Rationale: Measurement of greenhouse gas (GHG) concentrations and isotopic compositions in the atmosphere is a valuable tool for predicting their sources and sinks, and ultimately how they affect Earth’s climate. Easy access to unmanned aerial vehicles (UAVs) has opened up new opportunities for remote gas sampling and provides logistical and economic opportunities to improve GHG measurements.

Methods: This study presents synchronized gas chromatography/isotope ratio mass spectrometry (GC/IRMS) methods for the analysis of atmospheric gas samples (20-mL glass vessels) to determine the stable isotope ratios and concentrations of CO₂, CH₄ and N₂O. To our knowledge there is no comprehensive GC/IRMS setup for successive measurement of CO₂, CH₄ and N₂O analysis meshed with a UAV-based sampling system. The systems were built using off-the-shelf instruments augmented with minor modifications.

Results: The precision of working gas standards achieved for δ¹³C and δ¹⁸O values of CO₂ was 0.2‰ and 0.3‰, respectively. The mid-term precision for δ¹³C and δ¹⁵N values of CH₄ and N₂O working gas standards was 0.4‰ and 0.3‰, respectively. Injection quantities of working gas standards indicated a relative standard deviation of 1%, 5% and 5% for CO₂, CH₄ and N₂O, respectively. Measurements of atmospheric air samples demonstrated a standard deviation of 0.3‰ and 0.4‰ for the δ¹³C and δ¹⁸O values, respectively, of CO₂; 0.5‰ for the δ¹³C value of CH₄ and 0.3‰ for the δ¹⁵N value of N₂O.

Conclusions: Results from internal calibration and field sample analysis, as well as comparisons with similar measurement techniques, suggest that the method is applicable for the stable isotope analysis of these three important GHGs. In contrast to previously reported findings, the presented method enables successive analysis of all three GHGs from a single ambient atmospheric gas sample.

1 | INTRODUCTION

There is an increased awareness of the anthropogenic impact on climate change. Identifying the sources and sinks of greenhouse gases (GHGs) and monitoring their atmospheric abundance¹ are essential in managing the required global GHG emission reductions to achieve the 1.5°C target² or to establish pathways to zero emissions.³ GHG monitoring is a valuable input to facilitate technology improvement,
leading to more efficient resource utilization. The most important GHGs are carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). For 2018 the global mean concentrations of CO₂, CH₄ and N₂O were 407.8 ± 0.1 μmol mol⁻¹, 1869 ± 2 nmol mol⁻¹ and 331.1 ± 0.1 nmol mol⁻¹, respectively. In light of their low absolute concentrations, instrumentation has to be used that will ensure accurate and precise measurements. In addition to the compound concentration, the stable isotopic composition enables identification of GHG sources and sinks. However, the inclusion of isotopic analysis requires different considerations and an appropriate analyzer, such as an isotope ratio mass spectrometer, or optical devices based on tunable diode laser adsorption spectroscopy or Fourier transform infrared spectroscopy. While optical devices are customized to analyze specific compounds only (e.g. CO₂, H₂O or N₂O), isotope ratio mass spectrometry (IRMS) can be used to measure a multitude of compounds in addition to GHGs. The key process in efficient and accurate IRMS is sample preparation, which encompasses the various steps from specifically designed sample collection and manual sample preparation, through to introduction of the gases into the device and treatment options for specific gas separation.

Most IRMS systems use gas chromatography (GC) to separate and isolate gas compounds of similar physical and chemical behavior (e.g. CO₂ and N₂O). Furthermore, pre-concentration steps connected in series with GC are often needed, if injection volumes (e.g. 20 mL to 2.5 L) yield compound amounts (e.g. of CH₄, N₂O) below IRMS detection limits, which are in the range of hundreds of picomoles to nanomoles. A common pre-concentration approach is the use of cryogenic traps, filled with adsorbent material to trap CH₄ or N₂O while other residual compounds are vented away. In this setup the entire gas contents of the vessel, whatever the volume, are purged out though the trapping system with a carrier gas such as helium. Pre-concentrated CH₄ held on the trap can then be released and oxidized to CO₂ while trapped pre-concentrated N₂O requires no chemical transformation for detection. Both gases then undergo similar preparation to that for atmospheric CO₂ measurements. That is, compounds are focused and separated from any residuals using GC and transferred to the isotope ratio mass spectrometer, which measures the intensity of m/z 44, 45 and 46 to calculate the stable isotope ratios of carbon, oxygen or nitrogen of sampled CO₂, CH₄ or N₂O.

There are already numerous methods available to measure atmospheric samples for the concentration and isotopic composition of CO₂, CH₄ and N₂O. While the majority of published methods focus on one of the three GHGs only, the aim of the study reported here was to enable the measurement of all three gases from identical sample vessels in a single-push measurement approach. Specifically, taking into consideration the compatibility of the sampling approach with unmanned aerial vehicle (UAV)-based sampling systems, the key for success was the identification of appropriate sample vessels fitting the requirements of both the sampling system and the measurement setup. To our knowledge there is no comprehensive GC/IRMS setup for the successive measurement of CO₂, CH₄ and N₂O meshed with a UAV-based sampling system.

This paper presents a method for automated GC/IRMS based on simultaneous and/or successive measurement of atmospheric CO₂, CH₄ and N₂O provided by a single air sample. Therefore, sample vessels have been identified fitting the requirements of UAV-based sampling systems and GC/IRMS instrumentation. Such a UAV-based sampling system was also designed and tested, but will be presented elsewhere. In accordance with Schauer et al., the aim was to employ off-the-shelf instruments needing minor modification only, so that the presented methods can be considered by the scientific community as an alternative to specially designed instruments. It should also be kept in mind that, after adjusting the current measurement system, it is still ready to use for its ordinary purpose of analyzing a large variety of other gaseous and volatile compounds.

The presented methods were customized to the current abundance status of CO₂, CH₄ and N₂O in the atmosphere. The detection range for atmospheric CO₂ and CH₄ was established at 372 to 944 μmol mol⁻¹ and 1.7 to 5.0 μmol mol⁻¹, respectively. Appropriate limits of determination for tracing atmospheric gases are recommended at 100 μmol mol⁻¹ for CO₂ and 500 nmol mol⁻¹ for CH₄, in Schuyler and Guzman. For N₂O, a limit of determination of 300 nmol mol⁻¹ was the target to guarantee the measurement of current atmospheric global mean abundance.

2 | MATERIALS AND METHODS

In the process of setting up the methods described below, there have been many process iterations with several discarded options, in terms of sample vial specifications, sample transfer, GC columns, adsorbents and cryogenic trapping. These are summarized in the supporting information.

2.1 | Sample vial preparation

Air was sampled in 20-mL headspace vials (La-pha-pack GmbH, Langerwehe, Germany) sealed with grey butyl-PTFE-lined septa (DWK Life Sciences GmbH, Mainz, Germany) and aluminum crimp caps. The vials were pre-conditioned by flushing with helium or synthetic air for 1 min at an inlet pressure of 2 bar before evacuation for 1 min with a rotary vane pump (e.g. E2M-1.5, Edwards Ltd, Burgess Hill, UK) to a final pressure of approx. 0.05 Pa. Flushing was performed using two G26 51 mm Luer-lock side-bore needles (Hamilton Bonaduz AG, Bonaduz, Switzerland) while evacuation used a single needle only. Pre-conditioned or already filled vials can be stored for several weeks before measurement, having shown adequate tightness in internal tests and according to the literature.

2.2 | Sampling of CO₂ via direct injection to GC/C- HTC/IRMS

This method sought to achieve rapid accurate automated measurement, using a sequential sampling procedure for CO₂. Up to
64 samples can be loaded to the autosampler (Combi PAL, CTC Analytics AG, Zwingen, Switzerland) and an aliquot sample volume of 300 μL was transferred by the autosampler to a split/splitless injection port of the gas chromatograph (Trace GC Ultra, Thermo Fisher Scientific S.p.a., Rodano, Italy). A 1-mL syringe (1.0 mL HLT PTFE sealed G23, Innovative Laborsysteme GmbH, Stützerbach, Germany) maintained at room temperature was initially flushed with helium 5.0 taking two filling strokes before injecting the sample at 50 μL s⁻¹. The injector was maintained at 120°C housing a 3 mm inner diameter splitless liner (LNR TQ CE, Trajan Scientific and Medical, Ringwood, Australia). Sample compounds were separated and focused on a packed column (ShinCarbonST 80/100 mesh, 2 m × 1 mm inner diameter, Restek Corporation ordered from BGB Analytik AG, Rheinfelden, Switzerland) with a temperature program starting at 40°C, and increased at 10°C min⁻¹ to 110°C where it was held for 5 min before being increased at 50°C min⁻¹ to the final temperature of 180°C. Furthermore, it is important to note that the splitless time of the injector was 1 min and the septum purge was stopped for 1 min. The He carrier gas provided a constant pressure of 150 kPa. This procedure enables a sufficient separation of CO₂, but it can be altered if CH₄ and/or N₂O are present in concentrations similar to that of CO₂ (Figure 1).

The temperature program was then adjusted as follows. Starting at 40°C, the temperature was held for 1 min before being increased at 10°C min⁻¹ to 110°C where it was held for 5 min before being increased to 180°C at 20°C min⁻¹. In addition, the carrier gas pressure was maintained at 150 kPa for 8.4 min and increased to 180 kPa at 50 kPa s⁻¹ for the remaining time. Thereby CH₄, CO₂ and N₂O were separated and focused properly and the issue of interfering N₂ with CH₄ and H₂O with CO₂ and N₂O was overcome. After being eluted, CH₄ was passed through a Cu/Ni combustion/reduction reactor (1000°C) and oxidized to CO₂, while air–CO₂ and air–N₂O were passed through an empty Al₂O₃ tube maintained at 200°C (designed as a high-temperature-conversion (HTC) reactor operating at temperatures above 1000°C) to preserve their chemical state. All three analytes were successively transferred via a universal continuous flow gas interface (ConFlo IV, Thermo Fisher Scientific GmbH, Bremen, Germany) to the isotope ratio mass spectrometer (Delta V Advantage, Thermo Fisher Scientific GmbH) measuring the ion currents at m/z 44, 45 and 46. This approach of direct injection was shown to be consistent for the measurement of CO₂, CH₄ and N₂O at levels above 250 μmol mol⁻¹ in air.

2.3 | Sampling of CH₄ and N₂O via purge and trap GC/C-HTC/IRMS

For measurement of CH₄ or N₂O, concentration range of 0.3 to 3.5 μmol mol⁻¹ in air, the samples were switched to a purge and trap autosampler (VSP 4000, Envea™, SWR Engineering GmbH, Schliengen, Germany). The general procedure is illustrated in Figure 2. The autosampler was modified such that the cryo-trap (1/16” outer diameter, 0.8 mm inner diameter × 136 mm glass-lined tube) was filled along 21 mm with HayeSep D mesh 80/100 (HayeSeparations Inc., Bandera, TX, USA) following Miller et al. Water and CO₂ were trapped in front of the cryo-trap using a CO₂/ water trap (100 mm × 1/2” outer diameter glass tube, IVA Analysetechnik GmbH, Meerbusch, Germany) filled with an equal mixture of Ascarite and anhydrous magnesium perchlorate (Mg(ClO₄)₂). In order to enable the use of identical crimp vials to
those used for direct injection a specially designed needle plate was used. Similar to the gas-bench needle approach, a Pencan Paed G22 0.6 mm outer diameter needle (B. Braun Austria GmbH, Maria Enzersdorf, Austria) was cut at 100 mm, to serve as the purge gas outlet, and was inserted into a G19 1.0 mm outer diameter Luer-lock needle (Hamilton Bonaduz AG), cut at 50 mm, working as helium inlet, protruding by 3 mm. The G19 needle terminated inside a 1/16th stainless steel T-piece (Swagelok, ordered from AA-Solutions GmbH, Wiener Neudorf, Austria), sealed with a drilled-out 0.25 mm inner diameter SilTite ferrule (Fisher Scientific Austria, Vienna, Austria) connected to the helium inlet (1/16th stainless steel tube) and a 1/16th stainless steel connector (Swagelok, ordered from AA-Solutions GmbH) leading to the G22 needle, sealed with three drilled-out 1/16th x 0.5 mm inner diameter graphite/vespel ferrules (Restek Corporation ordered from BGB Analytik AG) to a 1/16th stainless steel tube purge gas outlet.

Vials were each purged with helium 5.0 for 10 min at a flow rate of 20 mL min⁻¹, while the cryo-trap was maintained at −150°C by cooling with liquid nitrogen (LN₂). Due to the limit of determination and calibration range of the presented method, measurement of atmospheric N₂O required a sample volume of three sample vials (61.5-mL), as shown in Figure 3, while the volume of a single vial (20.5-mL) was sufficient for the analysis of CH₄. Therefore, the software of the VSP 4000 had to be modified to enable the trapping of multiple vial volumes in a single measurement keeping the cryo-trap at −150°C while switching the purge procedure from vial to vial. To finalize the purge process, the cryo-trap was heated to 120°C at 50°C s⁻¹, desorbing the trap and transferring gaseous compounds for 120 s at a head pressure of 700 hPa. The VSP 4000 was connected via a temperature programmed transfer line (200°C) enabling on-column injection. In front of the GC column (Poraplot Q, 30 m x 0.32 mm inner diameter, 10 µm film, Agilent Technologies Austria GmbH, Vienna, Austria) a guard column was installed (3-m piece of Poraplot Q, 0.32 mm inner diameter, 10 µm film), which guided the transferred compounds from the transfer line outlet inside the gas chromatograph through a 1/16th stainless steel tube (U-shaped, length of 50 cm) mounted to the GC-Isolink Cold Trap Option (Thermo Fisher Scientific GmbH) piston cantilever. The stainless steel tube was immersed in a 3-L LN₂ Dewar flask to separate CH₄ from residual N₂ and O₂. Subsequently the guard column was linked back into the gas.
chromatograph and connected to the GC column. The cold trap was activated 30 s before the cryo-trap was heated up and was kept immersed in LN2 during and after the transfer time for a total of 240 s after cryo-trap desorption started. The GC temperature gradient was programmed to start at the beginning of the purge and trap transfer time keeping a temperature of 35°C for 8.7 min before it was increased to 120°C at 5°C min⁻¹ to reduce the amount of residual water inside the Poraplot Q. The outlet of the GC column was linked to a combustion reactor and a HTC reactor. While the combustion reactor was used for CH₄ conversion the HTC reactor was set to 200°C to enable the direct measurement of N₂O via the signals at m/z 44, 45 and 46. In order to enable simultaneous analysis of CH₄ and N₂O in a single run, the gas flow to the isotope ratio mass spectrometer was switched from combustion mode to HTC mode at 265 s after the cold trap had been lifted. Switching the reactor also required switching the gas configuration in the ISODAT software (Thermo Fisher Scientific GmbH) from CO₂ to N₂O.

2.4 Referencing and calibration of CO₂, CH₄ and N₂O

The isotopic compositions of CO₂, CH₄ and N₂O are reported in δ-notation (‰) and were referenced against laboratory working standard gases (CO₂, N₂O) which have been calibrated relative to the international standard Vienna Peedee Belemnite (VPDB) for δ¹³C and δ¹⁸O values and AIR-N₂ for the bulk δ¹⁵N value using internationally distributed isotopic reference materials. The δ-values were calculated as:

\[ \delta^{13}C = \frac{R_P}{R_{Std}} - 1 \]
\[ \delta^{18}O = \frac{R_P}{R_{Std}} - 1 \]
\[ \delta^{15}N_{bulk} = \frac{R_P}{R_{Std}} - 1 \]

where R is the ratio of the abundance of ¹³C to ¹²C, ¹⁸O to ¹⁶O and ¹⁵N to ¹⁴N of a sample (P) and a measurement standard (Std).²⁷

A CO₂ working gas (CO₂ 4.8 F50, Messer Austria GmbH, Gumpoldskirchen, Austria) and a CH₄ working gas (CH₄ 4.5 F10, Messer Austria GmbH) were calibrated using the above described direct injection method using two certified CO₂ gas standards (ISO-TOP, Messer Austria Gmbh) with a δ¹³C value of −6.7 ± 0.2‰ and −39.0 ± 0.2‰ and a δ¹⁸O value of −7.8 ± 0.2‰ and −20.4 ± 0.2‰ vs VPDB. The N₂O working gas (N₂O UHP F10, Messer Austria GmbH) was converted into N₂ using the GC-Isolink combustion/reduction reactor and was then measured against an N₂ working gas, used as the measurement reference gas (N₂ 5.0, F10, Messer Austria GmbH), which had been calibrated using elemental analyzer/IRMS (Flash 2000-ConFlo IV-DeltaV Advantage, Thermo Fisher Scientific GmbH, Cambridge, UK) using the international standard materials IAEA-N-1 (0.4 ± 0.1‰), IAEA-NO-3 (4.7 ± 0.1‰)³¹ and IAEA-600 (0.9 ± 0.1‰).³² In addition, pure N₂ and N₂O working gases were manually injected into the elemental analyzer and using the N₂ working gas as the measurement reference gas for IRMS to determine the bulk δ¹⁵N
value of the N2O working gas. The determination of the δ13C and δ18O value of CO2 and the δ13C value of CH4 as well as the bulk δ15N value of N2O followed the evaluation procedure of Paul and Skrzypek.33 The working gases indicated an isotopic composition and uncertainty of −29.5 ± 0.1‰ for the δ13C value and 1.2 ± 0.1‰ for the δ18O value of CO2 (n = 6), −40.3 ± 0.2‰ (n = 38) for the δ13C value of CH4 and −1.2 ± 0.1‰ (n = 4) for the bulk δ15N value of N2O.

Each reported sample run implies the use of one of the three working standard gases (CO2, CH4, N2O) as a measurement reference gas injected as a working gas standard for isotopic evaluation and compound quantification. For preparing working gas standards, CO2 was added pure, while CH4 and N2O were first diluted to a specific concentration range using pure gas addition to a glass gas mouse flushed and filled to laboratory air pressure with synthetic air (EPA-quality F50, Messer Austria GmbH). Samples and working gas standards were prepared under identical treatment,34 equilibrating the vials under pressure with sample gas (atmospheric air) or synthetic air using a 30-mL all-glass syringe (Fortuna® Optima®, Poulten & Graf GmbH, Wertheim, Germany) with a 51 mm G26 side-bore Luer-lock needle (Hamilton Bonaduz AG) installed using three filling strokes of sample gas in advance. Vials filled with synthetic air were used as working standard gases (CO2, CH4, N2O) as a measurement reference gas (CO2) disparities of the backflush and straight mode operation did not affect the calculated isotope ratios. The offset between the nominal and measured delta value of the CO2 working gas was 0.2 to 0.4‰ for δ13C values and −0.5 to 0.1‰ for δ18O values, both at decreasing amplitude of mass 44.

The corrected values were checked for outliers using the Grubbs test35 (setting a significance level of 5%). Therefore, values were grouped by nominal concentration to obtain three groups of ten values each. A single outlier was detected, which was discarded. The overall arithmetic mean value and standard deviation (SD) of the δ13C and δ18O values (n = 29) of the CO2 working gas standards were −4.3 ± 0.3‰ and −3.1 ± 0.3‰, respectively, with a maximum SD of 10 μmol mol−1 over the entire concentration range. A confidence interval of twice the SD (95%) for δ13C and δ18O values covered 93% and 90% of the values, respectively. Thereby, the overall arithmetic mean values slightly changed to −4.4‰ and −3.1‰ while the SD for δ13C and δ18O values dropped to 0.2‰ and 0.3‰, respectively. The results are shown in Figure S1 (supporting information) for individual data points of measured working gas standards and presented in Table 1, giving a summary of grouped data points.

3 RESULTS AND DISCUSSION
3.1 Internal calibration of CO2, CH4, N2O
3.1.1 CO2

Working gas standards of three nominal CO2 concentration levels (341, 488 and 732 μmol mol−1) were prepared in duplicate. Working gas standard vials were measured five times in succession spread over the sequence. The measured data were processed as follows. In order to calculate the concentration, the AreaAll value (V) was correlated with the vial’s respective nominal concentration by linear regression, resulting in a correlation coefficient (R2) of 1.0 and p < 2 x 10−16. Measurements of blanks, containing synthetic air only, showed an amplitude of mass 44 of 18 to 30 mV for the first to the last injection and did not affect the raw delta values of working gas standards or air samples. The raw delta values were checked and corrected to the mass spectrometer signal response (on source linearity), measurement reference gas (CO2) disparities of the backflush and straight mode operation, and offsets between the nominal and measured delta values of the CO2 working gas. Corrections for signal response linearity were calculated by a quadratic polynomial (R² > 0.98) that provided a better fit than a linear function35 (beam intensity of 300 to 6500 mV), resulting in corrections of 0.1 to 0.4‰ for δ13C values and 0.0 to −0.2‰ for δ18O values for an amplitude of mass 44 of 260 to 700 mV. Measurement reference gas disparities in the backflush and straight mode operation did not affect the calculated isotope ratios. The offset between the nominal and measured delta value of the CO2 working gas was 0.2 to 0.4‰ for δ13C values and −0.5 to 0.1‰ for δ18O values, both at decreasing amplitude of mass 44.

Internal calibration of CH4 and N2O covered the range 0.7–2.8 and 0.8–2.9 μmol mol−1, respectively. The purge and trap method, which was designed to measure ambient atmospheric CH4 and N2O, was tested by repeated preparation and measurement of atmospheric samples and working gas standards in six individual sequences across a period of two weeks. Samples and standards were measured from single and multiple vials with standard vials always containing both working standard gases (CH4 and N2O). The measurement results of the working gas standards were grouped by sequence and nominal concentration to calculate measured concentrations by linear regression of their AreaAll (Vs) and nominal concentration. All values were inside a 95%
**TABLE 2**

Results of CH$_4$ and N$_2$O working gas standard measurements: $n_{\text{tot}}$ represents the total number of measurements, and $n$ is the number of measurements inside a 95% confidence interval. Nominal concentrations are indicated by $c_{\text{nom}}$ in μmol mol$^{-1}$ and measured concentrations ($c_{\text{mean}}$) are calculated as arithmetic means of μmol mol$^{-1}$ with their standard deviation (SD). Delta values are given as arithmetic means in ‰ with their SD. For N$_2$O, the column $S_{\text{vol}}$ indicates the total sample volume, which can represent either a single vial volume (20.5 mL) or the volume of three vials (61.5 mL).

|       | CH$_4$ | N$_2$O |
|-------|--------|--------|
| $c_{\text{nom}}$ | $S_{\text{vol}}$ | $n_{\text{tot}}$ | $n$ | $c_{\text{mean}}$ ± SD | RSD (%) | $\delta^{13}$C ± SD | $c_{\text{nom}}$ | $S_{\text{vol}}$ | $n_{\text{tot}}$ | $n$ | $c_{\text{mean}}$ ± SD | RSD (%) | $\delta^{15}$N ± SD |
| 0.68  | 0.69 ± 0.04 | 6 | 6 | −40.3 ± 0.3 |  | 0.83 | 20.5 | 8 | 7 | 0.75 ± 0.10 | 13 | 4.6 ± 0.3 |
| 0.88  | 0.86 ± 0.04 | 5 | 5 | −40.3 ± 0.4 |  | 0.88 | 20.5 | 12 | 11 | 0.90 ± 0.05 | 6 | 4.6 ± 0.4 |
| 1.17  | 1.18 ± 0.05 | 4 | 4 | −40.2 ± 0.5 |  | 1.17 | 20.5 | 7 | 7 | 1.15 ± 0.02 | 2 | 4.6 ± 0.1 |
| 1.37  | 1.37 ± 0.11 | 8 | 8 | −40.1 ± 0.5 |  | 1.76 | 20.5 | 11 | 11 | 1.77 ± 0.09 | 5 | 4.6 ± 0.3 |
| 1.76  | 1.85 ± 0.11 | 6 | 6 | −40.3 ± 0.4 |  | 2.63 | 61.5 | 3 | 3 | 2.65 ± 0.01 | 0 | 4.6 ± 0.2 |
| 2.10  | 2.12 ± 0.10 | 5 | 5 | −40.3 ± 0.3 |  | 2.78 | 20.5 | 8 | 8 | 2.42 ± 0.20 | 8 | 4.6 ± 0.3 |
| 2.78  | 2.84 ± 0.16 | 6 | 6 | −40.2 ± 0.3 |  | 2.93 | 20.5 | 2 | 2 | 3.01 ± 0.00 | 0 | 4.5 ± 0.1 |
| 2.93  | 2.93 ± 0.01 | 0 | 0 | −40.2 ± 0.1 |  | 3.37 | 61.6 | 6 | 6 | 3.71 ± 0.23 | 6 | 4.6 ± 0.2 |

**FIGURE 4**

Progress of CO$_2$ concentration and isotopic composition in April to May 2020. Mean values are displayed as points with the minimum and maximum value from consecutive injections indicated as an error bar.
confidence interval. The regression coefficients settled between 0.97 and 1.0, and the p-values were kept below $4.5 \times 10^{-6}$ for both CH$_4$ and N$_2$O. Delta value corrections due to ion source linearity and measurement reference gas (CO$_2$, N$_2$O) offset between backflush and straight mode operation could be neglected due to their observed insignificant contribution. While there were no peaks at the retention time of N$_2$O in blank measurements, there was a small peak interfering with the CH$_4$ peak. These blank peaks were similar in AreaAll and $\delta^{13}$C values in measurements of multiple blank vials within each sequence which enabled a straightforward subtraction from calibration gas standards and sample values.

A Grubbs test did not identify any outliers for $\delta^{13}$C values of CH$_4$ or $\delta^{15}$N values of N$_2$O. The overall arithmetic mean value and SD of the $\delta^{13}$C and $\delta^{15}$N values was $-40.2 \pm 0.4\%o$ and $4.6 \pm 0.4\%o$, respectively. Excluding values outside a 95% confidence interval kept 94% and 96% of the values of each dataset, which are presented in Figure S2 (supporting information). The calculated mean values remained unchanged, while the SDs decreased to 0.4‰ and 0.3‰ for CH$_4$ and N$_2$O, respectively. A summary of the results grouped by the nominal compound amount is presented in Table 2. It should be noted that mean values were calculated by merging day-to-day measurements which gives the value information about the medium-term (period of two weeks) stability of the method.

Measurements of ambient atmospheric air samples indicated a necessary sample volume of 61.5 mL (volume of three vials). In order to save consumables and device run time, working gas standards were measured from single vial volumes. To ensure accurate quantification when standards and samples were measured from different vial volumes, the N$_2$O concentrations from single vial volumes and triple vial volumes were compared. As is evident from Table 2 for the nominal concentration of 0.88 and 1.17 $\mu$mol mol$^{-1}$ (from single vial volume, 20.5 mL) and 2.63 and 3.37 $\mu$mol mol$^{-1}$ (from triple vial volume, 61.5 mL), the delta values and concentrations showed consistency.

3.2 | Analysis of atmospheric air

3.2.1 | CO$_2$

The method for CO$_2$ measurements of atmospheric samples was tested by consecutive sampling of atmospheric air outside the institute building (WGS84 coordinates; E: 16.067816 N: 48.320476),
located in a suburb, and surrounded by agricultural land at a height of 3.4 m above ground, in March to May 2020. Figure 4 shows the δ¹³C and δ¹⁸O values and respective concentrations of CO₂ of the measured atmospheric samples. Each vial was measured four times and the results were filtered using a Gibbs test to detect outliers and a 95% confidence interval. The residual values comprised 97%, 91% and 87% of the initial datasets with a maximum SD of 0.3‰ and 0.4‰ for δ¹³C and δ¹⁸O values, respectively, and 9 μmol mol⁻¹ for concentrations. Figure 4 presents mean values with error bars indicating minima and maxima of filtered data points. The values of δ¹³C aligned with reported values of the three closest ESRL Global Monitoring Laboratory observation sites in Germany (Hohenpreisensburg – HPB; Ochsenkopf – OXK) and Hungary (Hegyhatsal – HUN). It was speculated that the trend of δ¹⁸O enrichment and the decrease in CO₂ concentration was driven by atmosphere/leaf diffusion processes and the CO₂ demand by photosynthesis. The values of δ¹³C further complemented by working gas standards, which always contained both CH₄ and N₂O working gases. The results, presented in Figure 4, show the δ¹³C values obtained by single- and triple-vial methods. The values were used for the quantification of CH₄ and N₂O concentrations. The SDs of the delta values and concentrations were from 0.1‰ to 0.5‰ and 0.03 to 0.19 μmol mol⁻¹ with all data points inside a 95% confidence interval.

3.2.2 | CH₄

Sampling of the atmosphere for CH₄ was carried out in March to April 2020 on four different days to test the repeatability of day-to-day measured samples. According to Miller et al., the expected seasonal variations of δ¹³C values of CH₄ should be minor on a day-to-day basis. The results indeed showed minor variations in the mean values, from −47.2‰ to −48.0‰ over the concentration range of 2.09 to 2.16 μmol mol⁻¹ (3 ≤ n ≤ 6), as presented in Figure 5. The SDs of the delta values and concentrations were from 0.1‰ to 0.5‰ and 0.03 to 0.19 μmol mol⁻¹ with all data points inside a 95% confidence interval.

3.2.3 | N₂O

N₂O and CH₄ can be measured using the same procedure but with the need to triple the sample volume for N₂O (61.5 mL) compared with the CH₄ evaluation. Atmospheric N₂O was sampled on the same days as atmospheric CH₄ and the samples were measured in the same sequences, complemented by working gas standards, which always contained both CH₄ and N₂O working gases. The results, presented in Figure 5, indicate natural variations in δ¹⁵N values (4.5–5.9‰; SD: 0.1–0.4‰; 3 ≤ n ≤ 6) and concentrations (0.33–0.43 μmol mol⁻¹; SD: 0.00–0.01 μmol mol⁻¹) as expected during springtime at a grassland and agriculture surrounded environment. The depletion in δ¹⁵N compared with the average tropospheric background of 6.55‰ was suspected to result from the impact of soil emissions (δ¹⁵N values below 0‰) and soil uptake and a probable application of fertilizers (δ¹⁵N value near 0‰) to agricultural land.

4 | CONCLUSIONS

The method precisions are 0.2‰ and 0.3‰ for the δ¹³C and δ¹⁸O values of CO₂, 0.4‰ for the δ¹³C value of CH₄ and 0.3‰ for the δ¹⁵N value of N₂O, and cannot reach precisions at the sub-0.0‰ level as presented by Ehleringer and Cook for CO₂, Rice et al. and Miller et al. for CH₄ or Kaiser and Röckmann for N₂O. They are, however, within reach of the precisions obtained for CH₄ or N₂O. Most of these and other publications showing the best precisions use a PreCon-based system, which was specially designed for CH₄ and N₂O analysis at atmospheric concentrations.

The as yet unsolved weakness of the presented methods relates to the CH₄ quantification. Despite the observed homogeneity of δ¹³C values obtained by single- and triple-vial methods, the measurement of single-vial volumes was used for the quantification of CO₂ concentration and isotopic ratios. It was therefore shown that successive quantification and stable isotopic analysis of all three GHGs in a single ambient atmospheric gas sample can be accomplished by modifying a purge and trap autosampler connected to a GC/C-HTC/IRMS system. Given that, the envisaged UAV-based air sampling system can be used to sample the atmosphere for GHGs. Such a system facilitates sampling campaigns at hard-to-access areas and enables automated sampling by remote control.

ACKNOWLEDGEMENTS

The authors acknowledge financial support by the Austrian Research Promotion Agency (FFG) within grant 866949 "UAV-based gas monitoring systems for the underpinning of urban, agricultural and industrial emission roadmaps" of the Beyond Europe 2nd Call Partner Application.

PEER REVIEW

The peer review history for this article is available at https://publons.com/publon/10.1002/rcm.8929

ORCID

Simon Leitner https://orcid.org/0000-0002-0889-1720
Rebecca Hood-Nowotny https://orcid.org/0000-0002-4398-3233
Andrea Watzinger https://orcid.org/0000-0002-9082-1544
REFERENCES

1. Rubino M, Etheridge DM, Thornton DP, et al. Revised records of atmospheric trace gases CO2, CH4, N2O, and 13C/12C over the last 2000 years from law dome, Antarctica. Earth Syst Sci Data. 2019;11(2):473-492. https://doi.org/10.5194/essd-11-473-2019.

2. Masson-Delmotte V, Zhai P, Pörtner H-O, et al., eds. Global Warming of 1.5°C. An IPCC Special Report on the Impacts of Global Warming of 1.5°C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change. 2018 https://www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SR15_Full_Report_High_Res.pdf. Accessed June 22, 2020.

3. Sachs JD, Schmidt-Traub G, Williams J. Pathways to zero emissions. Nat Geosci. 2016;9(11):799-801. https://doi.org/10.1038/geo2826.

4. WMO – World Meteorological Organization. WMO Greenhouse Gas Bulletin (GHG Bulletin), No. 15. 2019:8. https://library.wmo.int/doc_num.php?explnum_id=10100. Accessed April 16, 2020.

5. Hsueh DY, Krakauer NY, Randerson JT, Xu X, Trumbore SE, Southon JR. Regional patterns of radiocarbon and fossil fuel-derived CO2 in surface air across North America. Geophys Res Lett. 2007;34(2):6-11. https://doi.org/10.1029/2006GL027032.

6. Dlugokencky EJ, Nisbet EG, Fisher R, Lowry D. Global atmospheric methane: Budget, changes and dangers. Philos Trans R Soc A. 2011;369(1943):2058-2072. https://doi.org/10.1098/rsta.2010.0341.

7. Sherwood OA, Schwietzke S, Arling VA, Etiope G. Global inventory of gas geochemistry data from fossil fuel, microbial and burning sources, version 2017. Earth Syst Sci Data. 2017;9(2):639-656. https://doi.org/10.5194/essd-9-639-2017.

8. Keeling RF, Graven HD, Welp LR, et al. Atmospheric evidence for a global secular increase in carbon isotopic discrimination of land photosynthesis. Proc Natl Acad Sci. 2017;114(39):10361-10366. https://doi.org/10.1073/pnas.1619240114.

9. Shearer G, Kohl DH. Natural abundance of 15N: Fractional contribution of two sources to a common sink and use of isotope discrimination. In: Nitrogen Isotope Techniques. Cambridge, Massachusetts, USA: Academic Press; 1993:89-125. 10.1016/B978-0-08-092407-6.50009-2.

10. Brewer PJ, Kim JS, Lee S, et al. Advances in reference materials and measurement techniques for greenhouse gas atmospheric observations. Metrologia. 2019;56(3):034006. https://doi.org/10.1088/1681-7575/ab1506.

11. Merritt DA, Hayes JM, Des Marais DJ. Carbon isotopic analysis of atmospheric methane by isotope-ratio-monitoring gas chromatography-mass spectrometry. J Geophys Res. 1995;100(D1):1317-1326. https://doi.org/10.1029/94JD02689.

12. Miller JB, Mack KA, Dissly R, White JWC, Dlugokencky EJ, Tans PP. Development of analytical methods and measurements of 13C/12C in atmospheric CH4 from the NOAA climate monitoring and diagnostics laboratory global air sampling network. J Geophys Res Atmos. 2002;107(D13):4178. https://doi.org/10.1029/2001JD000630.

13. Rice AL, Gotch AA, Ajo H, Tyler SC. High-precision continuous-flow measurement of 13C/12C and 18O of atmospheric CH4. Anal Chem. 2001;73(17):4104-4110. https://doi.org/10.1021/ac0155106.

14. Brand WA. PreCon: A fully automated interface for the pre-GC concentration of trace gases on air for isotopic analysis. Isot Environ Health Stud. 1995;31(3-4):277-284. https://doi.org/10.1080/1025601950803671.

15. Ferretti DF, Lowe DC, Martin RJ, Brailsford GW. A new gas chromatograph-isotope ratio mass spectrometry technique for high-precision, N2O-free analysis of 13C/12C and 18O/16O in atmospheric CO2 from small air samples. J Geophys Res Atmos. 2000;105(D5):6709-6718. https://doi.org/10.1029/1999JD901051.

16. Ribas-Carbo M, Tans P, Berry J. Automated system for simultaneous analysis of 13C/12C, 18O/16O and CO2 concentrations in small air samples. Rapid Commun Mass Spectrom. 2002;16(5):339-345. https://doi.org/10.1002/rcm.582.

17. Schauer AJ, Lott MJ, Cook CS, Ehleringer JR. An automated system for stable isotopic and concentration analyses of CO2 from small atmospheric samples. Rapid Commun Mass Spectrom. 2005;19(3):359-362. https://doi.org/10.1002/rcm.1792.

18. Fisher R, Lowry D, Wilkin O, Sriskantharajah S, Nisbet EG. High-precision, automated stable isotope analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry. Rapid Commun Mass Spectrom. 2006;20(2):200-208. https://doi.org/10.1002/rcm.2300.

19. Berman ESF, Fladeland M, Lien J, Kolner R, Gupta M. Greenhouse gas analyzer for measurements of carbon dioxide, methane, and water vapor aboard an unmanned aerial vehicle. Sens Actuators B. 2012;169:128-135. https://doi.org/10.1016/j.snb.2012.04.036.

20. EPA United States Environmental Protection Agency. Air Sensor Guide. Washington, DC; 2014. https://cfpub.epa.gov/si/si_public_file_download.cfm?download_id=519616. Accessed June 22, 2020.

21. Schuyler T, Guzman M. Unmanned aerial systems for monitoring trace tropospheric gases. Atmosphere (Basel). 2017;8(12):206. https://doi.org/10.3390/atmos8120206.

22. Glatzel S, Well R. Evaluation of septum-capped vials for storage of gas samples during air transport. Environ Monit Assess. 2007;136(1-3):307-311. https://doi.org/10.1007/s10661-007-9686-2.

23. Sansone FJ, Popp BN, Rust TM. Stable carbon isotopic analysis of low-level methane in water and gas. Anal Chem. 1997;69(1):40-44. https://doi.org/10.1021/ac960241j.

24. Moeill PL, Sleep BE, Peepersd DJ, et al. Variations in expression of carbon isotope fractionation of chlorinated ethenes during biologically enhanced PCE dissolution close to a source zone. J Contam Hydrol. 2009;110(1-2):60-71. https://doi.org/10.1016/j.jconhyd.2009.08.006.

25. Stephan M, Jochmann MA, Schmidt TC, Gruyters M. Untersuchung von Bodenluft-Proben; 2009. https://www.glt-labor.de/forschung/chemie-physik/untersuchung-von-bodenluft-proben. Accessed June 22, 2020.

26. Mohn J, Guggenheim C, Tuzson B, et al. A liquid nitrogen-free preconcentration unit for measurements of ambient N2O isotope bymeters by QCLAS. Atmos Meas Tech. 2010;3(3):609-618. https://doi.org/10.5194/amt-3-609-2010.

27. Coplen TB, Brand WA, Gehre M, et al. New guidelines for 13C/12C measurements. Anal Chem. 2006;78(7):2439-2441. https://doi.org/10.1021/ac052027c.

28. Brand WA, Assonov SS, Coplen TB. Correction for the 17O interference in 12/13O measurements when analyzing CO2 with stable isotope mass spectrometry (IUPAC technical report). Pure Appl Chem. 2010;82(8):1719-1733. https://doi.org/10.1515/pac-2010-09-01-05.

29. Coplen TB. Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results. Rapid Commun Mass Spectrom. 2011;25(17):2538-2560. https://doi.org/10.1002/rcm.5129.

30. Böhlike KJ, Gwinn CJ, Coplen TB. New reference materials for nitrogen-isotope-ratio measurements. Geostand Geoanal Res. 1992;17(1):159-164. https://doi.org/10.1111/j.1751-908X.1993.tb00131.x.

31. INTERNATIONAL ATOMIC ENERGY AGENCY. Reference and Intercomparison Materials for Stable Isotopes of Light Elements, IAEA-TECDOC-825, IAEA, Vienna, 1995. ISBN 1011-4289.

32. Brand WA, Coplen TB, Vogt J, Rosner M, Prohaska T. Assessment of international reference materials for isotope-ratio analysis (IUPAC technical report). Pure Appl Chem. 2014;86(3):425-467. https://doi.org/10.1515/pac-2013-1023.
33. Paul D, Skrzypek G. Normalization of measured stable isotopic compositions to isotope reference scales – A review. *Rapid Commun Mass Spectrom*. 2007;3006-3014. https://doi.org/10.1002/rcm

34. Werner RA, Brand WA, Biogeochemistry M, Box PO. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Commun Mass Spectrom*. 2001;15(7):501-519. https://doi.org/10.1002/rcm.258

35. Kornfeld A, Horton TW, Yakir D, Turnbull MH. Correcting for nonlinearity effects of continuous flow isotope ratio mass spectrometry across a wide dynamic range. *Rapid Commun Mass Spectrom*. 2012;26(4):460-468. https://doi.org/10.1002/rcm.6120

36. Grubbs FE. Procedures for detecting outlying observations in samples. *Dent Tech*. 1969;11(1):1. https://doi.org/10.2307/1266761

37. Ohlsson KEA. Uncertainty of blank correction in isotope ratio measurement. *Anal Chem*. 2013;85(11):5326-5329. https://doi.org/10.1021/ac303968

38. Global Monitoring Laboratory – Earth System Research Laboratories (ESRL). https://www.esrl.noaa.gov/gmd/dv/data/index.php?category=Greenhouse%2BGases. Accessed June 8, 2020.

39. Farquhar GD, Lloyd J, Taylor JA, et al. Vegetation effects on the isotope composition of oxygen in atmospheric CO2. *Nature*. 1993;363(6428):439-443. https://doi.org/10.1038/363439a0

40. Denk TRA, Mohn J, Decock C, et al. The nitrogen cycle: A review of isotope effects and isotope modeling approaches. *Soil Biol Biochem*. 2017;105:121-137. https://doi.org/10.1016/j.soilbio.2016.11.015

41. Snider DM, Venkiteswaran JJ, Schiff SL, Spoelstra J. From the ground up: Global nitrous oxide sources are constrained by stable isotope values. *PLoS ONE*. 2015;10(3):e0118954. https://doi.org/10.1371/journal.pone.0118954

42. Wrage N, Lauf J, del Prado A, et al. Distinguishing sources of N2O in European grasslands by stable isotope analysis. *Rapid Commun Mass Spectrom*. 2004;18(11):1201-1207. https://doi.org/10.1002/rcm.1461

43. Ehleringer JR, Cook CS. Carbon and oxygen isotope ratios of ecosystem respiration along an Oregon conifer transect: Preliminary observations based on small-flask sampling. *Tree Physiol*. 1998;18(8-9):513-519. https://doi.org/10.1093/treephys/18.8-9.513

44. Kaiser J, Röckmann T. Complete and accurate mass spectrometric isotope analysis of tropospheric nitrous oxide. *J Geophys Res*. 2003;108(D15):4476. https://doi.org/10.1029/2003JD003613

45. Yarnes C. δ13C and δ2H measurement of methane from ecological and geological sources by gas chromatography/combustion/pyrolysis isotope-ratio mass spectrometry. *Rapid Commun Mass Spectrom*. 2013;27(9):1036-1044. https://doi.org/10.1002/rcm.6549

46. McIlvin MR, Casciotti KL. Fully automated system for stable isotopic analyses of dissolved nitrous oxide at natural abundance levels. *Limnol Oceanogr Methods*. 2010;8(2):54-66. https://doi.org/10.4319/locm.2010.8.54

47. INTERNATIONAL ATOMIC ENERGY AGENCY. Stable Isotope Measurement Techniques for Atmospheric Greenhouse Gases, IAEA-TECDOC-1268, IAEA, Vienna. 2002, ISSN 1011-4289.

**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

---

**How to cite this article:** Leitner S, Hood-Nowotny R, Watzinger A. Successive and automated stable isotope analysis of CO2, CH4 and N2O paving the way for unmanned aerial vehicle-based sampling. *Rapid Commun Mass Spectrom*. 2020;34:e8929. https://doi.org/10.1002/rcm.8929