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SPECIAL SECTION:
GRA N_2O CHAMBER METHODOLOGY GUIDELINES

Global Research Alliance N_2O chamber methodology guidelines: Considerations for automated flux measurement

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Abstract

Nitrous oxide (N_2O) 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 N_2O 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 N_2O and other significant greenhouse gases. This information will assist researchers across the world in the successful deployment and operation of automated N_2O chamber systems.

1 | INTRODUCTION

Nitrous oxide (N_2O) 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;

Abbreviations: AC, alternating current; CRDS, cavity ring-down spectroscopy; ECD, electron capture detector; FID, flame iodization detector; GC, gas chromatograph; KIT, Karlsruhe Institute for Technology; NANORP, National Agricultural Nitrous Oxide Research Program; QCL, quantum cascade lasers; TGA, trace gas analyzer; UIT, Umwelt- und Ingenieurtechnik.

Wagner-Riddle et al., 2017). The uncertainty of current global N_2O 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_2O 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_2O 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.

Core Ideas

- High-temporal-frequency N_2O measurements improve the accuracy of inventories.
- A range of analytical options now exists for direct and rapid N_2O analysis in the field.
- Automated systems are robust and proven for field deployment.

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_2O'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_2O, methane (CH_4), and carbon dioxide (CO_2) emissions are largely due to temperature variation (Christensen,

1983a; Maljanen, Martikainen, Aaltonen, & Sivola, 2002; Sass, Fisher, Turner, & Jund, 1991; Savage & Davidson, 2003). 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 is 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 N_2O 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 N_2O 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 N_2O 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 N_2O 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 N_2O production via denitrification (Savage & Davidson, 2003). Similar diurnal trends are also observed with CH_4 emissions from rice (*Oryza sativa* L.) systems (Buendia et al., 1998).

2.2 | Sample frequency

The highly episodic response of N_2O 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 N_2O 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 N_2O 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).

A number of field comparisons have been made of manual and automated chamber methods; however, all suffer from the difficulty of having to compare different techniques in different places or at different times, thus confounding the consideration of technique with either spatial or temporal heterogeneity. Rowlings et al. (2015) examined the impact of sampling frequency on the accuracy of annual flux estimates across multiple land uses (Table 1). At sampling intervals of 3 d or fewer, errors associated with sampling frequency were greater than the diurnal variability of N_2O emissions, suggesting that sampling interval is more critical than sampling time. At weekly intervals or greater, errors increased significantly, potentially overestimating emissions in excess of 100% for agricultural land uses. In all land uses, coarser sampling intervals tended to overestimate, rather than underestimate, cumulative emissions estimates. van der Weerden, Clough, and Styles (2013) conducted three short-term field trials where N_2O fluxes were measured from urine-affected pastoral soil and assessed bias in cumulative emissions created by infrequent sampling. They recommended flux measurements to be sampled twice a week between 1000 and 1200 h over the first 4–6 wk after urine deposition, with additional sampling after significant rain (e.g., >10 mm d^{-1}). This sampling regime produced a +4% bias, compared with cumulative emissions based on frequent, two-hourly, flux measurements. It was therefore considered to represent a balance between practicality and data quality for estimating cumulative emissions. Similarly, Reeves et al. (2016) found that bias in annual cumulative emissions from sugarcane (*Saccharum* spp.) crops could be reduced to <10%

TABLE 1 Maximum and minimum annual N_2O fluxes (percentage deviation from the mean) from three land uses in subtropical Queensland (Australia) using all possible sampling frequency permutations (Rowlings et al., 2015)

		Sampling frequency					
Land use	**Min./max.**	**1 d**	**2 d**	**3 d**	**7 d**	**14 d**	**30 d**
		g N ha^{-1} yr^{-1}	%				
Rainforest	Min.	516[a]	−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

[a] Annual estimate of N_2O emissions calculated using a fully automated greenhouse gas measurement system with 10 cycles per day over 2 yr.

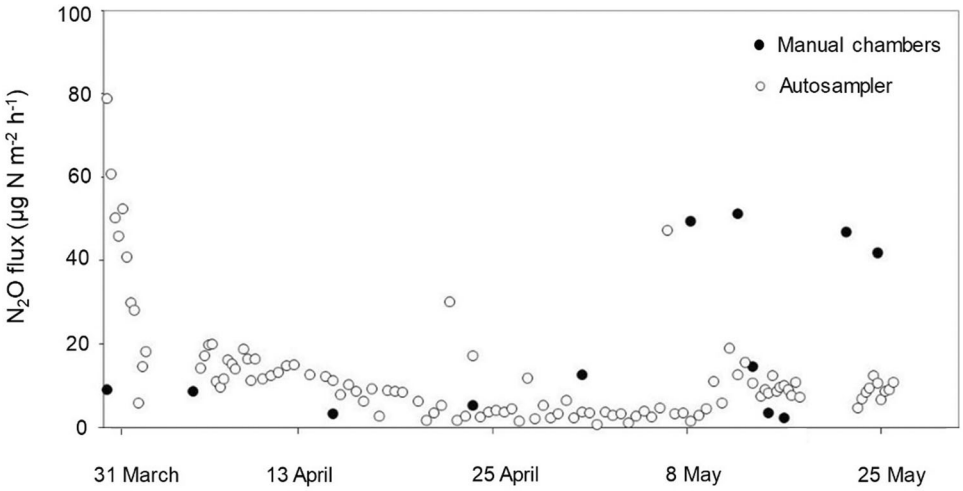

FIGURE 1 A comparison between N_2O fluxes measured from a grazed grassland in Scotland, using manual chambers and an autochamber. Data taken from a study by Ambus et al. (2010)

of the high-temporal-resolution estimates if sampling was conducted weekly rather than biweekly after rain events.

Scott, Ball, Crichton, and Aitken (2000) compared autochambers with manual chambers in measurements of N_2O emissions from grassland receiving either sewage sludge or synthetic fertilizer N. The manual chambers were sampled up to twice per week, and the autochambers were sampled up to six times per day over a 6-mo period. The study found that cumulative emissions from the sludge-treated plots over the 6-mo period measured by the autochambers were 20.6 kg N_2O-N ha^{-1}, compared with 13.3 kg N_2O-N ha^{-1} from the manual chambers. However, these differences were not significant due to a high CV (27.4%), and the manual chambers were better at identifying treatment effects, since (in this particular case) the increased replication of the manual chambers methods was able to take account of the spatial heterogeneity.

A variant of the autochamber technique has been reported 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_2O 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_2O 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 N_2O and potentially other gases, including CO_2 and CH_4. 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; McDaniel 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 N_2O, CH_4, and CO_2, or a subset of these gases. In some cases, an infrared gas analyzer is used for CO_2. 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 CO_2 (Kessavalou, Doran, Mosier, & Drijber, 1998), the optimum for N_2O 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.

FIGURE 2 Automated chambers developed by Queensland University of Technology (Australia) in collaboration with Karlsruhe Institute of Technology (Germany). In this picture, standard 37.5-L chambers are atop 125-L extensions to accommodate wheat

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, 2016; 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]) (Hube et al., 2016), India (International Crops Research Institute for the Semi-Arid Tropics [ICRISAT]),

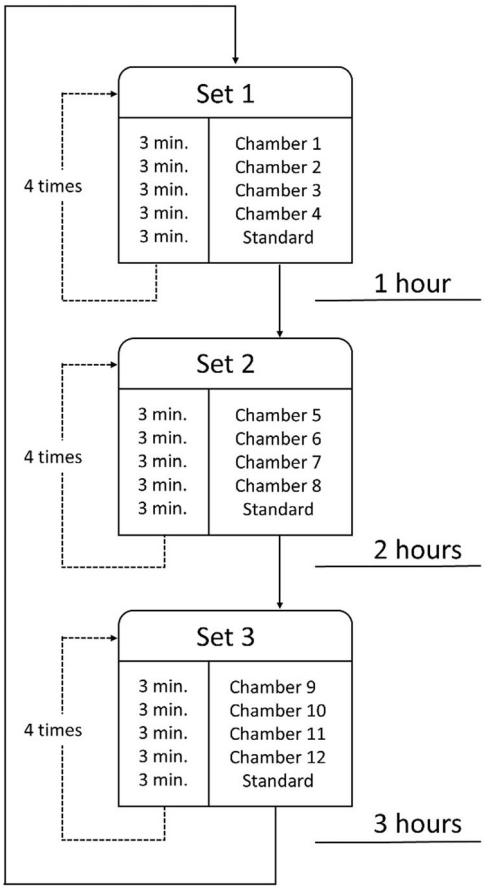

FIGURE 3 An example of a 12-chamber automated sampling sequence suitable for three replicates of four treatments

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).

Fluxes are calculated from the slope of the linear increase or decrease in N_2O 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 $\mu g\ g^{-1}$ 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 $\mu g\ g^{-1}$) 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.

The portable automated greenhouse gas measurement comprises two main parts: the automated chambers and the sampling unit, which also includes software to run the system and record data. Chamber operation, sampling, and data acquisition are computer controlled and run continuously. Mains (AC) power or a generator is required, and solar powered systems have also been deployed in remote locations (Li et al., 2016).

2.4 | Chamber design

The Queensland automated chambers are sealed airtight 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

FIGURE 4 Automated greenhouse gas chambers developed by AgResearch (New Zealand). Chamber open (left) and closed (right)

compressor). 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., CO_2 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).

FIGURE 5 The Karlsruhe Institute of Technology Robotic greenhouse has chamber system for mounting on lysimeters at the DE-Fen site within the TERENO (TERrestrial ENvironmental Observatories) network

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 N_2O 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 CO_2 analyzer (e.g., LI-820, LI-COR Biosciences), a GC (e.g., 8610C, SRI Instruments) containing a flame iodization detector (FID) for CH_4 and an electron capture detector (ECD) for N_2O, 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 CO_2 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 CH_4 and ECD for N_2O). 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 (N_2) 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 N_2O and CH_4 concentrations from chromatogram peak areas, and for calibrating the CO_2 sensor. For low-emitting systems, typical calibration standard concentrations are 0.5 $\mu g\ g^{-1}$ for N_2O, 4 $\mu g\ g^{-1}$ for CH_4, and 800 $\mu g\ g^{-1}$ for CO_2. 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 CO_2 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}

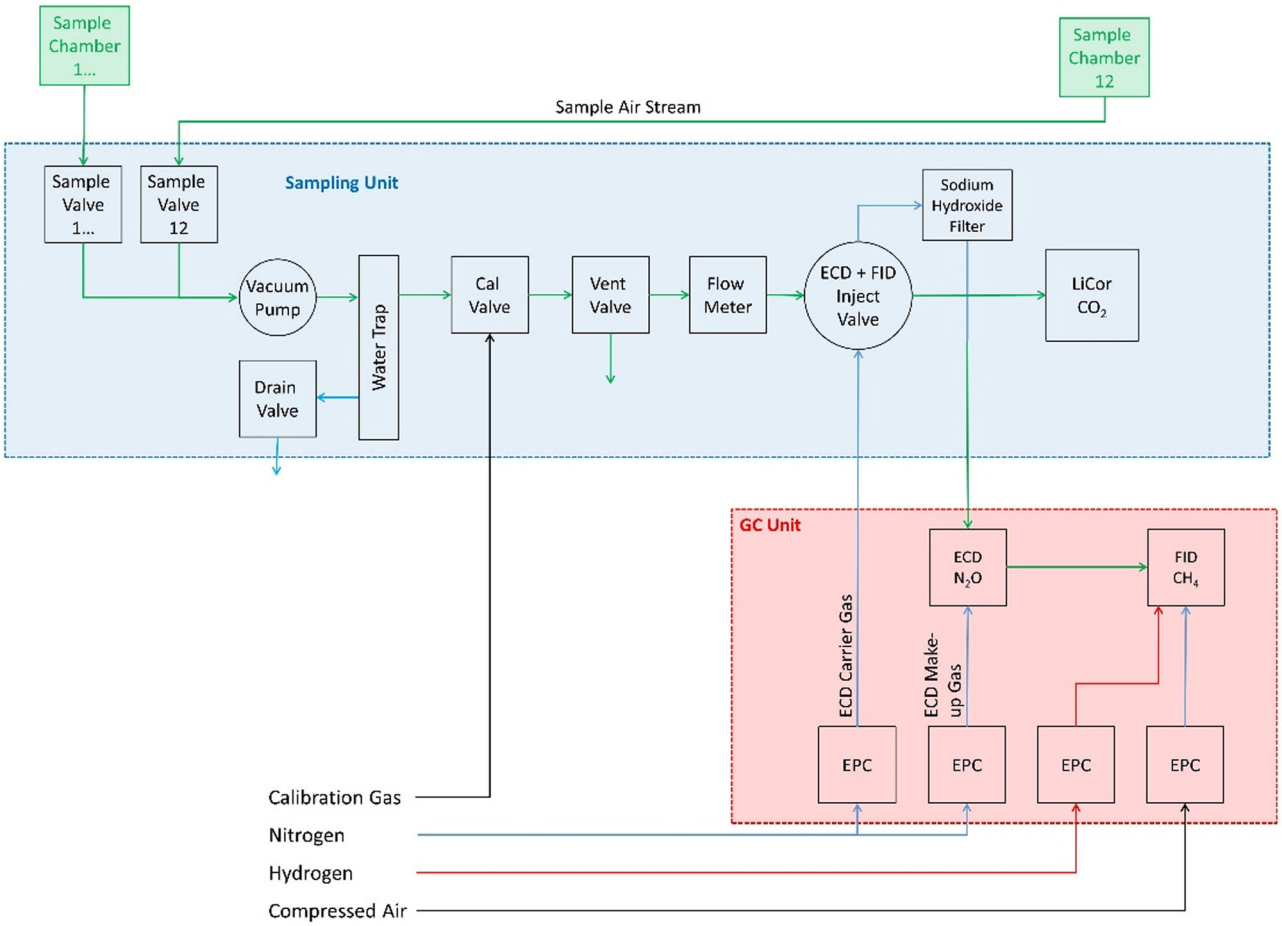

FIGURE 6 Gas sampling schematic of the Queensland automated greenhouse gas chamber system, showing the sample air path and carrier gases and calibration gas. ECD, electron capture detector; EPC, electronic pressure control; FID, flame iodization detector

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_2 and H_2O in the sample air must be removed (Zheng et al., 2008) before the online N_2O analysis in the GC can occur, as both gases are detected by the ECD and may interfere with the accuracy of the N_2O 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 ~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_2, and water vapor can be measured every 2 min. Because CO_2 interferes with the TGA's N_2O signal (de Klein, Harrison, & Lord, 1996), a correction factor is established, using a range of mixed CO_2 and N_2O gases of known concentration in N_2. In addition, CO_2 concentration in the air stream is minimized prior to

TGA analysis, using a soda lime trap (400-mm length × 10-mm diameter), which is renewed when CO_2 concentrations exceed 1,000 μg g^{-1} CO_2. 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 (R^2 between .93 and .98).

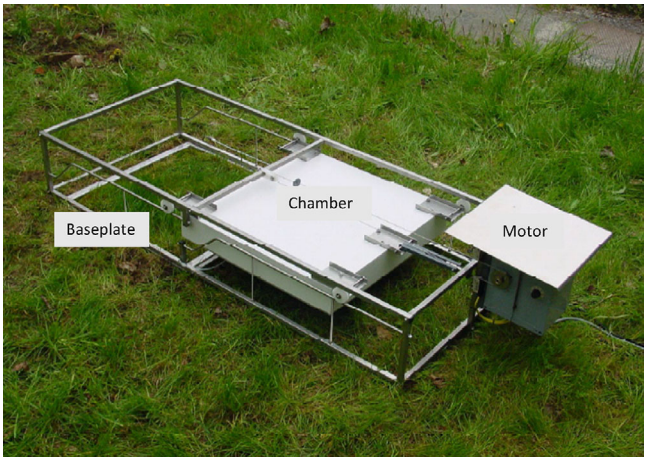

FIGURE 7 The chamber section of the Umwelt- und Ingenieurtechnik (UIT) autosampler, showing the moveable plastic chamber, rails, and electric motor

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 (N_2O, CO_2, and CH_4) 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} N_2O standard are injected from a certified calibration gas cylinder. Fluxes are calculated automatically using an 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 N_2O emission range. Typical sensitivity of QCL analyzers for N_2O is in the range of 0.03–1.0 ng g^{-1} for N_2O, 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 N_2O-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 N_2O-N ha^{-1} d^{-1} (2 μg N_2O-N m^{-2} h^{-1}) without chamber extensions, and 2.0 g N_2O-N ha^{-1} d^{-1} (8 μg N_2O-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 N_2O-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 N_2O-N ha^{-1} d^{-1} (3 μg N_2O-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

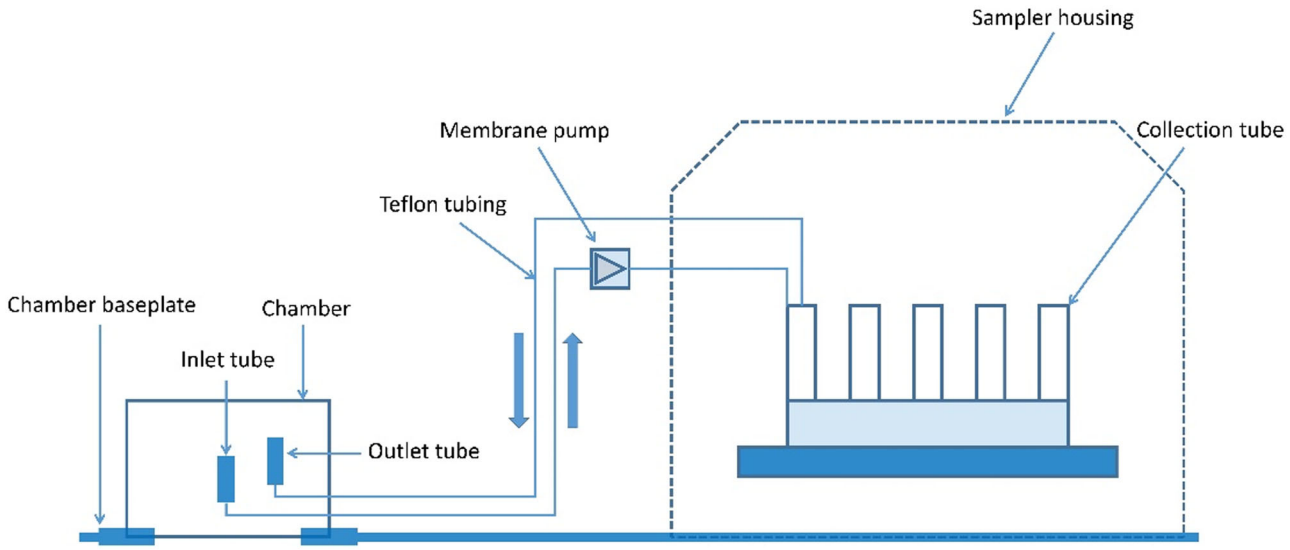

FIGURE 8 A diagrammatic sketch of the relationship between the auto-sampler and collection system used by the Umwelt- und Ingenieurtechnik (UIT) system

turntable and can be transferred directly onto the autosampling unit of a GC for N_2O 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 N_2O 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 CH_4 and N_2O concentrations (Courtois et al., 2019). Due to the high sensitivity of the CRDS instrument, a 2-min chamber closure time was sufficient to measure CH_4 concentrations, but for N_2O, a 25-min closure period was required in low-N_2O-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.

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CONFLICT OF INTEREST

The authors declare no conflict of interest

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