.e. δ¹⁵N(NO₃⁻) of the educt NH₄NO₃ salts S1/S4, were used to define a linear calibration function. δ¹⁵N⁰ cal values of S2-N₂O, S3-N₂O, S5-N₂O and S6-N₂O were calculated from measured δ¹⁵N⁰ using this correction function and compared against actual values (Table 6).

Results of δ¹⁵N⁰ cal/δ¹⁵N⁰ cal/δ¹⁵N⁰ cal for S2-N₂O and S3-N₂O agree within expanded uncertainties (2 x σcal, Equation 2) with the isotopic composition of the substrate NH₄NO₃ (S2, S3; Table 5). In contrast, for S5-N₂O and S6-N₂O, δ¹⁵N⁰ cal/δ¹⁵N⁰ cal/δ¹⁵N⁰ cal values of the N₂O gases show a significant deviation from δ¹⁵N(NO₃⁻)/δ¹⁵N(NH₄⁺)/δ¹⁵N(NO₃⁻) of the respective salts (S5, S6). Assuming similar fractionation effects for decomposition of all NH₄NO₃ salts (S1–S6), provided the comparable decomposition yield (Table S1, supporting information), we conclude that the deviation is caused by non-linearities either in N₂O isotope analysis by QCLAS or in δ¹⁵N(NO₃⁻) and δ¹⁵N(NH₄⁺) analyses of the NH₄NO₃ salts. The latter is more plausible, as the QCLAS analyses using the same calibration approach showed good agreement with independent IRMS measurements for N₂O RM with high ¹⁵N enrichment (see RM4, Table S2, supporting information). The observed deviations were highest for δ¹⁵N⁰ cal to δ¹⁵N(NH₄⁺) (e.g. S5), which agrees with earlier studies indicating challenges in δ¹⁵N(NH₄⁺) analysis, but this may also be due to the lack of available international standards for δ¹⁵N(NH₄⁺) that cover δ values above (+53.75 ± 0.24)%o (USGS26) and below (<−30.41 ± 0.27)%o (USGS25).

In summary, our results demonstrate consistency of the isotopic composition of the N₂O gases from around zero (S1-N₂O) to ¹⁵N-enriched (S4-N₂O) and of the substrate NH₄NO₃ salts (S1–S4). Thereby, our study covers a much larger range of δ values (> 50‰ in δ¹⁵N⁰ cal and δ¹⁵N⁰ cal) than earlier studies,¹,²,³ and provides a robust link to the Air-N₂ scale. At very high and low ¹⁵N enrichment

### Table 6 Consistency check for δ¹⁵N⁰ cal/δ¹⁵N⁰ cal/δ¹⁵N⁰ cal and δ¹⁵Ncal of N₂O gases (S2-N₂O, S3-N₂O, S5-N₂O, S6-N₂O) as analysed by QCLAS and referenced to the actual isotopic composition of S1-N₂O and S4-N₂O: against the actual isotopic composition of the same gases, expressed by δ¹⁵N(NO₃⁻), δ¹⁵N(NH₄⁺), δ¹⁵N(NO₃⁻)–δ¹⁵N(NH₄⁺) and δ¹⁵N(NO₃⁻) of the respective NH₄NO₃ substrates (S2, S3, S5, S6). For details see section 2.1.3. The number of repetitions (n) for S2-N₂O/S3-N₂O analysis is 3, for S5-N₂O and S6-N₂O it is 10. All values are reported in ‰

| Isotopic composition of N₂O as analysed by QCLAS (Sx-N₂O) | δ¹⁵N⁰ cal α | δ¹⁵N⁰ cal α | δ¹⁵N⁰ cal α | δ¹⁵N⁰ cal α | δ¹⁵N⁰ cal α | δ¹⁵N⁰ cal α |
|----------------------------------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| S2-N₂O                                                  | +13.20      | +13.99      | +0.23       | −0.79       | +0.37       | +13.60      | +13.70      | +13.07      | +0.17       | +0.36       | +0.24       | +13.34      | +0.26       | +0.31       | −50.03      | +0.24       | −1.27       | +0.30       | −50.60      | +0.30       |
| S3-N₂O                                                  | +113.53     | +103.67     | +0.24       | −9.78       | +0.41       | +108.60     | +14.04      | +0.09       | +0.19       | +0.08       | +13.85      | +0.12       | +7.31       | +114.37     | +0.15       | +101.22     | +0.34       | +13.16      | +0.37       | +107.90     | +0.13       |
| S6-N₂O                                                  | −50.47      | −49.01      | +0.08       | −1.46       | +0.21       | −49.87      | +13.69      | +0.07       | +14.26      | +0.13       | −0.57       | +0.15       | +14.14      | +14.04      | +0.09       | +14.26      | +0.13       | +14.14      | +0.15       | +14.14      | +0.13       |

| Actual isotopic composition derived from NH₄NO₃ (Sx) | δ¹⁵N(NO₃⁻) α | δ¹⁵N(NH₄⁺) α | δ¹⁵N(NO₃⁻) − δ¹⁵N(NH₄⁺) α | δ¹⁵N(NO₃⁻) α |
|--------------------------------------------------|-------------|-------------|--------------------------|-------------|
| S2                                               | +13.69      | +14.26      | +0.07                    | +14.14      |
| S3                                               | +14.04      | +14.26      | +0.09                    | +14.14      |
| S5                                               | +114.37     | +101.22     | +0.34                    | +107.90     |
| S6                                               | −50.47      | −49.01      | +0.08                    | −49.87      |
(S5-N2O, S6-N2O), the calibration approach using NH4NO3 decomposition is more challenging, probably due to less satisfying analytical accuracy of δ15N(NH4+) measurements to date. As the N2O gases S5-N2O and S6-N2O were not included in the analysis of N2O RMs, their enhanced uncertainty in δ15N(cal) and δ15N cal does not affect the data quality of N2O RMs.

3.2 Isotopic composition of N2O RMs

3.2.1 Isotopic composition of N2O RMs for δ15NISP by QCLAS and IRMS

The novel N2O RMs (RM1–RM5) were calibrated against Air-N2 by both QCLAS (Lab Empa) and IRMS (Lab TT) analyses. For QCLAS analyses, two N2O gases produced by NH4NO3 decomposition (S1-N2O, S4-N2O) were applied to define a calibration function and propagate the isotopic information of the NH4NO3 salts (δ15N(NO3−), δ15N(NH4+)) to the N2O RMs (δ15N, δ15NISP, δ15NIP and δ15N were calculated using definitions and their uncertainty estimated using the law of error propagation. In Table 7, δ15NISP values acquired by QCLAS (Lab Empa) using the calibration approach established in this study are compared with results provided by DI-IRMS (Lab TT) using a previously published link to the Air-N2 scale.1 The complete QCLAS and DI-IRMS datasets for N2O RMs are shown in Tables S2 and S3 (supporting information).

Results in Table 7 indicate a 1.5–2.7‰ offset in δ15NISP measurements by DI-IRMS (Lab TT, Tokyo Institute of Technology) and QCLAS (Lab Empa) across all N2O RMs. This is most likely attributable to the calibration of the position-dependent δ values with respect to Air-N2 via the NH4NO3 decomposition technique, which were performed independently for the two labs. Incidentally, for the NH4NO3 salts S1–S4, the δ15N(NO3−) results provided by Lab TT were always lower ((−0.63 ± 0.59)‰), while δ15N(NH4+) values were higher than the respective weighted mean values (+(0.49 ± 0.25)‰), which would lead to 1.12‰ lower δ15NISP values (Table 5).

A similar 1.5–2.0‰ difference in δ15NISP results was recently detected by Kanterová et al.24 using an independent approach, equilibrating N2O at 200 °C over a catalyst and comparing theoretical predictions with analytical results traceable to the δ15NISP scale of Lab TT. One previous comparison using an independent link to the Air-N2 scale also indicated 1.5‰ higher δ15NISP values: (+20.2 ± 2.1)‰ vs. (+18.7 ± 2.2)‰ for ambient tropospheric N2O.24 Other studies confirmed the δ15NISP measurements by the Tokyo Institute of Technology, using the NH4NO3 decomposition technique.23,25 The uncertainty of both approaches, however, was quite high.

### Table 7

|                  | Lab Empa (QCLAS) | Lab TT (DI-IRMS) | Difference δ15NISP (Lab Empa – Lab TT) |
|------------------|-----------------|-----------------|----------------------------------------|
| RM1A             | +0.47 ± 0.26    | +1.51 ± 0.95    | 0.95                                   |
| RM1B             | +0.30 ± 0.30    | +1.49 ± 0.96    | 0.96                                   |
| RM2              | +18.92 ± 0.24   | +1.92 ± 0.94    | 0.94                                   |
| RM3A             | −2.13 ± 0.37    | +2.00 ± 1.00    | 1.00                                   |
| RM3B             | +1.01 ± 0.23    | +1.69 ± 0.94    | 0.94                                   |
| RM4              | +0.00 ± 0.60    | +2.75 ± 1.11    | 1.11                                   |
| RM5              | +21.96 ± 0.33   | +1.76 ± 0.97    | 0.97                                   |

### Table 8

|                  | Lab TT | Lab MPI-I | Lab MPI-II | Lab UEA-I | Lab UEA-II | Air-N2 | δ15NSP       | δ15NSP       | δ15NSP       | δ15NSP       | δ15NSP       | Weighted mean ± σ |
|------------------|--------|-----------|------------|-----------|------------|--------|---------------|---------------|---------------|---------------|---------------|-------------------|
| RM1A             | −0.67  | +0.44     | +0.29      | +0.29     | +0.28      | 0.45   | 0.16          | 0.21          | 0.13          | 0.10          | 0.06          | −0.30 ± 0.05       |
| RM1B             | −0.53  | −0.33     | −0.20      | −0.24     | +0.19      | 0.45   | 0.14          | 0.21          | 0.10          | 0.10          | 0.06          | −0.22 ± 0.05       |
| RM2              | +7.31  | +7.09     | +6.95      | +6.73     | +6.94      | 0.45   | 0.16          | 0.21          | 0.07          | 0.06          | 0.06          | +6.88 ± 0.04       |
| RM3A             | +53.41 | +53.25    | +53.11     | +52.69    | +53.09     | 0.47   | 0.15          | 0.21          | 0.11          | 0.07          | 0.07          | +53.02 ± 0.05      |
| RM3B             | +16.45 | +16.14    | +16.09     | +15.96    | +16.08     | 0.46   | 0.14          | 0.21          | 0.17          | 0.06          | 0.06          | +16.08 ± 0.05      |
| RM4              | +104.54| +104.39   | +104.33    | +104.18   | +104.30    | 0.50   | 0.37          | 0.28          | 0.13          | 0.08          | 0.06          | +104.28 ± 0.06     |
| RM5              | +33.76 | +33.52    | +33.46     | +33.38    | +33.45     | 0.46   | 0.21          | 0.21          | 0.10          | 0.06          | 0.06          | +33.44 ± 0.05      |
We conclude that the realisation of the link between δ15Nsp and the Air-N2 scale with high accuracy is still challenging and the current realisation of the Air-N2 scale for δ15Nsp provided by USGS51 and USGS52\textsuperscript{26} may lead to too low δ15Nsp values and should be revisited in future studies.

3.2.2 Isotopic composition of N2O RMs for δ15N by IRMS

δ15N values of N2O RMs were analysed by IRMS in three different laboratories using independent links to the Air-N2 scale (Table 8). Results display a consistent offset of (±0.22 ± 0.05)% and (±0.46 ± 0.14)% between Lab MPI-I (EA/IRMS, Thermo Delta Plus, MPI-BGC) and Lab UEA-I (Sercon GEO 20-20, UEA) versus Lab TT (Thermo MAT252, Tokyo Institute of Technology). A slightly larger offset was detected for the N2O RMs USGS51 and USGS52 (Table 9) by a comparison of published provisional values (Lab TT)\textsuperscript{26} and results of MPI-II, with δ15N values of (+0.92 ± 0.22)% (USGS51) and (+0.07 ± 0.22)% (USGS52). These values fall between results published by laboratories 7 and 8 (USGS and BGC-IsoLab) in Ostrom et al.\textsuperscript{26} and are lower than results of the other laboratories, highlighting an ongoing scaling problem in δ15N(N2O) measurements. A similar offset between laboratories had already been detected earlier and was attributed to differences in the propagation of the Air-N2 scale to δ15N(N2O).\textsuperscript{20,25,26} To account for differences between individual approaches to anchor laboratory results to scales, a weighted mean value was calculated for N2O RMs.

### TABLE 9 DI-IRMS analyses of RMs, USGS51, USGS52 and NINO at MPI-BGC (MPI-II). Analyses were conducted in two campaigns in September 2019 and February 2021 on individual sample flasks. For RM1A, in each campaign three flask samples were analysed; for RM2, two flask samples were analysed in 2021. Referencing and 17O corrections considered actual Δ17O values: δ values were referenced to Air-N2 and VSMOW using the in-house working standard NINO (δ15N and USGS51 (δ18O)) and calculated according to Kaiser et al.\textsuperscript{47} n indicates the number of repeated analyses per campaign. Uncertainties for individual campaigns are calculated following the law of error propagation. For the uncertainty of the weighted mean, the uncertainty of the working standard was applied, which was considered as a conservative approach. All values are reported in ‰.

|               | Sep 2019 | Feb 2021 | Weighted mean ± σ |
|---------------|----------|----------|-------------------|
|               | Δ15N     | σΔ15N    | Δ18O              | σΔ18O   | n  |         | Δ15N              | σΔ15N |
|               |          |          |                   |         |    |         |                   |       |
| RM1A          | +0.30    | 0.22     | +39.51            | 0.35    | 9  |         | +0.29 ± 0.21      | +39.50 ± 0.34 |
| RM1B          | +0.20    | 0.23     | +39.14            | 0.36    | 3  |         | +0.19 ± 0.24      | +39.10 ± 0.38 |
| RM2           | +6.96    | 0.23     | +44.37            | 0.35    | 3  |         | +6.94 ± 0.24      | +44.32 ± 0.38 |
| RM3A          | +53.12   | 0.25     | +103.60           | 0.37    | 3  |         | +53.09 ± 0.26     | +103.50 ± 0.41 |
| RM3B          | +16.10   | 0.23     | +55.58            | 0.35    | 3  |         | +16.08 ± 0.24     | +55.55 ± 0.39 |
| RM4           | +104.33  | 0.28     | +154.93           | 0.38    | 3  |         | +104.33 ± 0.21    | +154.93 ± 0.38 |
| RM5           | +33.48   | 0.23     | +39.77            | 0.35    | 3  |         | +33.44 ± 0.25     | +39.74 ± 0.38 |
| USGS51        | +0.92    | 0.22     | +41.45\textsuperscript{a} | 0.35\textsuperscript{a} | 6  | n.a.   | +0.92 ± 0.22      | +41.45 ± 0.35 |
| USGS52        | +0.07    | 0.22     | +40.89            | 0.35    | 6  | n.a.   | +0.07 ± 0.22      | +40.89 ± 0.35 |
| NINO          | +0.54\textsuperscript{b} | 0.22\textsuperscript{b} | +39.90            | 0.35    | 6  | +0.53\textsuperscript{c} | +39.90\textsuperscript{c} | 0.38\textsuperscript{c} | 9  | +0.54 ± 0.21\textsuperscript{b} | +39.90 ± 0.34 |

n.a. not analysed.

\textsuperscript{a}Average of laboratory results from Ostrom et al.\textsuperscript{26} taken for referencing of δ18O

\textsuperscript{b}Value provided by EA/IRMS analysis (Table S4, supporting information), value taken for referencing of δ15N

\textsuperscript{c}Analysed as quality control.

### TABLE 10 δ18O analyses of N2O RMs by IRMS at the Tokyo Institute of Technology (Lab TT: Thermo MAT252), MPI-BGC (Lab MPI-II: Thermo MAT 253), and UEA (Lab UEA-I: Sercon GEO 20-20, Lab UEA-II: Finnigan MAT 253). All values are reported in ‰. The full set of analyses for all laboratories is provided in the supporting information (Lab TT: Table S3, Lab UEA-I: Table S5).

|               | Lab TT | Lab MPI-II | Lab UEA-I | Lab UEA-II | σ TT | σ MPI-II | σ UEA-I | σ UEA-II | Weighted mean ± σ |
|---------------|--------|------------|-----------|------------|------|----------|---------|---------|-------------------|
| RM1A          | +39.37 | +39.50     | +39.06    | +39.22     | 1.24 | 0.34     | 0.25    | 0.22    | +39.22 ± 0.15     |
| RM1B          | +38.86 | +39.12     | +38.77    | +38.83     | 1.24 | 0.34     | 0.24    | 0.22    | +38.86 ± 0.15     |
| RM2           | +44.08 | +44.35     | +43.69    | +44.02     | 1.25 | 0.34     | 0.24    | 0.22    | +43.96 ± 0.15     |
| RM3A          | +103.21| +103.55    | +103.04   | +102.78    | 1.30 | 0.34     | 0.27    | 0.24    | +103.04 ± 0.16    |
| RM3B          | +55.28 | +55.57     | +54.98    | +55.13     | 1.26 | 0.34     | 0.26    | 0.22    | +55.17 ± 0.15     |
| RM4           | +154.35| +154.93    | +155.17   | +153.63    | 1.36 | 0.38     | 0.39    | 0.24    | +154.25 ± 0.18    |
| RM5           | +39.50 | +39.76     | +39.43    | +39.50     | 1.29 | 0.34     | 0.24    | 0.22    | +39.52 ± 0.15     |
In contrast, differences between analytical techniques applied within one lab, thus using the same link to the scale, were smaller than offsets between laboratories: (+0.10 ± 0.04)% for Lab MPI and (+0.12 ± 0.14)% for Lab UEA. This indicates that both EA/IRMS and GC-IRMS and DI-IRMS can achieve high accuracy, provided that an accurate link to the scale and Δ17O data are available. Consistency of N2O RM flask subsamples was demonstrated using DI-IRMS (Lab MPI-II, Table 9) by replicate sampling and analysis in two campaigns in September 2019 and February 2021. For RM1A, a total of six independent flask samples were analysed; the results agreed to within 0.02% for δ15N(N2O) and 0.03% for δ18O(N2O) (2σ, data not shown).

### 3.2.3 | Isotopic composition of N2O RMs for δ18O and δ17O by IRMS

δ18O values of N2O RMs were analysed by IRMS in three different laboratories (Table 10). Results show deviations of (+0.30 ± 0.13)%o, (+0.22 ± 0.24)%o and (+0.07 ± 0.38)%o between Lab TT and Lab MPI-II, Lab UEA-I and Lab UEA-II, respectively. Differences were highest for N2O RMs with high δ18O values (RM3A, RM4), indicating a potential scaling or scale compression issue. Measurements were not completely independent for all laboratories, as the results for Lab MPI-II were referenced to average δ18O values of USGS51 in Ostrom et al.,26 which in turn was determined by seven laboratories.

δ17O values were determined by GC/IRMS at UEA (Lab UEA-I) and showed a (0.98 ± 0.27)%o offset to prototypical measurements by HR-IRMS (MAT253 ULTRA) at the Tokyo Institute of Technology (Lab TT; Table 11). Consistency of GC/IRMS results agreed with an approximation, where the δ17O was calculated from the 17O content of the 18O-labelled H2O used for 18O-labelled NH4NO3 and N2O production (certificate of analysis provided by Medical Isotopes Inc., USA; see Supplementary Method 2, supporting information). A 1% error in δ17O results in around −0.1% error in δ15N⁎, when used for correction of DI-IRMS measurements.

### 4 | CONCLUSIONS

Within the SIRS project, we established seven pure N2O isotope RMs, which were analysed by specialised laboratories against the international isotope-ratio scales. The established N2O isotope RMs offer a wide coverage of δ values (Table 12) beyond the currently available standards USGS51 and USGS52. This will enable future users to implement the recommended two-point calibration approach for IRMS instrumentation, and, upon dilution with an appropriate gas matrix, for laser spectroscopic techniques as well.19,55 In addition, the gases have been characterised for their δ17O signatures in order to improve data quality/correction algorithms with respect to δ15N⁎ and δ15N analysis by mass spectrometry. In summary, the novel N2O isotope RMs are expected to improve compatibility between laboratories and accelerate the progress in this emerging field of research.

### ACKNOWLEDGMENTS

This project, 16ENV06 Metrology for Stable Isotope Reference Standards (SIRS), received funding from the EMPIR program co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation program. Longfei Yu was supported by the Swiss National Science Foundation (SNSF; grant number 200021_163075), as well as the EMPAPPOSTDOCS-II program, which received funding from the European Union’s H2020 Marie Skłodowska-Curie Actions (EMPAPPOSTDOCS-II; grant number 754364). Kristýna Kantnerová was supported by the SNSF (grant number 200021_166255) and the bilateral Japanese Science and Technology Program (JSPS International Fellowship for Research in Japan; grant number GR18108). The authors would like to thank Daniel Zindel from ETH Zurich for providing laboratory equipment and space for the synthesis of the 18O-labelled NH4NO3. Open Access Funding provided by ETH-Bereich Forschungsanstalten.

| TABLE 11 | δ17O analyses of N2O RMs by GC/IRMS at UEA (Lab UEA-I), HR-IRMS at the Tokyo Institute of Technology (Lab TT), and predictions based on mixing of 18O-labelled N2O with commercial N2O. All values are reported in ‰ |

| Lab TT | Lab UEA-I | Predicted | σ TT | σ UEA-I |
|--------|-----------|-----------|------|---------|
| RM1A   | +21.60    | +20.33    | +20.4 | 0.08    | 0.59    |
| RM1B   | +20.88    | +20.2     | 0.56  |         |         |
| RM2    | +20.87    | +20.8     | 0.40  |         |         |
| RM3A   | +24.40    | +23.78    | +24.5 | 0.21    | 0.54    |
| RM3B   | +21.22    | +21.5     | 0.24  |         |         |
| RM4    | +27.75    | +26.71    | +27.6 | 0.35    | 0.83    |
| RM5    | +20.90    | +20.6     | 0.44  |         |         |

| TABLE 12 | Weighted mean δ values for the N2O RMs. All values are reported in ‰ |

|            | δ15N⁎   | σ | δ15N   | σ | δ18O   | σ | δ17O   | σ |
|------------|---------|---|--------|---|--------|---|--------|---|
| RM1A       | −1.04   | 0.91  | −0.30  | 0.05 | +39.22 | 0.15 | +20.33 | 0.59 |
| RM1B       | −1.19   | 0.91  | −0.22  | 0.05 | +38.86 | 0.15 | +20.88 | 0.56 |
| RM2        | +17.00  | 0.91  | +6.88  | 0.04 | +43.96 | 0.15 | +20.87 | 0.40 |
| RM3A       | −4.13   | 0.93  | −5.02  | 0.05 | +103.04 | 0.16 | +23.78 | 0.54 |
| RM3B       | −0.68   | 0.91  | +16.08 | 0.05 | +55.17 | 0.15 | +21.22 | 0.24 |
| RM4        | −2.75   | 0.93  | +104.28 | 0.06 | +154.25 | 0.18 | +26.71 | 0.83 |
| RM5        | +20.20  | 0.91  | −33.44 | 0.05 | +39.52 | 0.15 | +20.90 | 0.44 |
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