Global Research Alliance N₂O chamber methodology guidelines: Considerations for automated flux measurement

Peter R. Grace¹,² | Tony J. van der Weerden³ | David W. Rowlings¹
Clemens Scheer¹,⁴ | Christian Brunk¹ | Ralf Kiese⁴ | Klaus Butterbach-Bahl⁴
Robert M. Rees⁵ | G. Philip Robertson² | Ute M. Skiba⁶

Abstract
Nitrous oxide (N₂O) emissions are highly episodic in response to nitrogen additions and changes in soil moisture. Automated gas sampling provides the necessary high temporal frequency to capture these emission events in real time, ensuring the development of accurate N₂O inventories and effective mitigation strategies to reduce global warming. This paper outlines the design and operational considerations of automated chamber systems including chamber design and deployment, frequency of gas sampling, and options in terms of the analysis of gas samples. The basic hardware and software requirements for automated chambers are described, including the major challenges and obstacles in their implementation and operation in a wide range of environments. Detailed descriptions are provided of automated systems that have been deployed to assess the impacts of agronomy on the emissions of N₂O and other significant greenhouse gases. This information will assist researchers across the world in the successful deployment and operation of automated N₂O chamber systems.

1. INTRODUCTION

Nitrous oxide (N₂O) is a long-lived greenhouse gas typically emitted from soils in response to nitrogen (N) fertilization, tillage, episodic wetting, and freeze–thaw events (Dusenbury, Engel, Miller, Lemke, & Wallander, 2008; Molodovskaya et al., 2012; Ruan & Robertson, 2017;
Wagner-Riddle et al., 2017). The uncertainty of current global N$_2$O estimates from agricultural soils (Wang et al., 2019) may partly be attributed to the sampling frequency of the datasets selected for inclusion in any analysis (Barton et al., 2015). For example, less than one-third of the 464 studies included in the global meta-analysis by Stehfest and Bouwman (2006) measured N$_2$O on at least a daily basis, with 50% of the data collected 3 d per week, or less than weekly (Barton et al., 2015). Infrequent sampling has the potential to overlook both diurnal variability and day-to-day variability, and subsequently is considered one of the major disadvantages of using manual sampling methods (Reeves, Wang, Salter, & Halpin, 2016).

Nitrous oxide emissions can be measured at high temporal frequency using automated systems, which allow both the collection and analysis of greenhouse gases at high temporal resolution in real time in the field. The basic requirements of chamber design and the need to minimize soil, plant, and environmental disturbance are identical to those for static chambers and are discussed in more detail by Clough et al. (2020). This paper covers additional aspects and requirements specific to automated systems.

Previous efforts to automate chamber-based measurements of greenhouse gas emissions from agricultural soils (Ambus & Robertson, 1998; Christensen, 1983b; Denmead, 1979) relied on near-continuous flow systems. However, since the turn of the 21st century, more emphasis has been placed on the modification and automation of the static chamber, non-steady state, non-flow-through technique (Breuer, Papen, & Butterbach-Bahl, 2000; Butterbach-Bahl & Papen, 2002; Kiese & Butterbach-Bahl, 2002; Smith & Dobbie, 2001; Wassmann, Neue, & Lantin, 2000).

Automation ensures the capture of emissions associated with unforeseen episodic events, such as significant rainfall after a dry period. Automation allows gas measurements to be taken at high temporal frequencies and define the shape of the N$_2$O response curve to N fertilization, irrigation, or other disturbances. This is especially the case at sites where manual chambers would be difficult to access when significant emission events are occurring (e.g., heavy clay soils after rain, dense and/or tall closed canopies, or freeze–thaw events). Automation also reduces the impact of soil disturbance on measurements, which can be an issue with repeated manual sampling events, especially after irrigation or rainfall events.

Automation also allows for detailed assessments in remote locations (e.g., savannah woodlands, Livesley et al., 2011; and semiarid croplands, Li et al., 2016) using generators or solar power, where labor and travel costs for episodic manual sampling might be uneconomic. Automated chambers are considerably more expensive than manual chambers, but they can be used in conjunction with manual chambers in order to characterize temporal variability (Wang et al., 2016). This can be a useful approach in experiments where a large number of treatments are compared and in which it is not possible to deploy large numbers of autochambers. The overall cost of automated equipment is dependent on the choice of chamber design, the automated gas sampling system, the gas analysis technology, and operational costs.

With respect to gas analysis equipment in the field, gas chromatography is the cheapest option, especially if AC (alternating current) power is available, but N$_2$O's relatively slow retention time (of 2–3 min) in most gas chromatography columns places limitations on the number of chambers that can realistically be sampled over a defined closure period without compromising linearity (Livingston, Hutchinson, & Spartalian, 2006).

Modern laser systems (described in more detail below), together with autochambers, could provide a less labor-intensive alternative. Instrument costs are likely to be at least twice the cost of a system using gas chromatography but in the long term may outweigh the labor costs associated in the operating costs and maintenance of gas chromatography systems. Spectra can be obtained in a fraction of a second, making optical techniques ideally suited to measure trace gas fluxes (Rapson & Dacres, 2014); however, applications can be challenging, mainly due to spectral interferences with other atmospheric constituents (Harris et al., 2020).

### 2 | FACTORS INFLUENCING SAMPLE ACQUISITION

#### 2.1 | Diurnality

Diurnality (time of day) in the context of manual chambers and sampling has been discussed by Charteris et al. (2020). One of the main advantages of automated sampling is the ability to capture diurnal fluctuations in emissions—a laborious task when repeated manual sampling is undertaken over a 24-h period. Diurnal variations in soil derived N$_2$O, methane (CH$_4$), and carbon dioxide (CO$_2$) emissions are largely due to temperature variation (Christensen,
...Nitrous oxide fluxes are generally higher during the day and increase exponentially with soil temperature (Flessa, Potthoff, & Loftfield, 2002). Temperature sensitivity is also moisture and substrate dependent, with the rate of change greatest when the soil moisture level approaches field capacity (Meyer et al., 2001) or shortly after N fertilization (Rowlings, Grace, Scheer, & Kiese, 2013, Scheer et al., 2014).

Several studies have found a close relationship between N₂O fluxes and surface soil temperature, but others have found a lag of several hours between maximum flux and maximum temperature. For example, using automated chambers, Scheer, Grace, Rowlings, and Payero (2012) found that the diurnal variation of N₂O fluxes from subtropical irrigated wheat (Triticum aestivum L.) was >10-fold for some chambers, with maximum emissions between 1800 and 2400 h and minimums between 0800 and 1400 h. In contrast, a U.K. study on an oilseed rape (Brassica napus L.) field observed maxima N₂O fluxes in the afternoon, which were associated with photosynthetically active radiation rather than temperature (Keane et al., 2018). Land use must also be taken into account. Rowlings, Grace, Scheer, and Liu (2015) disaggregated 2 yr of high-temporal-resolution data, comprising 10 automated samples per day for adjacent land uses in subtropical Queensland. They found that errors arising from single daily calculations of average daily N₂O flux rates could be minimized if rainforest, pasture, and lychee (tree crop, Litchi chinensis Sonn.) sites were sampled in the morning, at noon, and in the afternoon, respectively, due to the shading effect of different canopy densities. Diurnal patterns may not be consistent throughout the year (Du, Lu, & Wang, 2006; Yao et al., 2009) and can be obscured by dry and/or wet conditions causing rapid anoxic conditions, which stimulate N₂O production via denitrification (Savage & Davidson, 2003). Similar diurnal trends are also observed with CH₄ emissions from rice (Oryza sativa L.) systems (Buendia et al., 1998).

2.2 Sample frequency

The highly episodic response of N₂O emissions to changes in soil water status, and the availability of labile sources of organic carbon and N fertilization, means that the sampling frequency throughout the year or season has a profound effect on the calculation of seasonal or annual emissions. A major limitation of a manual chamber sampling strategy is that it cannot adequately handle the impact of climatic variability: potentially large emission pulses are not captured. For instance, Scheer et al. (2016) observed high fluxes after a >100-mm rainfall event which resulted in up to 79% of the annual emissions occurring over just 7 d. A less frequent sampling regime based on weekly linear interpolation would have either greatly overestimated some treatments or completely missed this event. Considering this study was examining the N₂O mitigation potential of enhanced efficiency fertilizers, a very different conclusion may have resulted from these errors. The high temporal frequency of automated measurements greatly improves the ability to measure (and ultimately predict) the effects of rapidly changing soil water content on emissions and their interaction with management events such as N fertilizer applications (Savage & Davidson, 2003). Likewise, Ruan and Robertson (2017) found in a Michigan (USA) wintertime cropland experiment that episodic fluxes after freeze–thaw events lasted only hours but accounted for the majority of wintertime N₂O fluxes, which were especially significant under reduced snow cover conditions. A biweekly or monthly sampling frequency would have substantially misrepresented cumulative fluxes over the same period of time, which is consistent with the observations of Parkin (2008).

...
Table 1 Maximum and minimum annual N\textsubscript{2}O fluxes (percentage deviation from the mean) from three land uses in subtropical Queensland (Australia) using all possible sampling frequency permutations (Rowlings et al., 2015)

| Land use | Min./max. | Sampling frequency | 1 d | 2 d | 3 d | 7 d | 14 d | 30 d |
|----------|-----------|-------------------|-----|-----|-----|-----|------|------|
|          |           | g N ha\textsuperscript{−1} yr\textsuperscript{−1} |     |     |     |     |      |      |
|          |           | %                 |     |     |     |     |      |      |
| Rainforest | Min.     | 516               | −3  | −4  | −16 | −19 | −34  |      |
|          | Max.     |                   | 3   | 2   | 15  | 26  | 183  |      |
| Pasture  | Min.     | 1,827             | −3  | −10 | −22 | −32 | −53  |      |
|          | Max.     |                   | 3   | 16  | 30  | 32  | 183  |      |
| Lychee   | Min.     | 1,712             | −2  | −2  | −34 | −48 | −67  |      |
|          | Max.     |                   | 2   | 3   | 28  | 58  | 108  |      |

\textsuperscript{a} Annual estimate of N\textsubscript{2}O emissions calculated using a fully automated greenhouse gas measurement system with 10 cycles per day over 2 yr.

A comparison between N\textsubscript{2}O fluxes measured from a grazed grassland in Scotland, using manual chambers and an autochamber. Data taken from a study by Ambus et al. (2010) (Figure 1). They compared manual chambers with two different autochamber systems. In the first, samples were collected and stored in sample vials, but in a variant of the autosampler approach (SIGMA), samples were collected and stored in foil bags. Samples collected on each occasion were added to the previous sample. The advantage of this system is that it provides an accurate assessment of cumulative gas fluxes over time with significantly lower analytical costs. Their study found no significant differences in the accumulation of N\textsubscript{2}O in standard autochambers, manual chambers, and SIGMA autochambers, and all three approaches were able to capture aspects of temporal variability in fluxes, but at different timescales. Again, spatial heterogeneity was considered as an important explanation of the differences observed. Smemo et al. (2011) used a similar approach to sample unattended, periodically closed chambers by trapping accumulated gases on molecular sieve over days to weeks of periodic chamber closures, with N\textsubscript{2}O later released for analysis in the laboratory.
2.3 Operating principles

The basic principle of current automated systems is to use the static closed chamber technique (non-steady-state, non-through-flow) to capture soil fluxes of N₂O and potentially other gases, including CO₂ and CH₄. The system may consist of numerous automated chambers linked to a sampling system and an in situ gas chromatograph (GC; Kiese, Hewitt, Graham, & Butterbach-Bahl, 2003; Rowlings, Grace, Kiese, & Weier, 2012; Scheer, Grace, Rowlings, Kimber, & van Zwieten, 2011), tuneable diode laser (TDL; Officer et al., 2015), Fourier transfer infrared (FTIR) spectrometer (Kelly, Phillips, & Baigent, 2008; McDaniels et al., 2017), photo-acoustic infrared spectroscopy (Tirol-Padre et al., 2014; van der Weerden et al., 2013; Yamulki & Jarvis, 1999), or quantum cascade lasers (QCL; Bruemmer et al., 2017; Savage, Phillips, & Davidson, 2014) for N₂O, CH₄, and CO₂, or a subset of these gases. In some cases, an infrared gas analyzer is used for CO₂. Alternatively, the autosampler may be used to transfer gas samples to vials in the field, which are subsequently analyzed using standard gas chromatography methods (Ambus et al., 2010; Scott et al., 2000).

Sensors also collect high-temporal-resolution environmental data, including soil temperature moisture both within and outside the chamber. Fluxes are derived by measuring the increase or decrease in gas concentration inside the chambers headspace over the closure time (normally 30–60 min) fitting the change in concentration over time using a linear or nonlinear model (Venterea et al., 2020). Each chamber is sampled repeatedly (a minimum of three times) over the defined closure time, allowing multiple flux rates to be measured for each chamber per day. Gas concentration in an enclosed atmosphere can build up to levels where there is a decline in the vertical concentration gradient, which may inhibit the normal emission rate (Livingston et al., 2006). Although a closure period of up to 30 min is considered acceptable for CO₂ (Kessavalou, Doran, Mosier, & Drijber, 1998), the optimum for N₂O can be longer (Jury, Letey, & Collins, 1982) or shorter (Venterea et al., 2020). At low to moderately high flux rates (<2 g ha⁻¹ h⁻¹), nonlinearity may be of minor importance compared with other commonly observed errors associated with chamber disturbance and fluctuations in temperature and pressure during the closure period (Bruemmer et al., 2017). Optimisation of closure periods under specific measurement conditions, with application to both manual and automated chambers, is addressed in detail by Venterea et al. (2020).

All systems should be designed with sensor-based alarms, which activate during certain climatic conditions. For example, when the chambers are closed for gas sampling, they potentially become miniature greenhouses (i.e., under high solar radiation, the interior temperature of the chambers can rise excessively). In this case, the alarm will interrupt the gas sampling and open the chamber lids to allow air circulation to lower the temperature, ensuring the vegetation inside the chamber is not harmed. A rain gauge should also be used so that the chambers will open automatically during rain, or sprinkler irrigation.

The following is a working example of one of the more popular automated sampling systems, which consists of twelve 37.5-L chambers (Figure 2), allowing multiple treatments to be assessed at a single location. This unit is based on the original system as described in Breuer et al. (2000) and has been used extensively in Australia (Barton et al., 2008; Barton, Butterbach-Bahl, Kiese, & Murphy, 2010; De Antoni Migliorati et al., 2015, 2016; De Rosa et al., 2016, 2018; Kiese & Butterbach-Bahl, 2002; Mumford, Rowlings, Scheer, De Rosa, & Grace, 2019; Rowlings et al., 2012, 2013, 2015; Scheer et al., 2011, 2012, 2014, 2016; Schwenke et al., 2015, 2016; Schwenke & Haigh, 2016; van Delden, Rowlings, Scheer, & Grace, 2016; van Delden, Rowlings, Scheer, De Rosa, & Grace, 2018; Wang, Dalal, Reeves, Butterbach-Bahl, & Kiese, 2011; Wang et al., 2016) as a key component of the Australian National Agricultural Nitrous Oxide Research Program (NANORP) (Grace et al., 2010). The modified system, which we call the “Queensland” system, is now produced by Queensland University of Technology (Brisbane, Australia) in collaboration with Karlsruhe Institute of Technology (Garmisch, Germany) (Figure 2). This system has been deployed in the United States at Michigan State University (Ruan & Robertson, 2017), Kansas State University, and the USDA (Idaho), Chile (Instituto de Investigaciones Agropecuarias [INIA]) (Hubel et al., 2016), India (International Crops Research Institute for the Semi-Arid Tropics [ICRISAT]),
Fluxes are calculated from the slope of the linear increase or decrease in N$_2$O concentration during the chamber lid closure, then corrected for air temperature, atmospheric pressure, and the ratio of chamber volume to surface area, as described in detail by Scheer et al. (2014). At the commencement of each field campaign and after any major flow rate adjustments, a six-point calibration curve ranging from 0.25 to 25 μg g$^{-1}$ is run manually on the GC to test for the detector’s linearity. Using this information, a linear model is used to calculate fluxes within the linear response of the curve (typically below 0.8–1 μg g$^{-1}$) using the real-time single-point calibration. Fluxes above these thresholds are filtered off and run with a detector-specific nonlinear response. Flux quality control is performed using a combination of diagnostics on the 15-min calibration standards to check performance of the GC and CO$_2$ linearity (where no plants are in chambers) to ensure the chambers are sufficiently sealed. The $r^2$ for the linear regression is normally calculated and used as a final quality check for the measurement. More details on flux calculations and correlations can be found in Venterea et al. (2020); however, the fact remains that a single automatic chamber produces up to 3,000 individual flux estimates per year, which ensures significantly increased temporal accuracy compared with manual chamber approaches.

The experience of the many users of these automatic systems within the Australian NANORP is that the vast majority of chamber data have an $r^2 > .9$ in a well-maintained, functioning autosystem. However, as discussed by Venterea et al. (2020), high $r^2$ values by themselves do not necessarily ensure that linear regression will be the best calculation method for determining fluxes. That article also describes how additional factors, including measurement precision and the number of samples collected during each chamber closure period, should be considered in making the decision whether to apply a linear or nonlinear calculation approach.

2.4 Chamber design

The Queensland automated chambers are sealed air-tight during gas sampling by two lids edged with either closed cell foam or a rubber gasket, which open and close via pneumatic actuators (with air supplied from a

Brazil (Empresa Brasileira de Pesquisa Agropecuária [EMBRAPA]), and the United Kingdom (Marsden, Holmberg, Jones, & Chadwick, 2018; Marsden et al., 2019).

The normal layout is three sets of four chambers, of which one set is sampling at any one time. This allows for up to four treatments to be sampled during any measurement period, each replicated three times. The chambers are normally within 50 m of the automated sampling unit and the GC. Air samples are taken sequentially from each closed chamber, followed by a single-point known standard (i.e., after every fourth sample) for calibration and drift correction. In total, each chamber is sampled four times (every 15 min) over 60 min. When the current set of chambers open, the next set of four chambers close and begin the sampling sequence (see Figure 3). It takes 180 min for all chambers to be sampled in one measurement cycle. During the measurement cycle, the chambers can be programmed to open automatically during high-intensity rainfall events or when air temperature inside the chambers exceeds a certain threshold (e.g., 45 °C; Li et al., 2016). To reduce heat building up within chambers, nondegradable transparent film can be applied to the Perspex sheeting (Rowlings et al., 2015).
The standard chambers (500 × 500 × 150 mm) are stainless steel frames, with transparent acrylic panes that have external outlet and inlet ports (3.175 mm [1/8 inch])—the latter a vent to ensure equalization of pressure during gas sampling (Hutchinson & Livingston, 2001). The outlet port is connected to an internal stainless steel sampling line with multiple holes, which extends to the center of the chamber. Extensions of either 300 or 500 mm (or both) can potentially be fitted to raise the height of the chambers for use with a variety of agricultural crops; however, this significantly increases the detection limit. A sampling manifold with multiple vertical inlets can be fitted in the extended chamber to provide a representative gas sample (Li et al., 2016). Ideally, the plants in the chamber will mimic the surrounding environment as closely as possible but can introduce artifacts (e.g., CO₂ fertilization), although this can be minimized by shifting the chamber position regularly during the season. Neither is it practicable to enclose tall crops such as maize (Zea mays L.) and sugarcane, so chambers are normally placed between the rows.

A second example of a working system is one developed by AgResearch in New Zealand (Figure 4), based on that reported by Ambus and Robertson (1998). This system (termed the “AgResearch” system) resembles the Queensland system in many aspects. However, the design and construction of the nine chambers differ, with the use of linear motors to move a one-piece lid into the closed position, where electronic proximity switches inform the software of the lid’s position (fully open, closed, or in between). Aluminum is used for the main construction of the 500-mm × 500-mm × 180-mm chambers, with acrylic lids on top allowing light penetration for pasture or crops (van der Weerden et al., 2013).

Another system that was developed by the Karlsruhe Institute for Technology (KIT), Germany (termed the “KIT” system) uses a large cylindrical chamber (1-m diameter, variable height according to vegetation development state) on a grassland lysimeter cluster (Kiese et al., 2018). It is controlled by a robotic system that moves on rails sequentially from lysimeter to lysimeter and lowers the rubber-sealed static dark chamber on top of a collar at each location (Figure 5). An advantage of the moving chamber is that it keeps the soil and plants inside the soil collar under as natural of conditions as possible and does not alter rainfall intensity or solar radiation when no sample is taken. The SkyBeam, a similar approach using many small chambers, was developed by York University, UK, (Keane, Morrison, McNamara, & Ineson, 2019).

In some applications, fans mix the chamber air (Yao et al., 2009), and it is commonly assumed in chamber studies that the air space is therefore well mixed. However, this assumption may not be correct regarding measurements over a deep, dense crop, when N₂O emitted from soil is likely to build up to a much higher concentration at the bottom of the canopy. Using a model, Meyer et al. (2001) found that trace gas transport through the canopy is unlikely to introduce errors into the flux estimates, despite
a significant concentration gradient. Thus, complete mixing within the air space of the chamber is not always necessary for valid chamber measurements. However, to reduce uncertainty when extensions are fitted, the internal sampling port can be extended vertically to ensure gas is sampled from throughout the chamber.

Tinted acrylic is recommended for the chamber lids and sides to prevent heat buildup during closure. This reduces incoming infrared radiation bands with minimal impact on photosynthetically active radiation bands. Reflective or insulated films can also be used in high-temperature environments, but their impact on heat and photosynthetic activity within the chambers should be assessed. In both examples described here, the chambers are attached by quick-release clamps to stainless steel bases featuring sharp edges for easy insertion ~100 mm into the soil. This gives an airtight enclosure with the topsoil. To minimize the memory effect of the chamber on soil properties and plant growth, at least two bases should be located in each treatment replicate, allowing the chambers to be regularly moved.

3 | SAMPLING UNITS

3.1 | The Queensland system

The Queensland system’s (Scheer et al., 2016) unit houses a sample pump, sample valves, calibration gas valve, eight-port sample injector valves, a sample flow meter, an infrared CO₂ analyzer (e.g., LI-820, LI-COR Biosciences), a GC (e.g., 8610C, SRI Instruments) containing a flame ionization detector (FID) for CH₄ and an electron capture detector (ECD) for N₂O, a pneumatic air regulator and filtering system, and a program logic controller (PLC). The PLC controls all sample and pneumatic air actuators and receives and processes sensor data. It is connected to a computer, which serves as an interface for system control and data storage.

The chambers are connected to the sampling unit by a nonreactive, Teflon-coated sample line, two pneumatic air lines (for opening and closing the lids), and any external temperature and soil moisture sensors required. Each field chamber is connected to the sampling unit by a 3.175-mm (1/8-inch) Teflon tube, which is in turn connected to a bank of chamber selection valves (sample valves). When a sample valve opens, a suction pump extracts the sample air from the corresponding chamber. The sample then passes through a water trap to remove any excess moisture. The sample air is then pumped through two eight-port, two-way Valco (Valco Instruments Company) injector valves, filling sample loops. The remaining sample air flows to the CO₂ analyzer.

After the 3-min sampling time, the injector valves switch, allowing a carrier gas to push the sample out of the sample loops and into the separation columns of the GC, and then onto to the detectors for analysis (FID for CH₄ and ECD for N₂O). The function of the carrier gas is to “flush” the 3-ml sample from the sample loops of the Valco injector valves, through the separation columns of the GC and into the FID and ECD detectors. The carrier gas needs to be an inert gas, providing a stable baseline signal from the detectors. The automated greenhouse gas measurement system uses high-purity dinitrogen (N₂) as the single carrier gas with no requirement for a makeup gas. There are two independent carrier gas streams: one each for the ECD and FID. Their flows are controlled by electronic pressure controllers positioned in the GC.

A calibration gas is also injected into the GC at regular intervals throughout the sampling cycle via a two-way valve, located before the injector valves. The calibration standard is required for calculating N₂O and CH₄ concentrations from chromatogram peak areas, and for calibrating the CO₂ sensor. For low-emitting systems, typical calibration standard concentrations are 0.5 μg g⁻¹ for N₂O, 4 μg g⁻¹ for CH₄, and 800 μg g⁻¹ for CO₂. See Harvey et al. (2020) for details on the calibration of the GC, especially noting the nonlinearity of ECD detectors.

Where a field scenario emits large amounts of greenhouse gas, it is recommended that a higher concentration standard curve be used, especially for the nonlinear ECD detector response. This can be done for short periods at monthly intervals, or anytime flow settings on the GC are modified. A schematic diagram of the overall sampling process is provided in Figure 6.

The Valco injector valve sends a specific volume of sample air from the automated chambers to the detectors of the GC for analysis. The standard volume used with this system is 3 ml. The injector valve is fitted with two 3-ml sample loops. The sample from one loop goes into the ECD, followed by the FID, and the other loop on to the LI-COR CO₂ analyzer.

A flow meter controls the flow of sample air. The sample flow rate needs to be high enough to ensure that the sample air from the chamber adequately flushes the injector valves, filling the sample loops within the 3-min sampling time. However, the volume of air extracted from the chambers should be minimized, to reduce dilution of the headspace with external air through the chamber vent. A chamber dilution of <5% is recommended. This is determined by the volume of the sample removed, divided by the chamber volume (including extensions if fitted).

The minimum sample flow rate (ml min⁻¹) is calculated by dividing the volume of the longest allowable sample line (e.g., 50 m) by the 3-min sampling time. The recommended flow rate is between 200 and 300 ml min⁻¹.
under normal conditions. The flow rate can, however, be adjusted to the site conditions, taking into consideration the length of sample lines and the use of chamber extensions.

Any CO\textsubscript{2} and H\textsubscript{2}O in the sample air must be removed (Zheng et al., 2008) before the online N\textsubscript{2}O analysis in the GC can occur, as both gases are detected by the ECD and may interfere with the accuracy of the N\textsubscript{2}O detection. A pre-column filter, containing sodium hydroxide coated in silicate (i.e., Ascarite) is normally sufficient. The sodium hydroxide will absorb any moisture contained in the sample air.

### 3.2 The AgResearch system

The AgResearch system (van der Weerden et al., 2013) includes a mobile caravan housing an Innova 1312 photoacoustic trace gas analyzer (TGA, Lumasense Technologies), sample valves and controllers, and purpose-designed software using Labview (National Instruments). The system can be powered by mains supply or by six 125-W solar panels and four 6-V, 420-A h, wet cell Trojan batteries, with a backup generator with a 100-A direct current (DC) alternator, powered by a 7.457-kW (10-hp) petrol engine with a 25-L fuel tank. When the battery voltage drops below 24 V, the generator will autostart and run for 1 h, increasing battery voltage to \( \sim 28 \) V. All data, including calculated fluxes, are sent via modem to a secure web address, allowing access from any internet connection.

Each chamber has two 20-m-long, nonreactive Teflon-coated sample lines that connect to a solenoid valve manifold in the caravan. The software communicates with the TGA and solenoid valve controllers to ensure a closed loop is created between a single chamber and the TGA, before switching airlines to the next chamber. The TGA’s internal pump, flowing at up to 1.9 L min\(^{-1}\), circulates air from the chamber headspace into the TGA sample cell, then back to the chamber. Nitrous oxide, CO\textsubscript{2}, and water vapor can be measured every 2 min. Because CO\textsubscript{2} interferes with the TGA’s N\textsubscript{2}O signal (de Klein, Harrison, & Lord, 1996), a correction factor is established, using a range of mixed CO\textsubscript{2} and N\textsubscript{2}O gases of known concentration in N\textsubscript{2}. In addition, CO\textsubscript{2} concentration in the air stream is minimized prior to
TGA analysis, using a soda lime trap (400-mm length \times 10-mm diameter), which is renewed when CO₂ concentrations exceed 1,000 μg g⁻¹ CO₂. Water vapor interference is automatically compensated for by the analyzer.

To provide a check on calculated fluxes from the automated system, three manual gas samples are periodically collected from chamber headspaces at 25- to 30-min intervals, following the same method used for manual static chambers, with access to the headspace provided by a rubber septa inserted into the chamber lid. These gas samples, stored in 6-ml vials, are analyzed by gas chromatography, and calculated fluxes are compared with those produced by the automated system. To date, the comparisons have been favorable (R² between .93 and .98).

3.3 | The KIT system

The sampling control unit and the analytical system of the KIT system is housed in a mobile container, which is located onsite next to the robotized chamber system. The measuring chamber is connected to the sampling unit by a nonreactive, Teflon-coated sample line and sequentially moved from one lysimeter position to the next. Each lysimeter is sampled four times per day by lowering the rubber-sealed chamber on top of a collar at each location for a closure time of 15 min. During the closure time, headspace air of the chamber is extracted via a diaphragm pump, which provides constant air flow (250 ml min⁻¹) to the sampling unit. A 0.45-μm coalescing filter and Nafion dryer filter system removes particulate and water vapor from the gas sample. Changes in headspace gas concentrations (N₂O, CO₂, and CH₄) are then measured automatically and at high precision using Quantum Cascade Laser Absorption Spectroscopy (QC-TILDAS DUAL, Aerodyne Research). After each lysimeter has been sampled two reference standards consisted of ambient air samples and a 0.4 μg g⁻¹ N₂O standard are injected from a certified calibration gas cylinder. Fluxes are calculated automatically using R script and stored on an external server via an internet connection.

4 | DETECTION LIMITS

Detection limits of automated chamber systems depend on the sensitivity of the TGA, the closure time, and the headspace volume of the chamber (Venterea et al., 2020). Thus, the detection limit can potentially be lowered by reducing the chamber headspace and increasing the closure time. However, these parameters need to be adjusted according to the field conditions, the sensitivity of the gas analyzer, and the expected N₂O emission range. Typical sensitivity of QCL analyzers for N₂O is in the range of 0.03–1.0 ng g⁻¹ for N₂O, whereas gas chromatography systems are usually in the range of 5 ng g⁻¹. Accordingly, the use of a QCL system can considerably lower the detection limit compared with gas chromatography systems, and minimum detectable fluxes of 0.5 μg N₂O-N m⁻² h⁻¹ for such systems have been reported (Savage et al., 2014).

The detection limit of the Queensland system is ~0.5 g N₂O-N ha⁻¹ d⁻¹ (2 μg N₂O-N m⁻² h⁻¹) without chamber extensions, and 2.0 g N₂O-N ha⁻¹ d⁻¹ (8 μg N₂O-N m⁻² h⁻¹) with the 50-cm chamber extension in place (Scheer et al., 2012). The detection limit of the AgResearch system is ~10.0 g N₂O-N ha⁻¹ d⁻¹ (van der Weerden et al., 2013), due to the lower sensitivity of the Innova analyzer compared with the GC. The detection limit of the KIT system is ~0.7 g N₂O-N ha⁻¹ d⁻¹ (3 μg N₂O-N m⁻² h⁻¹) with the 70-cm headspace. These limits should be independently determined for each system.

A commercially available automated system in which gas samples are collected in vials and returned to the laboratory for analysis has been developed by Umwelt- und Ingenieurtechnik (UIT) in Germany and deployed by Ambus et al. (2010). This battery-operated system (illustrated in Figures 7 and 8) collects samples from an automatically operated chamber, which opens and closes by the action of an electric motor that moves the chamber across a set of guide rails. The chamber closes by being placed on the baseplate and sealed with a silicone tube in the lower rim of the coverbox. Once the chamber is closed, a hypodermic double needle is inserted into 20-ml glass vials, and a membrane pump then flushes the vial with gas sampled from the closed chamber. At the end of the closure period, the chamber is moved away from the baseplate. Samples are stored in airtight glass vials on a sample
FIGURE 8 A diagrammatic sketch of the relationship between the auto-sampler and collection system used by the Umwelt- und Ingenieurtechnik (UIT) system

turntable and can be transferred directly onto the autosampling unit of a GC for N₂O analysis in the laboratory. The system requires a power supply to run the motor that moves the chamber and power the vacuum pump. This can be supplied either by an AC supply, or by rechargeable batteries. The system is fully programmable but is normally set to collect three gas samples over 40 min (at 0, 20, and 40 min). Although chambers could theoretically close every hour, it is not advisable to do this, especially when plants are enclosed. Ideally these chambers are only closed every 6 h.

An example of N₂O measured by a UIT autosampler compared with that from static chambers is provided in Figure 1. The autosampler has a greater potential to capture temporal variability in fluxes. The spatial heterogeneity within the site reduces the possibility to determine any statistical difference in the cumulative flux estimated by the two methods. The UIT autosampler and similar systems have the advantage of relative simplicity in that it is used only for the collection and storage of samples. The analysis of samples is undertaken in controlled laboratory environments, avoiding the need for maintenance of delicate analytical equipment in the field. Arnold, Tubbs, Arnold, and Walker (2010) present a further example of a similar chamber sampling system developed by the USDA.

A more recent automated chamber development is the combination of relatively small-diameter (~20 cm) autochambers, originally designed for soil respiration measurements, and connected to a cavity ring-down spectroscopy (CRDS) instrument to measure CH₄ and N₂O concentrations (Courtois et al., 2019). Due to the high sensitivity of the CRDS instrument, a 2-min chamber closure time was sufficient to measure CH₄ concentrations, but for N₂O, a 25-min closure period was required in low-N₂O-flux ecosystems, such as tropical forests. The CRDS instruments require an external pump. Unfortunately, power consumptions are high, and relying on fuel-based generators may be a problem in remote regions.

5 CONCLUSIONS

Fully automated greenhouse gas sampling systems for field deployment are now highly portable and robust and can be paired with a wide variety of analytical instruments. The automated systems can capture highly episodic emissions, and the characteristic diurnality in emissions, by multiple sampling events over any 24-h period. Large discrepancies in annual and seasonal estimates of emissions are apparent when using low-temporal-frequency manual sampling strategies versus high-temporal-frequency automated measurements. Automated systems also offer the essential high-temporal-resolution data necessary for model calibration, which can potentially be supplemented with a low-temporal-frequency manual sampling network for model validation.

Where relative differences in emissions associated with different management treatments are used for decision making, well-replicated manual chambers remain important tools. Improvements in analytical, sampling, and computing technologies have made automated systems more affordable and robust. Ultimately, their utility and uptake within the research community depend on country-specific labor and associated operational costs.
ACKNOWLEDGMENTS
We are thankful for support for the publishing costs from the New Zealand Government, in support of the objectives of the Livestock Research Group of the Global Research Alliance on Agricultural Greenhouse Gases.

CONFLICT OF INTEREST
The authors declare no conflict of interest

ORCID
Peter R. Grace https://orcid.org/0000-0003-4136-4129
Tony J. van der Werde https://orcid.org/0000-0002-6999-2584
David W. Rowlings https://orcid.org/0000-0002-1618-9309

REFERENCES
Ambus, P., & Robertson, G. P. (1998). Automated near-continuous measurement of carbon dioxide and nitrous oxide fluxes from soil. Soil Science Society of America Journal, 62, 394–400. https://doi.org/10.2136/sssaj1998.03615995006200015x
Ambus, P., Skiba, U., Drewer Jones, S. K., Carter, M. S., Albert, K. R., & Sutton, M. A. (2010). Development of an accumulation-based system for cost-effective chamber measurements of inert trace gas fluxes. European Journal of Soil Science, 61, 1365–2389. https://doi.org/10.1111/j.1365-2389.2010.01272.x
Arnold, S. L., Tubbs, R. S., Arnold, N. S., & Walker, A. E. (2010). Automated collector of terrestrial systems used for the gathering of soil atmospheric-gas emissions. Communications in Soil Science and Plant Analysis, 41, 638–648. https://doi.org/10.1080/00103620903531201
Barton, L., Butterbach-Bahl, K., Kiese, R., & Murphy, D. (2010). Nitrous oxide emissions from a grain–legume crop (narrow-leafed lupin) grown in a semiarid climate. Global Change Biology, 17, 1153–1166. https://doi.org/10.1111/j.1365-2486.2010.02260.x
Barton, L., Kiese, R., Gatter, D., Butterbach-Bahl, K., Buck, R., Hinz, C., & Murphy, D. (2008). Nitrous oxide emissions from a cropped soil in a semi-arid climate. Global Change Biology, 14, 177–192. https://doi.org/10.1111/j.1365-2486.2007.01474.x
Barton, L., Wolf, B., Rowlings, D., Scheer, C., Kiese, R., Grace, P., ... Butterbach-Bahl, K. (2015). Sampling frequency affects estimates of annual nitrous oxide fluxes. Scientific Reports, 5. https://doi.org/10.1038/srep15912
Breuer, L., Papen, H., & Butterbach-Bahl, K. (2000). N₂O emission from tropical forest soils of Australia. Journal of Geophysical Research, 105, 26353–26367. https://doi.org/10.1029/2000JD900424
Bruemmer, C., Lyshede, B., Lempiö, D., Delorme, J-P., Ruffer, J. J., Fub, R., ... Kutsch, W. L. (2017). Gas chromatography vs. quantum cascade laser-based N₂O flux measurements using a novel chamber design. Biogeosciences, 14, 1365–1381. https://doi.org/10.5194/bg-14-1365-2017
Buendia, L. V., Neue, H. U., Wassman, R., Lantin, R. S., Javellana, A. M., Arah, J. ... Charoen Silp, N. (1998). Anefficientsamplingstratificationinhibitor3,4-dimethylpyrazolephosphate. Soil Research, 36, 395–407. https://doi.org/10.1017/S00045-6535(97)00283-X
Butterbach-Bahl, K., & Papen, H. (2002). Four years continuous record of CH₄-exchange between the atmosphere and untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany. Plant & Soil, 240, 77–90. https://doi.org/10.1023/A:1015856617553
Charteris, A. F., Chadwick, D. R., Thorman, R. E., Vallejo, A., de Klein, C. A. M., Rochette, P., & Cardenas, L. M. (2020). Global Research Alliance N₂O chamber methodology guidelines: Recommendations for deployment and accounting for sources of variability. Journal of Environmental Quality. https://doi.org/10.1002/jeq2.20126
Christensen, S. (1983a). Nitrous oxide emission from a soil under permanent grass: Seasonal and diurnal fluctuations as influenced by manuring and fertilization. Soil Biology & Biochemistry, 15, 531–536. https://doi.org/10.1016/0038-0717(83)90046-9
Christensen, S. (1983b). Nitrous oxide emission from the soil surface: Continuous measurement by gas chromatography. Soil Biology & Biochemistry, 15, 481–483. https://doi.org/10.1016/0038-0717(83)90015-9
Clough, T. J., Rochette, P., Thomas, S. M., Pihlatie, M., Christiansen, J. R., & Thorman, R. (2020). Global Research Alliance N₂O chamber methodology guidelines: Design considerations. Journal of Environmental Quality. https://doi.org/10.1002/jeq2.20117
Courtois, E. A., Stahl, C., Burban, B., Van den Berge, J., Berveiller, D., Bréchet, L., ... Janssens, I. A. (2019). Automatic high-frequency measurements of full soil greenhouse gas fluxes in a tropical forest. Biogeosciences, 16, 785–796. https://doi.org/10.5194/bg-16-785-2019
De Antoni Migliorati, M., Bell, M., Lester, D., Rowlings, D. W., Scheer, C., de Rosa, D., & Grace, P. R. (2016). Comparison of grain yields and N₂O emissions on Oxisol and Vertisol soils in response to fertiliser N applied as urea or urea coated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate. Soil Research, 54, 552–564. https://doi.org/10.1071/SR15336
De Antoni Migliorati, M., Parton, W. J., Del Grosso, S. J., Grace, P. R., Bell, M. J., Strazzabosco, A., ... Harch, G. (2015). Legumes or nitrification inhibitors to reduce N₂O emissions from subtropical cereal cropping systems in Oxisols. Agriculture, Ecosystems & Environment, 213, 228–240. https://doi.org/10.1016/j.agee.2015.08.010
De Klein, C. A. M., Harrison, R., & Lord, E. I. (1996). Comparison of N₂O flux measurements using gas chromatography and photoacoustic infrared spectroscopy. In O. Van Cleemput, G. Hofman, & A. Vernoesen (Eds.), Progress in nitrogen cycling studies (pp. 533–536). Dordrecht, the Netherlands: Kluwer Academic. https://doi.org/10.1007/978-94-011-5450-5_87
De Rosa, D., Rowlings, D. W., Biala, J., Scheer, C., Basso, B., & Grace, P. R. (2018). N₂O and CO₂ emissions following repeated application of organic and mineral N fertiliser from a vegetable crop rotation. Science of the Total Environment, 637–638, 813–824. https://doi.org/10.1016/j.scitotenv.2018.05.046
De Rosa, D., Rowlings, D., Scheer, C., Basso, B., McGree, J., & Grace, P. R. (2016). Effect of organic and mineral N fertilizers on N₂O emissions from an intensive vegetable rotation. Biology & Fertility of Soils, 52, 896–908. https://doi.org/10.1007/s00374-016-1117-5
Denmead, O.T. (1979). Chamber systems for measuring nitrous oxide emissions from soils in the field. Journal of Environmental Quality, 89–95. https://doi.org/10.2136/jeq1979.0361599500430010016x
Dui, R., Lu, D., & Wang, G. (2006). Diurnal, seasonal, and inter-annual variations of N₂O fluxes from native semi-arid grassland soils of inner Mongolia. Soil Biology & Biochemistry, 38, 3474–3482. https://doi.org/10.1016/j.soilbio.2006.06.012
Dusenbury, M. P., Engel, R. E., Miller, P. R., Lemke, R. L., & Wallander, R. (2008). Nitrous oxide emissions from a northern great plains soil as influenced by nitrogen management and cropping systems. *Journal of Environmental Quality, 37*, 542–550. https://doi.org/10.2134/jeq2006.0395

Flessa, H., Potthoff, M., & Lottffiels, N. (2002). Greenhouse estimates of CO₂ and N₂O emissions following surface application of grass mulch: Importance of indigenous microflora of mulch. *Soil Biology and Biochemistry, 34*, 875–879. https://doi.org/10.1016/S0038-0717(02)00028-7

Grace, P. R. (2016). Foreword: Nitrous oxide from soils. *Soil Research, 54*, 1–ii. https://doi.org/10.1071/0r54n5 FO

Grace, P. R., Barton, L., Chen, D., Eckard, R., Graham, J., Hely, S., … Wang, W. (2010). The Australian Nitrous Oxide Research Program. In R. Gilkes & N. Prakongkep (Eds.), *Proceedings 19th World Congress of Soil Science* (pp. 247–248). Brisbane, QLD, Australia: International Union of Soil Sciences.

Hutchinson, G. L., & Livingston, G. P. (2001). Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. *European Journal of Soil Science, 52*, 675–682. https://doi.org/10.1046/j.1365-2399.2001.00415.x

Hube, S., Alvaro, M., Scheer, C., Brunk, C., Ramirez, L., Rowlings, D., & Grace, P. R. (2016). Effect of a nitrification and urease inhibitors on nitrous oxide and methane emissions from an oat crop in a volcanic ash soil. *Agriculture, Ecosystems & Environment, 238*, 46–54. https://doi.org/10.1016/j.agee.2016.06.040

Jury, W. A., Letey, J., & Collins, T. (1982). Analysis of chamber methods used for measuring nitrous oxide production in the field. *Soil Science Society of America Journal, 46*, 250–255. https://doi.org/10.1007/BF02375448

Keane, B. J., Ineson, P., Vallack, H. W., Blei, E., Bentley, M., Howarth, S., … Toet, S. (2018). Greenhouse gas emissions from the energy crop oilseed rape (*Brassica napus*); the role of photosynthetically active radiation in diurnal N₂O flux variation. *Global Change Biology Bioenergy, 10*, 306–319. https://doi.org/10.1111/gcbb.12491

Keane, J. B., Morrison, R., McNamara, N. P., & Ineson, P. (2019). Real-time monitoring of greenhouse gas emissions with tall chambers reveals diurnal N₂O variation and increased emissions of CO₂ and N₂O from miscanthus following compost addition. *Global Change Biology Bioenergy, 11*, 1456–1470. https://doi.org/10.1111/gcbb.12653

Kelly, K. B., Phillips, F. A., & Baigent, D. R. (2008). Impact of dicynanidamide application on nitrogen oxide emissions from urine patches in northern Victoria, Australia. *Australian Journal of Experimental Agriculture, 48*, 156–159. https://doi.org/10.1071/EA07251

Kessavalou, A., Doran, J. W., Mosier, A. R., & Drijber, R. A. (1998). Greenhouse gas fluxes following tillage and wetting in a wheat-fallow cropping system. *Journal of Environmental Quality, 27*, 1105–1116. https://doi.org/10.2134/jeq1998.00472425002700050016x

Kiese, R., & Butterbach-Bahl, K. (2002). N₂O and CO₂ emissions from three different tropical forest sites in the wet tropics of Queensland, Australia. *Soil Biology & Biochemistry, 34*, 975–987. https://doi.org/10.1016/S0038-0717(02)00031-1

Kiese, R., Fersch, B., Baessler, C., Brosy, C., Butterbach-Bahl, K., Chwala, C., … Schmid, H. P. (2018). The TERENO Pre-Alpine Observatory: Integrating meteorological, hydrological, and biogeochemical measurements and modeling. *Vadose Zone Journal, 17*. https://doi.org/10.2136/vzj2018.03.0060

Kiese, R., Hewitt, B., Graham, A., & Butterbach-Bahl, K. (2003). Seasonal variation of N₂O emissions and CH₄ uptake by tropical rainforest soils of Queensland, Australia. *Global Biogeochemical Cycles, 17*, 1043–1056. https://doi.org/10.1029/2002GB002014

Harris, S. J., Liisberg, J., Xia, L., Wei, J., Zeyer, K., Yu, L., … Blunier, T. (2020). N₂O isotopologue measurements using laser spectroscopy: Analyzer characterization and intercomparison. *Atmospheric Measurement Techniques, 13*, 2797–2831. https://doi.org/10.5194/amt-13-2797-2020

Harvey, M. J., Sperlich, P., Clough, T. J., Kellifer, F. M., Martin, R. J., & Moss, R. (2020). Global Research Alliance N₂O chamber methodology guidelines: Recommendations for air sample collection, storage, and analysis. *Journal of Environmental Quality*. https://doi.org/10.1002/jeq2.20129

Li, G. D., Conyers, M. K., Schwenke, G. D., Hayes, R. C., Li Liu, D., … Lowrie, R. J. (2016). Tillage does not increase nitrous oxide emissions under dryland canola (*Brassica napus L.*) in a semiarid environment of south-eastern Australia. *Soil Research, 54*, 512–522. https://doi.org/10.1071/IR15289

Livesley, S. J., Grover, S., Hutley, L. B., Jamali, H., Butterbach-Bahl, K., Fest, B., … Arndt, S. K. (2011). Seasonal variation and fire effects on CH₄, N₂O, and CO₂ exchange in savanna soils of northern Australia. *Agricultural & Forest Meteorology, 151*, 1440–1452. https://doi.org/10.1016/j.agrformet.2011.02.001

Livingston, G. F., Hutchinson, G. L., & Spartalian, K. (2006). Trace gas exchange in chambers: A non-steady-state diffusion model. *Soil Science Society of America Journal, 70*, 1459–1469. https://doi.org/10.2136/sssaj2005.0322

Maljman, M., Martikainen, P. J., Aaltonen, H., & Sivola, J. (2002). Short-term variation in fluxes of carbon dioxide, nitrous oxide and methane in cultivated and forested organic boreal soils. *Soil Biology & Biochemistry, 34*, 577–584. https://doi.org/10.1016/S0038-0717(01)00213-9

Marsden, K. A., Holmberg, J. A., Jones, D. L., & Chadwick, D. R. (2018). Sheep urine patch N₂O emissions are lower from extensively-managed than intensively-managed grasslands. *Agriculture, Ecosystems & Environment, 265*, 264–274. https://doi.org/10.1016/j.agee.2018.06.025

Marsden, K. A., Holmberg, J. A., Jones, D. L., Charteris, A. F., Cárdenas, L. M., & Chadwick, D. R. (2019). Nitrification represents the bottle-neck of sheep urine patch N₂O emissions from extensively grazed organic soils. *Science of the Total Environment, 695*. https://doi.org/10.1016/j.scitotenv.2019.133786

McDaniel, M. D., Simpson, R. R., Malone, B. P., McBratney, A. B., Minasny, B., & Adams, M. A. (2017). Quantifying and predicting spatio-temporal variability of soil CH₄ and N₂O fluxes from a seemingly homogeneous Australian agricultural field. *Agriculture, Ecosystems & Environment, 240*, 182–193. https://doi.org/10.1016/j.agee.2017.02.017

Meyer, C. P., Galbally, I. E., Wang, Y. P., Weeks, I. A., Jamie, I. M., & Griffith, D. W. T. (2001). *Two automatic chamber techniques for measuring soil-atmosphere exchanges of trace gases and results of their use in the OASIS field experiment*. Aspendale, VIC, Australia: CSIRO Atmospheric Research.

Molodovskaya, M., Singurindy, O., Richards, B. K., Warland, J., Johnson, M. S., & Steenhuis, T. S. (2012). Temporal variability of nitrous oxide from fertilized croplands: Hot moment analysis. *Soil Science Society of America Journal, 76*, 1728–1740. https://doi.org/10.2136/sssaj2012.0039
Mumford, M. T., Rowlings, D. W., Scheer, C., De Rosa, D., & Grace, P. R. (2019). Effect of irrigation scheduling on nitrous oxide emissions in intensively managed pastures. *Agriculture, Ecosystems & Environment*, 272, 126–134. https://doi.org/10.1016/j.agee.2018.11.011

Officer, S. J., Phillips, F., Kearney, G., Armstrong, R., Graham, J., & Partington, D. (2015). Response of soil nitrous oxide flux to nitrogen fertiliser application and legume rotation in a semi-arid climate, identified by smoothing spline models. *Soil Research*, 53, 227–241. https://doi.org/10.1017/S12049

Parkin, T. B. (2008). Effect of sampling frequency on estimates of cumulative nitrous oxide emissions. *Journal of Environmental Quality*, 37, 1390–1395. https://doi.org/10.2134/jeq2007.0333

Rapson, T., & Dacrees, H. (2014). Analytical techniques for measuring nitrous oxide. *Trends in Analytical Chemistry*, 54, 65–74. https://doi.org/10.1016/j.trac.2013.11.004

Rowlings, D. W., Scheer, C., & Kiese, R. (2013). Influence of nitrogen fertiliser application and timing on greenhouse gas emissions from a lychene (*Lithichinensis*) orchard in humid subtropical Australia. *Agriculture, Ecosystems & Environment*, 136, 123–133. https://doi.org/10.1016/j.agee.2012.04.008

Rowlings, D. W., Grace, P. R., Kiese, R., & Weier, K. L. (2012). Environmental factors controlling temporal and spatial variability in the soil-atmosphere exchange of CO₂, CH₄, and N₂O from an Australian subtropical rainforest. *Global Change Biology*, 18, 726–738. https://doi.org/10.1111/j.1365-2486.2011.02563.x

Scheer, C., Rowlings, D. W., Scheer, C., & Grace, P. R. (2013). The effect of biochar amendment on the soil-atmosphere exchange of CO₂, CH₄, and N₂O emissions under N₂-fixing legumes and N-fertilised canola: A reappraisal of emissions factor calculations. *Agriculture, Ecosystems & Environment*, 202, 232–242. https://doi.org/10.1016/j.agee.2015.01.017

Ruan, L., & Robertson, G. P. (2017). Reduced snow cover increases wintertime nitrous oxide (N₂O) emissions from an agricultural soil in the upper U.S. Midwest. *Ecosystems*, 20, 917–927. https://doi.org/10.1007/s10021-016-0077-9

Sass, R. L., Fisher, F. M., Turner, F. T., & Jund, M. F. (1991). Methane emissions from rice fields as influenced by solar radiation, temperature, and straw incorporation. *Global Biogeochemical Cycles*, 5, 335–350. https://doi.org/10.1029/91GB02586

Savage, K. E., & Davidson, E. A. (2003). A comparison of manual and automated systems for soil CO₂ flux measurements: Trade-offs between spatial and temporal resolution. *Journal of Experimental Botany*, 54, 891–899. https://doi.org/10.1038/sj.jxb.121

Savage, K., Phillips, R., & Davidson, E. (2014). High temporal frequency measurements of greenhouse gas emissions from soils. *Biogeochemistry*, 11, 2709–2720. https://doi.org/10.5194/bg-11-2709-2014

Scheer, C., Grace, P. R., Rowlings, D., Kimber, S., & van Zwieten, L. (2011). Effect of biochar amendment on the soil-atmosphere exchange of greenhouse gases from an intensive subtropical pasture in northern New South Wales, Australia. *Plant & Soil*, 345, 47–58. https://doi.org/10.1007/s11104-011-0799-1

Scheer, C., Grace, P. R., Rowlings, D. W., & Payero, J. (2012). Nitrous oxide emissions from irrigated wheat in Australia: Impact of irrigation management. *Plant & Soil*, 359, 351–362. https://doi.org/10.1007/s11104-012-1197-4

Scheer, C., Rowlings, D. W., De Antoni Migliorati, M., Lester, D. W., Bell, M. J., & Grace, P. R. (2016). Effect of enhanced efficiency fertilizers on nitrous oxide emissions in a sub-tropical cereal cropping system. *Soil Research*, 54, 544–551. https://doi.org/10.1017/S0038076416000208

Schwenke, G. D., & Haigh, B. M. (2016). The interaction of seasonal rainfall and nitrogen fertiliser rate on soil N₂O emission, total N loss and crop yield of dryland sorghum and sunflower grown on sub-tropical Vertosols. *Soil Research*, 54, 604–618. https://doi.org/10.1017/S15286

Schwenke, G. D., Herridge, D. F., Scheer, C., Rowlings, D. W., Haigh, B. M., & McMullen, K. G. (2015). Soil N₂O emissions under N₂-fixing legumes and N-fertilised canola: A reappraisal of emissions factor calculations. *Agriculture, Ecosystems & Environment*, 202, 232–242. https://doi.org/10.1016/j.agee.2015.01.017

Smith, K. A., & Dobbie, K. E. (2001). The impact of sampling frequency and sampling times on chamber-based measurements of N₂O emissions from fertilized soils. *Global Change Biology*, 7, 933–945. https://doi.org/10.1046/j.1365-2486.2001.00450.x

Scott, A., Ball, B. C., Crichton, I. J., & Aitken, M. N. (2000). Nitrous oxide and carbon dioxide emissions from grassland amended with sewage sludge. *Soil Use & Management*, 16, 36–41. https://doi.org/10.1111/j.1475-2743.2000.tb00170.x

Snemo, K. A., Ostrom, N. E., Odpkye, M. R., Ostrom, P. H., Bohn, S., & Robertson, G. P. (2011). Improving process-based estimates of N₂O emissions from soil using temporally extensive chamber techniques and stable isotopes. *Nutrient Cycling in Agroecosystems*, 91, 145–154. https://doi.org/10.1007/s10705-011-9452-2

Stehfest, E., & Bouwman, L. (2006). N₂O and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. *Nutrient Cycling in Agroecosystems*, 74, 207–228. https://doi.org/10.1007/s10705-006-9000-7

van Delden, L., Rowlings, D. W., Scheer, C., & Grace, P. R. (2016). Urbanisation-related land use change from forest and pasture into turf grass modifies soil nitrogen cycling and increases N₂O emissions. *Biogeoosciences*, 13, 6095–6106. https://doi.org/10.5194/bg-13-6095-2016

van Delden, L., Rowlings, D., Scheer, C., De Rosa, D., & Grace, P. (2018). Effect of urbanization on soil methane and nitrous oxide fluxes in sub-tropical Australia. *Global Change Biology*, 24, 5705–5707. https://doi.org/10.1111/gcb.14444

van der Weerden, T. J., Clough, T. J., & Styles, T. M. (2013). Using near continuous measurements of N₂O emission from urine-affected soil to guide manual gas sampling regimes. *New Zealand Journal of
Agriculture Research, 56, 60–76. https://doi.org/10.1080/00288233.2012.747548
Venterea, R. T., Petersen, S. O., de Klein, C. A. M., Pedersen, A. R., Noble, A. D. L., Rees, R. M.,… Parkin, T. B. (2020). Global Research Alliance N₂O chamber methodology guidelines: Flux calculations. Journal of Environmental Quality. https://doi.org/10.1002/jeq2.20118
Wagner-Riddle, C., Congreves, K. A., Abalos, D., Berg, A. A., Brown, S. E., Ambadan, J. T.,… Tenuta, M. (2017). Globally important nitrous oxide emissions from croplands induced by freeze-thaw cycles. Nature Geoscience, 10, 279–283. https://doi.org/10.1038/ngeo2907
Wang, Q., Zhou, F., Shang, Z., Ciais, P., Winiwarter, W., Jackson, R. B.,… Canadell, J. G. (2019). Data-driven estimates of global nitrous oxide emissions from croplands. National Science Review, 7, 441-452. https://doi.org/10.1093/nsr/nwz087
Wang, W., Dalal, R. C., Reeves, S. H., Butterbach-Bahl, K., & Kiese, R. (2011). Greenhouse gas fluxes from an Australian subtropical cropland under long-term contrasting management regimes. Global Change Biology, 17, 3089–3101. https://doi.org/10.1111/j.1365-2486.2011.02458.x
Wang, W., Park, G., Reeves, S., Zahmel, M., Heenan, M., & Salter, B. (2016). Nitrous oxide emission and fertiliser nitrogen efficiency in a tropical sugarcane cropping system applied with different formulations of urea. Soil Research, 54, 572–584. https://doi.org/10.1071/SR15314
Wassmann, R., Neue, H. U., & Lantin, R. S. (2000). Characterization of methane emissions from rice fields in Asia. 1. Comparison among field sites in five countries. Nutrient Cycling in Agroecosystems, 58, 1–12. https://doi.org/10.1023/A:1009848813994
Yamulki, S., & Jarvis, S. C. (1999). Automated chamber technique for gaseous flux measurements: Evaluation of a photoacoustic infrared spectrometer-trace gas analyzer, Journal of Geophysical Research, 104, 5463–5469. https://doi.org/10.1029/1998JD100082
Yao, Z., Zheng, X., Xie, B., Liu, C., Mei, B., Dong, H.,… Zhu, J. (2009). Comparison of manual and automated chambers for field measurements of N₂O, CH₄, CO₂ fluxes from cultivated land. Atmospheric Environment, 43, 1888–1896. https://doi.org/10.1016/j.atmosenv.2008.12.031
Zheng, X., Mei, B., Wang, Y., Xie, B., Wang, Y., Dong, H.,… Gu, J. (2008). Quantification of N₂O fluxes from soil-plant systems may be biased by the applied gas chromatograph methodology. Plant and Soil, 311, 211–234. https://doi.org/10.1007/s11104-008-9673-6

How to cite this article: Grace PR, van derWeerden TJ, Rowlings DW, et al. Global Research Alliance N₂O chamber methodology guidelines: Considerations for automated flux measurement. J. Environ. Qual. 2020;49:1126–1140. https://doi.org/10.1002/jeq2.20124