

SPECIAL SECTION:
GRA N₂O CHAMBER METHODOLOGY GUIDELINES

Global Research Alliance N₂O chamber methodology guidelines: Recommendations for deployment and accounting for sources of variability

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Abstract

Adequately estimating soil nitrous oxide (N₂O) emissions using static chambers is challenging due to the high spatial variability and episodic nature of these fluxes. We discuss how to design experiments using static chambers to better account for this variability and reduce the uncertainty of N₂O emission estimates. This paper is part of a series, each discussing different facets of N₂O chamber methodology. Aspects of experimental design and sampling affected by spatial variability include site selection and chamber layout, size, and areal coverage. Where used, treatment application adds a further level of spatial variability. Time of day, frequency, and duration of sampling (both individual chamber closure and overall experiment duration) affect the temporal variability captured. We also present best practice recommendations for chamber installation and sampling protocols to reduce further uncertainty. To obtain the best N₂O emission estimates, resources should be allocated to minimize the overall uncertainty in line with experiment objectives. Sometimes this will mean prioritizing individual flux measurements and increasing their accuracy and precision by, for example, collecting four or more headspace samples during each chamber closure. However,

Abbreviations: CBC, Chamber bias correction; EF, emission factor; NSS, non-steady-state; QCL, quantum cascade laser; WFPS, water-filled pore space.

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where N₂O fluxes are exceptionally spatially variable (e.g., in heterogeneous agricultural landscapes, such as uneven and woody grazed pastures), using available resources to deploy more chambers with fewer headspace samples per chamber may be beneficial. Similarly, for particularly episodic N₂O fluxes, generated for example by irrigation or freeze–thaw cycles, increasing chamber sampling frequency will improve the accuracy and reduce the uncertainty of temporally interpolated N₂O fluxes.

1 | INTRODUCTION

Static (or non-steady-state [NSS]) chambers are widely used for measuring nitrous oxide (N₂O) emissions worldwide (Rochette, 2011). They are simple, inexpensive, and versatile, but their (necessarily) small size (Clough et al., 2020) makes obtaining spatially representative and accurate field-scale N₂O fluxes challenging, and manual sampling imposes sampling frequency and duration constraints. Automated chamber methods that better account for temporal variability are becoming increasingly available (Grace et al., 2020), but manual sampling methods still represent the majority of measurements. Soil is not a homogeneous medium and most ecosystems (including agronomical plots) are a mosaic of N₂O sources of various intensities (Matthews, Chadwick, Retter, Blackwell, & Yamulki, 2010; Yanai et al., 2003). Spatial variability in management practices (e.g. fertilizer or water inputs) exacerbates this soil heterogeneity. Nitrous oxide emissions from agricultural systems also vary over time, responding to nitrogen (N) additions (e.g., manufactured fertilizer, manure, crop residues, or grazing returns) and rainfall-induced (or irrigation-induced) changes in soil moisture (Parkin, 2008). Capturing spatial and temporal variability and reducing the uncertainty of N₂O emission estimates requires careful experimental design and chamber deployment. Moreover, resource limitations restrict chamber numbers and sampling frequencies, necessitating design and sampling strategy optimization to generate accurate and comprehensive flux datasets which, in conjunction with ancillary data, achieve experiment aims.

Optimization of data collection must consider all sources of uncertainty relating to chamber deployment and N₂O measurement protocols. The relative importance of different sources of uncertainty depends on the specific experiment aims and site characteristics. The flux calculation method used (Venterea et al., 2020) has been found to be the single largest source of uncertainty in hourly flux estimates from individual chambers (Levy et al., 2011). More refined flux calculation methods require a greater number of headspace samples to be taken during chamber closure. This approach may give the best overall results if

the aim is to calculate accurate N₂O fluxes from individual chambers but becomes resource intensive as a larger number of chambers and/or sampling dates are required to adequately capture the spatial and temporal variability of N₂O emissions. McDaniel et al. (2017) recorded a mean temporal CV of >1,200% and a mean spatial CV of nearly 400% for automated chambers sampling at a high frequency compared with a static chamber array. However, a wider range (and SD) of N₂O fluxes was recorded from the static chambers (−19 to 476 $\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$, approximately −129 to 63 $\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}$ for the autochambers). The uncertainties associated with the spatial and temporal variability of N₂O fluxes vary with experimental site and could sometimes be larger than those relating to individual chambers or the flux calculation method.

The 2015 Nitrous Oxide Chamber Methodology Guidelines (de Klein, Harvey, et al., 2020) provided guidance on chamber methodologies for sampling N₂O emitted from soils. The papers presented in this special section provide updates on the 2015 guidelines. Here, we focus on updating recommendations for chamber deployment to reduce the uncertainty associated with the spatial, temporal, and experimental variability in N₂O fluxes. Our recommendations center on NSS chamber use to assess emissions from treatments and determine emission factors (EFs) but are applicable to any N₂O emission study using static chambers (e.g., using chamber arrays to assess the spatial variability of N₂O emissions and/or determine representative emissions in a particular environment; Charteris et al., unpublished data, 2020).

2 | FACTORS RESPONSIBLE FOR THE VARIABILITY OF N₂O FLUXES

Soil N₂O fluxes are spatially and temporally extremely variable. Large ranges in N₂O fluxes have been measured in “snapshot” spatial variability studies. For example, Turner et al. (2008) recorded fluxes of 45–765 ng N₂O-N m^{−2} s^{−1} (average = 165 ng N₂O-N m^{−2} s^{−1}) and 20–953 ng N₂O-N m^{−2} s^{−1} (average = 138 ng N₂O-N m^{−2} s^{−1}) for two experiments in summer and autumn, respectively,

on an Australian irrigated dairy pasture, whereas Cowan et al. (2015) recorded fluxes varying from 2,000–79,000 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ from 100 sampling points across an intensively managed, grazed 7-ha grassland in central Scotland. Temporal monitoring studies have similarly recorded large ranges, with episodic behavior in N_2O fluxes, even when spatial variations are excluded (e.g., 6.5–39.7 $\text{mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ from cropland in the United States measured using eddy covariance; Molodovskaya et al., 2012).

Soil-derived N_2O is produced largely via microbial processing, usually mainly by incomplete denitrification or during nitrification (Butterbach-Bahl, Baggs, Dannenmann, Kiese, & Zechmeister-Boltenstern, 2013). Denitrification is an anaerobic process that is favored by higher soil moisture contents (percentage water-filled pore space [% WFPS] > 70%), whereas nitrification is an oxidative process favored by lower % WFPS (Bateman & Baggs, 2005). In addition, both processes are subject to other important controls, such as N substrate, carbon (C) availability, and pH. Nitrous oxide fluxes therefore differ spatially with the variation of these processes in soil (depending on edaphic conditions, which in turn can depend on slope, aspect, larger scale features, management, weather, etc.) and temporally with changes in these conditions (due to weather and management). Soil N_2O fluxes are typically low, and commonly the emissions contributing to spatial integrations or annual budgets are observed from hotspots (Cowan et al., 2015) or during peaks that can last from a few hours to several weeks after events (e.g., soil disturbance, rainfall, irrigation, spring thaw, or N addition; Chadwick et al., 2011; Loick et al., 2017; Molodovskaya et al., 2012; Schelde et al., 2012). In both cases, uncertainties in measured fluxes result from uncertainties associated with properly capturing the underlying spatial and temporal heterogeneity of N_2O fluxes and those relating to NSS chamber protocols.

3 | ACCOUNTING FOR THE SPATIAL VARIABILITY IN N_2O FLUXES

3.1 | Site selection

Experimental site locations are often determined by a combination of practicalities and overall project and experiment goals. Where some choice remains, site selection should be considered in the context of wider local, regional, and national ecosystems, land uses, soil types, and climatic conditions and whether the site and management are representative.

In experiments aiming to determine emissions from a treatment (and often then calculate EFs), fluxes occurring prior to or without treatment are considered “background”

Core Ideas

- Account for spatial variation in site selection and chamber placement and coverage.
- Account for temporal variability with strategic sampling over a sufficient duration.
- Allocate resources to minimize the overall uncertainty of N_2O fluxes.

or control emissions (Pennock, Yates, & Braidek, 2006). Selecting relatively uniform areas helps to minimize interference from spatial heterogeneity in background emissions, although care needs to be taken to ensure site selection is still representative. Identification of homogeneous areas, in terms of N_2O fluxes, within a landscape (e.g., a grazed paddock or cropped field) can be achieved through exploratory flux sampling. Where this is not possible, the selection of areas within which landscape characteristics (e.g., aspect, slope or topography, distance from field features), management (both recent and historic; e.g., N application or irrigation), vegetation and soil type (or preferably properties, determined by basic soil sampling and analysis; e.g., pH, electrical conductivity, C/total organic C, N/extractable ammonium and nitrate) are consistent should reduce spatial variability in background emissions. Note, however, that fluxes may vary according to different factors at different sites (Charteris et al., unpublished data, 2020), and it may be difficult to estimate the spatial structure in N_2O fluxes. In addition, some soil properties are dynamic, so for maximum utility, soil sampling for baseline soil variables would need to be conducted shortly before the gas sampling experiment. For grazed pastures, the distribution of animals within the field, additional heterogeneity of grazing returns, and persistence time of these effects should be considered (Supplemental Section 1).

3.2 | Experiment spatial structure and spatial coverage

A plot is a discrete area to which a single treatment is applied. Plots should be kept as small as possible for improved homogeneity but must be large enough to allow for all sampling (N_2O and other ancillary measurements) required for the duration of the experiment. However, tradeoffs often exist between keeping plots as small as possible (while ensuring a large enough area for all sampling activities), and ensuring that the chambers cover as much of the plot as possible for accurate plot N_2O flux estimates (while leaving space for other sampling activities), without exceeding a chamber size that meets the requirements

for good chamber design (Clough et al., 2020) or using many small chambers that would be resource intensive. The size of the experimental plots (and number of chambers required per plot) can also be minimized by sampling some ancillary variables, such as soil pH and soil moisture content, at a lower spatial resolution than N_2O fluxes. Alternatively, pooling of pseudoreplicate soil samples prior to analysis to integrate plot-scale spatial variability and reduce resource demand is a common practice. Recently, this approach has been extended to gas samples (Arias-Navarro et al., 2013).

Each plot should have at least one NSS chamber on it. Where larger plots are required (e.g., for yield assessments), such that a single chamber can no longer provide an acceptable plot-scale estimate of N_2O fluxes, multiple static chambers are recommended to account for within-plot spatial variability and improve plot N_2O emission estimate accuracy. Chadwick et al. (2014) assessed the reliability of the standard deviation of the N_2O flux calculated from two, three, four, and five of the five chambers deployed on each experimental plot and found that there was a 10-fold reduction in the error as replication increased from two chambers to five. These multiple chambers per plot are pseudoreplicates but can be used to assess the within-plot spatial variability in N_2O fluxes. Only the average fluxes from each plot can be used in statistical analysis of treatment effects (Cardenas et al., 2019).

Statistical analysis of treatment effects also requires a minimum of three replicate plots of each treatment. More replicates will increase the ability of the experiment to identify treatment differences. This is the statistical power of the experiment, or the probability (expressed as a percentage) that a difference of a specified size will be detected as significant at a specified significance level (such as 5%, which equates to accepting a 5% probability of a false positive). The power is the probability of a true positive being detected and is commonly set at 80%. Given a required power, statistical software packages can calculate the ideal number of replicates required for the experiment. However, this may exceed available resources, necessitating compromise.

Fully replicated untreated control plots are recommended to assess background emissions, which will vary spatially and temporally and are required for the calculation of EFs (de Klein, Alfaro, et al., 2020). In addition, pretreatment N_2O flux measurements for treated plots provides information on preexisting spatial patterns of emissions, which can be used as covariates in statistical analyses.

Within the identified experimental area, and in the absence of any flux spatial structure, plots and chambers should be located randomly. Where differences or a trend in background emissions or conditions across the site are

present, replicate plots should be divided between areas that are uniform in themselves but differ from one another (blocks). Blocking enables variability between these areas to be isolated from the overall background variability and treatment effects. In a study exploring within- and between-block variability, Giltrap, Berben, Palmada, and Sagggar (2014) found spatial variability at both scales, highlighting the need for multiple replicates (and if plot size requires it, multiple chambers per plot) to obtain representative N_2O emission estimates.

Good plot spatial coverage by chambers is essential to obtain representative plot N_2O fluxes. If this cannot be achieved within the available resources, consider reducing (a) the number of plots (via fewer sites, treatments, or replicates), or (b) the number of headspace samples per chamber deployment. Due to the high spatial variability of N_2O fluxes, care must be taken when reducing treatment replicates below four for sufficient statistical power. Additionally, reducing the number of plots may reduce the overall experiment spatial coverage, leading to measured N_2O fluxes that are not representative at the site or experiment scale. The number of headspace samples can be reduced by replacing individual initial closure (t_0) headspace samples with average ambient air samples (Section 5.3.1), and/or reducing the number of headspace samples taken during chamber closure (Section 5.3). This approach reduces both sampling and analytical workloads and costs, leaving more resources to increase plot and site spatial coverage. However, a reduction in the number of headspace samples increases the uncertainty in individual chamber flux calculations (Venterea et al., 2020) and could affect the choice of calculation method, which has previously been shown to be a large contributor to uncertainty (Levy et al., 2011). Reduced headspace sampling must therefore not offset the benefits of increased spatial coverage.

3.3 | Chamber size

Dimension requirements for good chamber design are discussed in Clough et al. (2020). The effect of chamber height on flux-calculation accuracy and precision is discussed in Venterea et al. (2020). In this paper, we consider chamber area and height in terms of capturing spatial variability and minimizing the uncertainty in measured N_2O fluxes. The interaction between chamber height and closure duration is discussed in Section 4.1.

3.3.1 | Chamber area

Chamber areal coverage affects the spatial variability captured (Giltrap et al., 2014) and uncertainty in N_2O fluxes.

The greater the plot area covered by static chamber(s), the more accurate the plot-scale N_2O flux will be (although again note that accurate plot-scale N_2O fluxes do not equate to representative field- or landscape-scale fluxes, which depend on larger scales of spatial variability being captured by the overall experiment design). Larger chambers integrate fluxes over a larger area, averaging spatial variability at that scale. In studies seeking to understand spatial variability, multiple small chambers (ideally at variable spacings) can be used to determine its magnitude. However, it is recommended that the chamber area/perimeter ratio be ≥ 10 cm to minimize the relative error associated with a poor chamber seal, which decreases as chamber area increases (Rochette & Eriksen-Hamel, 2008).

Chambers covering an area up to 2 m^2 have been used, but most common designs have an area smaller than 0.5 m^2 . There have been few studies investigating the impact of differences in chamber area on the CV determined for a study area. Ambus, Clayton, Arah, Smith, and Christensen (1993) compared N_2O emissions from $15\text{-m}^2 \times 0.0078\text{-m}^2$ cylindrical chambers with $4\text{-m}^2 \times 0.49\text{-m}^2$ chambers along a transect. Emission patterns from the small chambers along the transect, and a higher than anticipated CV for the large chambers (40%) compared with the small chambers (77%), showed that mesoscale variation in N_2O emissions was present alongside small-scale N_2O hotspots. A statistically indistinguishable mean N_2O flux, but higher variability from 20 smaller cylindrical chambers (0.049 m^2) compared with eight larger rectangular chambers (0.5 m^2), was similarly observed in another study (Saggar, Tate, Giltrap, & Singh, 2008). The extent to which chamber shape (cylindrical vs. square) might also have affected variation (e.g., if one shape has a greater propensity for leaks) was not discussed in either paper. Smith et al. (1994) found that the CV for 24 small (0.13 and 0.49 m^2) chambers was 75% across an ungrazed field but estimated (by geostatistical analysis) that the CV for 51 simulations of a much larger (62 m^2) chamber would be much lower (25%), indicating spatial heterogeneity at the 10- to 100-m scale was present in the field. Thus, chamber size can affect the variability measured due to the scale of spatial N_2O variability (Section 2) captured by the chamber size (as well as layout, see Sections 3.2 and 3.4).

3.3.2 | Chamber height

Increasing chamber height (and hence headspace volume) reduces the physical impacts of enclosure but increases the minimum detectable flux (requiring longer chamber closures). It also affects the relative performance of

different flux-calculation schemes depending on measurement precision (Venterea et al., 2020; note, however, that chambers with higher *permanent* bases can cause greater within-chamber differences via, e.g., sun and rain shadows). Venterea et al. (2020) describe methods for quantitatively assessing the impacts of varying chamber height on flux-calculation accuracy and precision in the context of other important factors. These methods are recommended for site-specific evaluation, including evaluating the use of larger chamber heights to accommodate growing crops or for paddy crops (Bertora, Peyron, Pelissetti, Grignani, & Sacco, 2018; Olfs et al., 2018; Section 3.4.; note that for paddy crops, the headspace volume above the water level affects the uncertainty of N_2O flux measurements and should be recorded). Similar to Venterea et al. (2020), along with raising the minimum detectable flux, Lammi-rato, Lebender, Tierlingand, and Lammel (2018) found the uncertainty of individual N_2O flux estimates (calculated by linear regression over five headspace sampling points) increased with increasing chamber volume (perhaps indicating that headspace mixing is required; Clough et al., 2020).

3.4 | Strategic chamber placement

In many instances, management practices or cropping characteristics can create additional spatial variability (e.g., crop rows, irrigation patterns, grazed pasture, etc.). Adequately capturing field-scale N_2O emissions in these environments requires special consideration. Row crops may produce inter-row gradients in soil water and N content, which can be accounted for by an adequate sampling pattern (e.g., by placing chambers to include both row and inter-row areas; Cai, Ding, & Luo, 2012). Indeed, Olfs et al. (2018) describe a new chamber design to account for both row and inter-row areas (Clough et al., 2020). On irrigated crops, different irrigation systems can lead to different patterns of water distribution and, accordingly, soil moisture (Supplemental Section 2). This needs to be considered for chamber location (e.g., by selecting wetter and drier areas and ensuring some chambers are located on each), as does the N application method (e.g., band spreading, broadcast, drip fertigation), which affects N distribution and thereby appropriate chamber orientation (e.g., on bands and between bands, or encompassing a full band and half the space between bands on either side to obtain emissions from the full N gradient). Nitrous oxide emission calculations per hectare need to include the area of each sampled component (e.g., bands and between bands). This is also the case for animal urine patches (Supplemental Section 3).

3.5 | Treatment application

As discussed above, background spatial variability can be separated from treatment-induced effects via good experimental design. However, spatial variability is also associated with treatment application. For example, an experiment designed to measure the effects of adding manure, animal urine, crop residues, manufactured N fertilizer, or other treatments can be conducted in three ways: (a) prescribed amounts of N can be manually applied within the chambers in situ within their subplot (e.g., for urine and dung to pasture; Krol et al., 2016), (b) N can be applied to a larger area than the chamber (e.g., to a small plot before placing the chamber; Nicholson et al., 2017), or (c) N can be applied via farm-scale spreading equipment and chambers placed over the amended soil (Thorman et al., 2007). For all methods, there will be variability between plots of the same treatment due to underlying differences in the potential to produce N₂O emissions (i.e., spatial variability in the soil environment). However, Methods a and b usually reduce spatial variability, compared with Method c, as uneven amendment distribution by farm machinery will contribute further to the spatial variability of N₂O emissions. For Method c, the heterogeneity of the application method may require more chambers to be used. The treatment application method depends on the experiment objective(s) and whether typical agricultural practices need to be represented.

Moreover, N amendments to the soil affect both an immediate soil area and volume, as well as a greater diffusional area and volume which develops over time. Buckthought, Clough, Cameron, Di, and Shepherd (2016) recovered 21.5% of the ¹⁵N applied to a central urine patch in diffusional zones outside the central patch. Furthermore, Marsden, Jones, and Chadwick (2016b) showed that the N₂O EF including the diffusional area of a simulated urine patch applied to a moist soil (70% WFPS) was larger than the EF measured from the wetted area only. Different vegetation cover and soil types and textures (and even soil moisture content) affect urine patch diffusion. The relative importance of emissions from the wetted and diffusional treatment areas therefore varies with patch size, site, and season.

Several different approaches to treatment application (e.g., urine patches) for NSS chambers exist in the literature. Chadwick et al. (2018), for example, applied urine to a 60-cm × 60-cm area and then placed a 40-cm × 40-cm area chamber within this, excluding N₂O emissions from the diffusive area. Other researchers have taken the opposite approach and applied a single small urine patch within a chamber, allowing for patch diffusion within the chamber area and thereby accounting for all diffusive area N₂O emissions. For example, Marsden, Jones, and Chad-

wick (2017) and Marsden, Holmberg, Jones, and Chadwick (2018) used 150–385 ml sheep urine with wetted areas of 113–300 cm² within 50-cm × 50-cm chambers. Depending on the treatment concentration, however, for smaller patches this can lead to treatment N₂O emissions that are low or more difficult to detect. Accordingly, Marsden et al. (2019) used three sheep urine patches (each 195 ml with wetted areas of ~100 cm²) in 50-cm × 50-cm chambers, where the sum of the areas of the three patches represented 12% (by wetted area) of the chamber area.

Recent work has indicated the total amount of N applied, rather than the concentration of N, determines N₂O losses from urine patches (i.e., N₂O emissions from a small, high-concentration patch are similar to those from a large, low-concentration patch; Hoogendoorn, Saggar, Palmada, & Berben, 2018; Loick et al., 2017; Marsden, Jones, & Chadwick, 2016a; Orwin et al., 2009). However, the spatial distribution of equal amounts of urine N to several small areas or one large area may affect N₂O emissions (Marsden et al., 2016a; Orwin et al., 2009).

Different approaches also exist in calculating treatment EFs from static chambers with partial treatment coverage, with some researchers using only the wetted area and others the whole chamber area in calculations (López-Aizpún et al., 2020; Mori & Hojito, 2015). Care must therefore be taken when comparing EFs between studies. In addition, the delivery methods of treatments with additives (e.g., N amendments with nitrification inhibitors or ¹⁵N-labeled tracers) can be a source of variability. Premixing of amendments and inhibitors or tracers (Chadwick et al., 2018; Guardia, Vallejo, Cardenas, Dixon, & García-Marco, 2018) or spray application of inhibitors after the N source has been applied (Misselbrook et al., 2014) are common approaches. Repeated applications of treatments and inhibitors (e.g., additional urine patches to represent patch overlap) have also been used (Di, Cameron, & Sherlock, 2007) and may further complicate EF calculations. Furthermore, inhibitors often add further N to treatment plots (e.g., dicyandiamide [DCD] contains 67% N), and not all studies account for this in EF calculations. Greater standardization in experimental protocols and EF calculations are required to facilitate the use of EFs as comparable indicators (de Klein, Alfaro, et al., 2020).

To minimize the uncertainty in N₂O estimates and EF calculations due to treatment application, researchers should consider (a) the treatment application method; (b) appropriate application rates for the treatment being investigated, but ensuring sufficient treatment or N to induce a discernible effect; (c) the treatment area (and potential diffusive area) and distribution within the plot (and the necessary chamber size; Section 3.3.); (d) the delivery method of treatments with additives; (e) how repeated or overlapping treatments will be accounted for; and (f) the EF

calculation (de Klein, Alfaro, et al., 2020), to ensure the chosen approach is appropriate to the study aim(s) and site(s). Table 1 summarizes our recommendations for reducing uncertainty from the spatial variability of N_2O fluxes.

4 | ACCOUNTING FOR THE TEMPORAL VARIABILITY IN N_2O FLUXES

Given the episodic nature of N_2O fluxes, high frequency or continuous measurement techniques such as automated chamber systems (Grace et al., 2020) or micrometeorological methods (e.g., eddy covariance; Cowan et al., 2020) can provide better estimates of integrated N_2O emissions (Jones et al., 2011). However, these approaches require expensive equipment and experienced operators, beyond the scope of many project budgets. Additionally, measurement techniques that integrate fluxes over large areas are not suited for exploring statistical differences between typical replicated treatment plots, and eddy covariance systems are ill-suited to some environments (e.g., steep slopes or short fetches). Thus, most cumulative N_2O emission estimates, such as the amendment induced EFs used for national soil N_2O inventories, are determined using data obtained from manual NSS chambers (Bell et al., 2015; Cardenas et al., 2019; Chadwick et al., 2018). These chambers are typically deployed for short durations, sampled daily at best, and used for experiments of up to ~12 mo. Sufficiently capturing N_2O fluxes for accurate temporal integration can therefore be challenging.

4.1 | Chamber closure duration

Changes in the within-chamber physical environment, the risk of leaks, and potential for diffusional feedbacks due to accumulating headspace concentrations (Rochette & Eriksen-Hamel, 2008) increase with deployment time (Clough et al., 2020; Venterea et al., 2020). Long closure times have been found to significantly increase N_2O flux uncertainties when linear regression is used to calculate the N_2O flux (Cowan, Famulari, Levy, Anderson, Bell, et al., 2014). Although short deployment periods can lead to low chamber N_2O concentrations, 30-min closures for 0.2-m-high chambers should produce headspace N_2O concentrations ($>3 \mu\text{g N m}^{-2} \text{ h}^{-1}$) detectable by gas chromatographs (Rochette & Eriksen-Hamel, 2008). However, when using nonlinear flux calculation methods for estimating the flux at t_0 (Venterea et al., 2020), the flux estimate is independent from deployment time, and a longer closure duration allows researchers to take more gas samples per chamber. This in turn provides more options

in choice of flux calculation method (Venterea et al., 2020). More recently, technological advances have enabled infrared quantum cascade lasers (QCLs) to be used with NSS chambers (Cowan, Famulari, Levy, Anderson, Reay, et al., 2014; Cowan et al., 2015), providing lower detection limits ($<2 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$) with shorter (5 min) closure times (Cowan, Famulari, Levy, Anderson, Bell, et al., 2014). In addition, there is a greater chance that the assumption of a linear increase in chamber headspace N_2O concentrations is satisfied over a shorter closure period. However, the guidance provided by Venterea et al. (2020) for the selection of a flux calculation method should still be considered. The disadvantages of QCL systems are their relatively high purchase costs and power supply requirements, which can limit mobility and reach (Cowan, Famulari, Levy, Anderson, Bell, et al., 2014).

Where higher chambers are required (e.g., over growing crops), duration may be increased. Additionally, a longer closure duration (60 min) with smaller chambers (35.6-cm diam. \times 11-cm height) is required in ^{15}N tracer experiments to obtain detectable $^{15}\text{N}_2\text{O}$ headspace concentrations (Guardia et al., 2018). For logistical reasons, the chamber deployment duration used in experimental protocols may also depend on (a) the number of headspace samples taken during the enclosure period (Section 5.3.), (b) the number and spacing of simultaneously deployed chambers, and (c) the number of field operators.

4.2 | Approximating daily mean emissions

Soil N_2O fluxes vary diurnally (Cardenas et al., unpublished data, 2020), but manual static chambers can usually only be deployed once per day at best (both for practical reasons and to avoid excessive disturbance; Sections 4.4. and 5.1.). Daily deployments therefore aim to capture N_2O fluxes approximately equal to the daily mean. In the absence of transient fluxes after a disturbance of soil N_2O -producing processes (e.g., N application, soil tillage, or rainfall), fluxes are largely controlled by soil temperature (Livesley et al., 2008). Thus, NSS chamber deployment at the time of the daily mean soil temperature (e.g., measured in the plow layer at arable sites) will often capture the daily mean N_2O flux (Laville, Lehuger, Loubet, Chaumartin, & Cellier, 2011; Supplemental Section 4). Alternatively, periodic measurements of the diurnal pattern in soil N_2O emissions during an experiment are an adequate way to determine the deployment time representative of daily mean N_2O fluxes. However, such measurements have resource implications.

Smith and Dobbie (2001) reported that deployments at 0300, 1100, and 1900 h yielded fluxes similar to mean

TABLE 1 Summary of aspects of variability and recommendations discussed in this paper

Aspect	Recommendation to account for variability and reduce uncertainty
Aspect of spatial variability	
Site selection	Identify representative area and assess whether spatial structure in N ₂ O fluxes exists.
Experiment spatial structure	Divide area into homogenous sections (blocks) and stratify sampling. If no spatial structure, select plots and place chambers randomly. Each plot must have at least one chamber. A minimum of three replicate plots is required. A statistical “power” analysis to determine the required level of replication is recommended.
Spatial coverage	Chambers should cover an area as large as practical, while providing information at the smallest scale for which it is needed, and avoiding resource-intensive large numbers of small chambers, to achieve good coverage at a small scale.
Background emissions and control plots	Pretreatment N ₂ O flux measurements indicate underlying flux patterns and can be useful as covariates in statistical analyses. Replicated untreated control plots are recommended to estimate background emissions throughout and are required to calculate emission factors (de Klein, Alfaro, et al., 2020).
Chamber size	Chambers having larger areal coverage integrate spatial variability. Chambers should integrate N ₂ O fluxes at the desired scale and meet other requirements for good design with respect to area, height, and other considerations (Clough et al., 2020; Venterea et al., 2020).
Strategic chamber placement	Chamber placement must account for local features (e.g., crop row and inter-row gradients, irrigation-induced soil moisture gradients, or urine and dung patches) by either spanning chambers across features to integrate them or locating individual chambers on all desired features and accounting for the feature area as a proportion of the total and sampled areas in total calculations.
Treatment application	Different approaches exist (e.g. including/excluding urine patch diffusional areas), options should be considered, and approach selected reported in detail (including calculation details) to facilitate comparison between studies (see also de Klein, Alfaro, et al., 2020).
Aspect of temporal variability	
Chamber closure duration	Effect of closure time depends on flux-calculation method used and other factors (e.g., soil properties). Longer closures tend to increase uncertainty with linear regression and can have varying effects for nonlinear methods (Venterea et al., 2020).
Daily mean emissions	Previously, sampling between 1000 and 1200 h was recommended to capture the daily mean N ₂ O flux in temperate climates (Alves et al., 2012; Parkin, 2008; Smith & Dobbie, 2001). However, recent studies have suggested that an earlier time period might be better for some sites. Whenever possible, researchers should determine local diurnal N ₂ O emission patterns to assess times that best represent the daily mean N ₂ O flux for their study. At a minimum, researchers should assess the time that best represents the mean daily soil temperature, at a depth appropriate to their experimental study.
Temporal coverage	A strategic sampling frequency in response to events is preferred, but the whole “envelope” of an N ₂ O emission peak (pre- and post-event) must be included to avoid cumulative emission overestimation. Sampling frequency should be as high as resources allow. As a minimum, when higher soil N ₂ O emissions are occurring, chambers should be deployed at least twice per week and at higher intensities around events. When N ₂ O fluxes are low, deployment frequencies of once per week are appropriate. Deployment intervals may be increased only when near-zero or background fluxes are sustained (e.g., in dry or cold soils).

(Continues)

TABLE 1 (Continued)

Aspect	Recommendation to account for variability and reduce uncertainty
Duration of the experiment	Ideally, continue the experiment until there is no significant difference between pre- or control and post-treatment N ₂ O emissions and/or driving soil properties (e.g., soil NH ₄ ⁺ and NO ₃ ⁻ concentrations) are not statistically different from the background or control. Recent work (Vangeli et al., unpublished data, 2020) provides guidance for shortening experiments while still capturing 90% of 365-d N ₂ O emissions. For emission factor measurements for inventories, measurements should ideally be continued for 12 mo.
Practical/experimental aspects	
Chamber installation and site disturbance	Chamber bases must be inserted at least 24 h before the first sampling occasion and their GPS locations recorded. Minimize soil disturbance around chambers. Chamber relocation may be considered if within-chamber soil conditions become different from those externally, but there will be implications for data analysis.
Sequence and grouping of chamber measurements	Experiments should be sampled per block (rather than per treatment) to minimize within-block differences, and the order of block sampling should be rotated. Multiple operators allow the experiment size to be increased, but training to ensure protocol standardization is essential.
Headspace air sampling	Ideally, four or more headspace samples per flux measurement should be used to determine accurate fluxes for individual chambers (Venterea et al., 2020). However, when spatial variability is high (e.g., when within-treatment variability is similar to between treatment variability), overall uncertainty may be reduced by deploying more chambers with fewer headspace samples. In such cases, (non)linearity must be investigated and the potential bias introduced by assuming a linear increase in headspace N ₂ O concentrations stated.
^a <i>t</i> ₀ sample	<i>t</i> ₀ headspace air samples should be taken immediately after chamber closure. If ambient air samples are used to estimate <i>t</i> ₀ N ₂ O concentrations, researchers need to establish that ambient air N ₂ O concentrations are not significantly different from within chamber <i>t</i> ₀ samples.
Ancillary measurements	The need for additional measurements depends on the experiment objectives. Measurements of soil water content, bulk density, and temperature allow for application of the chamber bias correction (CBC) method (Venterea et al., 2020). To interpret N ₂ O fluxes, soil and air temperature and rainfall should be measured on a daily or hourly basis; soil moisture should be measured as often as needed to provide a representative estimate of conditions on each gas sampling occasion; soil mineral N should be measured as often as resources allow and especially after N additions; and soil bulk density, pH, organic C, and total N content should be measured at least once during the experiment. When possible, all ancillary measurements should be made in order to meet requirements for eventual flux calculations using mathematical models.

^a *t*₀, initial chamber headspace.

daily values, whereas estimates by Parkin (2008) at 0600 and 1200 h were 14% lower and 8% greater, respectively, than daily means. Measurements by Alves et al. (2012) in Scotland and Brazil suggested that in both countries, despite the contrasting climatic conditions, the times that best represented daily mean N_2O fluxes were 0900–1000 and 2100–2200 h. In a New Zealand study using near-continuous measurements of N_2O emissions from urine patches, van der Weerden, Clough, and Styles (2013) found mean daily fluxes occurred between 1000–1200 and 1800–2100 h. Recent work by Cardenas et al. (unpublished data, 2020) based on the N_2O fluxes measured in three pastures over 6 yr using automated chambers indicated that the mean time of the daily mean N_2O flux (across all years, months, and pasture types) was 0900 or 2100 h. A sampling time of 0900 h is earlier than previously suggested (1000–1200 h) for N_2O sampling in temperate climates (Alves et al., 2012; Parkin, 2008; Smith & Dobbie, 2001).

Most experimental designs and measurement protocols assume that diurnal emissions patterns are the same for all treatments and throughout the year, which may not be the case. If treatments alter soil surface albedo or insulation, for example, the time of daily minimum and maximum soil temperature near the surface soil will likely differ. Similarly, placing N fertilizers at different depths can also produce different temporal patterns in surface fluxes. Corrections can be made using “flux vs. temperature” relationships but fully accounting for these biases is difficult (Parkin & Kaspar, 2006).

4.3 | Temporal coverage

Static chambers are deployed for short periods (<1 h) and typically sampled at relatively long intervals (from 1 to 14 d). Therefore, they provide direct estimates of soil N_2O fluxes for a very small fraction of the time over which they are intended to estimate the cumulative emissions (month, season, year). Using 28-yr-long autochamber datasets spanning three continents (Europe, Asia, and Australia), Barton et al. (2015) found that daily sampling was required to generate an estimate of annual N_2O emissions within 10% of the best estimate for each dataset. As N_2O flux peak duration and chamber sampling frequency decrease, the error associated with time-integrated emissions of a soil N_2O emission peak will increase (Parkin, 2008). Maximum errors are observed when an emission peak occurs between two consecutive deployments, and when infrequent measurements coincide with short-lived peaks. Consequently, it is crucial to select an adequate number and time of sampling events when linear inter-

polation is used to integrate emissions between sampling points.

The maximum number of sampling dates during an experiment is finite and depends on available resources, the number of chambers, and the site characteristics (distance from the laboratory, spatial arrangement of plots). Therefore, sampling frequency can vary from daily, for simple experiments located at nearby sites, to weekly or longer for those at remote locations. However, as the weighting of individual measurements increases as sampling frequency lessens, intervals >7 d are usually only appropriate when conditions are conducive to near-zero fluxes (Parkin, 2008). This is most likely when soils remain dry for long periods (e.g., during the summer in rainfed Mediterranean regions; Sanchez-Martin, Dick, Bocary, Vallejo, & Skiba, 2010), or cold for extended periods.

A fixed sampling interval is often used, but a better option is usually to vary the frequency based on whether emission peaks are expected (e.g., due to triggers such as rainfall or fertilizer application; Barton et al., 2015; Saha, Kemanian, Rau, Adler, & Montes, 2017). If this approach is used, the whole “envelope” of an N_2O emission peak (before and after the event) should be captured to prevent overestimating cumulative fluxes. For example, where soils are irrigated in summer and evaporation and evapotranspiration rates are high, soil moisture in the top layers can fluctuate from dry to very wet to dry again, and high N_2O sampling frequencies (depending on moisture loss rates but ideally daily until dry conditions are restored) are required to reduce bias in the total calculated emissions (Guardia et al., 2018; Supplemental Section 5). Similarly, despite cold conditions, freeze–thaw cycles can increase N_2O emissions and should be monitored (Ruan & Robertson, 2017). Rapid gas sample analysis allows responsive monitoring and helps determine when the sampling frequency can be reduced.

Finally, consideration should be given to whether conditions during the studied period were representative (e.g., of the season), and the number of replicate experiments over time or different years required to accurately assess seasonal or annual emissions at that site. Differences in weather between years can affect N_2O emissions considerably, so EFs based on 1 yr of measurements only may misrepresent emissions. Accordingly, journals are increasingly requiring more than one site year of N_2O flux data. Researchers should consider this in grant applications, experiment planning, and overall use of the resulting emissions data, as single-year measurements are still useful for model validation and in future meta-analyses (especially if appropriate meta-data are included in the study; de Klein, Alfaro, et al., 2020).

4.4 | Duration of the experiment

In studies intended to quantify the emissions induced by a climatic event, agricultural practice (e.g., N fertilizer application), or experimental treatment (e.g., nitrification inhibitor or fertilizer form and application method), measurements should continue for as long as soil properties affecting the N_2O emission are changed by the event or practice (to capture the entire treatment-induced “emission envelope”). This can be achieved by continuing emission measurements until soil ammonium and nitrate concentrations in the treated soil are not statistically different from the control. Alternatively, Vangeli et al. (unpublished data, 2020) provides guidance on experiment duration by determining the minimum duration of measurements required to capture 90% of 365-d N_2O emissions from different excretal N sources, using a database of spring, summer, and autumn U.K. and Irish studies. On average, periods of 3, 5, 7, and 9 mo were sufficient for urine, farmyard manure, dung, and slurry treatments, respectively. The season of application did affect this average, however, with spring applications requiring the shortest duration of measurements and summer applications the longest.

If the measurements are to be used to determine EFs for soil N_2O inventories, they must ideally be taken over a year to comply with Intergovernmental Panel on Climate Change (IPCC) recommendations. There can be challenges in measuring fluxes over long periods, however. Soil compaction from repeated foot traffic next to the sampling sites can bias flux measurements by modifying gas production and vertical transfer (Section 5.1). Additionally, sometimes soil conditions are not suited to NSS chamber use, such as during flooding or when covered by thick snow. The resulting gaps in the coverage of annual emissions must then be estimated by other means—for example, by using a gap-filling approach (Dorich et al., 2020). Table 1 summarizes our recommendations for reducing uncertainty associated with the temporal variability of fluxes.

5 | PRACTICAL RECOMMENDATIONS FOR EXPERIMENT DESIGN AND CHAMBER DEPLOYMENT

5.1 | Chamber installation and site disturbance

Static chamber base installation causes soil disturbance, which may affect gas emissions (Matthias, Yarger, & Weinbeck, 1978; Norman, Garcia, & Verma, 1992). Bases should be installed long enough before chamber deployments to allow for soil and crop conditions to return to a steady state

approximating undisturbed conditions. On bare soil, this might take as little as one hour for coarse-textured soils, or a few days for clay soils (P. Rochette, personal communication, 2012). Pavelka et al. (2018) recommend installation at least 24 h prior to the first N_2O flux measurement.

Base installation in vegetated areas often damages roots, so several days or perhaps weeks (even months) will be required to allow root regrowth (Rochette & Hutchinson, 2005). This will avoid any potential impact of root death, which will disrupt C and N cycling and affect N_2O production in the soil profile. This is important if the study aims to assess the effects of root C leakage on N_2O emissions (Luo et al., 2018). Otherwise, shallower wall insertions may be needed, (such as in forest ecosystems; Pavelka et al., 2018), but only if other criteria for good design and deployment are used (Clough et al., 2020). Alternatively, control treatments experiencing the same root damage effects can be used to exclude this factor from the assessment of treatment effects.

For annual crops, bases should ideally be installed either shortly after sowing, to allow roots to grow within the inner area, or between the rows, depending on the research question. Chamber extensions are usually used to keep the crop within the chamber height, but this can reduce sensitivity in detecting N_2O emissions, and chamber closure periods often need to be extended, which has some disadvantages (Section 4.1). Additionally, farm activities (e.g., cultivation, drilling, reseeding, fertilizer application, etc.) may require temporary chamber or base removal. Accordingly, it is recommended that exact chamber locations are recorded (e.g., using a GPS) to enable same-location reinstallation after activity for consistency. Even if chambers are unlikely to be removed and replaced, recording exact locations is good practice and may later be useful for comparisons between years at that site.

Soil water content can affect chamber performance in several ways. Researchers walking around the chambers, especially in very wet conditions, can displace soil gases as well as compact the soil. For this reason, when chambers are located on a slope, it is advisable chambers are accessed from the downslope position to minimize the impact of sampling on the chamber soil conditions. Sampling in wet conditions can disturb the soil and modify N_2O production and vertical transport. Walking boards reduce this, but sampling NSS chambers in saturated soil often causes site deterioration that requires bases to be relocated. The implications of this for subsequent data analysis must be considered. Bases may also affect lateral surface water flow, and they should be relocated when soil water content differs from surroundings (Rochette & Bertrand, 2008). In paddy fields, where saturated conditions are the norm, wooden access bridges have been used (Bertora et al., 2018). Finally, under very dry conditions, clay soils may shrink away

from the edge of the chamber base. In such circumstances, researchers should loosen and tamp down the soil at the outer edge of the base prior to measurement to fill the gap and improve the seal between the soil and the base.

5.2 | Sequence and grouping of chamber measurements

Grouping and sequence of chamber measurements vary depending on deployment duration, experimental design, and human resources. The number of chambers that can be handled by one operator increases with deployment duration but decreases with the number of headspace samples and distance between bases. Chamber size and height, or stacking requirement (tall crops), may also affect the number of chambers an operator can handle safely and competently. The time interval between sampling two chambers varies, depending on their location, but it is usually ≥ 60 s. Where an operator samples a different chamber every minute, the four air samples (at 0, 8, 16, and 24 min) for eight chambers will be completed in 32 min.

For experiments with treatment replicates (or blocks), a full set of each treatment (i.e., Replicate 1 of Treatments A, B, and C, or one whole block) should be sampled as a group in as short a period as possible, before moving on to sample the second replicate of each treatment (or the next block). This reduces differences between treatments or within blocks due to sampling time and facilitates statistical analysis. The sampling sequence should also vary between sampling dates (e.g., the next day start with Replicate 2 of Treatments A, B, and C, or Block 2), to avoid any potential bias from always sampling in a particular order. This is also avoided through multiple operators for chamber sampling (e.g., one per block), as they can each measure a different block at the same time. Increasing the number of operators is also useful for larger experiments. In both cases, however, training is required to ensure the same sampling protocol is used by all operators.

5.3 | Headspace air sampling

When deploying chambers for measuring N_2O emissions, it is important to determine the requisite number of headspace samples to provide the least biased flux estimate (Venterea et al., 2020). The more headspace samples taken, the better the characterization of N_2O accumulation, and thus the less biased each individual flux estimate. However, resources are finite, and excessive headspace samplings from a small chamber may induce unwanted effects.

Rochette (2011) proposed that four or more air samples should be taken during static chamber deployment, to ade-

quately assess the quality of the calculated flux (detection of outliers and technical problems during handling and analysis of samples), and to account for the increased likelihood of a nonlinear N_2O flux with increasing deployment time. Venterea et al. (2020) similarly advocate for the collection of four or more headspace samples *alongside soil data*. In this paper, we reinforce this recommendation but also acknowledge that a less intensive chamber headspace sampling protocol may be acceptable for certain situations. An analysis by Levy et al. (2011) suggested that prioritizing the number of headspace samples per chamber, rather than the number of chambers, improved estimation of the mean flux at that point in time. In addition, Lammirato et al. (2018) suggested that since reducing the number of headspace samples increases the uncertainty of the estimated flux and the detection limit, it may not be appropriate to reduce the number of headspace samples when very low (near baseline) fluxes are expected. Subsequently, Jungkunst, Meurer, Jurasinski, Niehaus, and Günther (2018) concluded that although the above holds for shorter term studies, longer term studies (e.g., annual budgets) or those with high spatial heterogeneity (e.g., within-treatment variability is similar to between treatment variability) may benefit from better spatial coverage (Section 3.2) with fewer headspace sampling points. Moreover, very low fluxes do not contribute greatly to annual budgets, so the additional uncertainty associated with them may not be important. Any consideration regarding reducing headspace sampling intensity should be based on minimizing the overall uncertainty of the N_2O emission estimate.

Venterea et al. (2020) provide guidance on the selection of flux-calculation method depending on the number of headspace samples available, and the relative favorability of sampling options where four or more headspace samples, plus soil data, cannot be achieved. If fewer (two to three) headspace samples are taken, it is essential to quantify any potential bias introduced. This can be done by taking a random subset of chambers on each sampling occasion and conducting four or more headspace samples during the two- or three-point sampling strategy (Cardenas et al., 2010). Treatment effects (e.g., different application methods or high N application rates) do not seem to alter the tendency for linearity (Chadwick et al., 2014; Pedersen, Petersen, & Schelde, 2010), so a random subset of chambers should be used for this assessment. Each dataset of four or more headspace samples should be statistically analyzed to determine (non)linearity. Researchers should summarize this information, provide a percentage of cases when linearity was observed, and cite this alongside their calculated flux (Chadwick et al., 2014; Thorman et al., 2020). This provides an indication of the bias in the results that may have been introduced by assuming linearity in the flux

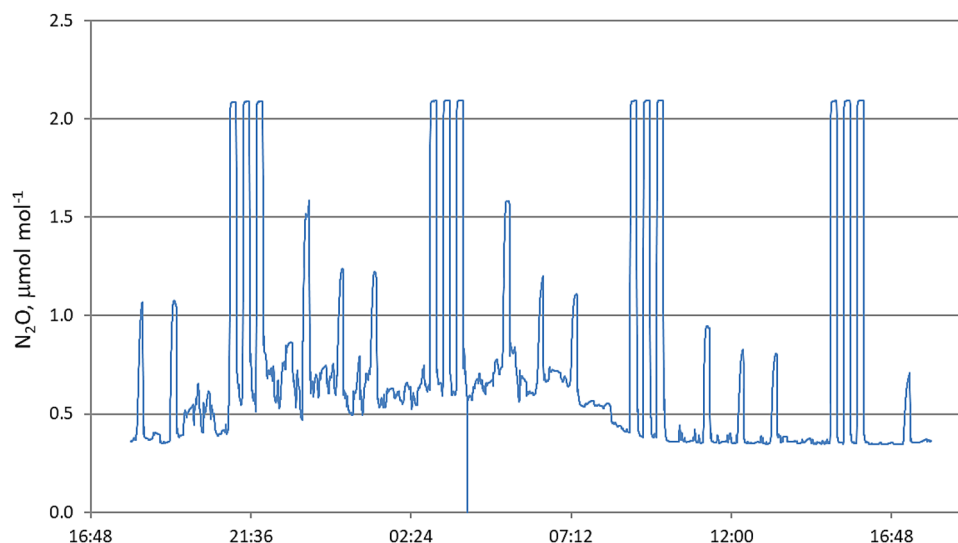


FIGURE 1 Example of ambient N_2O concentrations over a 24-h period from a field study of N_2O emissions at a raised bog in northern Denmark (Store Vildmose) drained for agriculture. The data show high background air concentrations of N_2O through the nighttime, which interfered with flux measurements during that period, and which were subsequently discarded. The analytical setup included a LI-8100A automated soil gas flux system (LI-COR) interfaced with a N_2O isotope analyzer (Los Gatos Research). A reference gas was analyzed between 6-h cycles. Data from S.O. Petersen (personal communication, 2020)

calculations. In the analysis of 1970 chamber measurements with four or more headspace samples over a 40- to 60-min closure period from nine U.K. studies (27 experimental treatments), Chadwick et al. (2014) found that, on average, only 8% increased nonlinearly (varying from 0 to 22% of measurements by site, or 0 to 14% where measurements with no net flux due to dry soil conditions were excluded). The level of bias can be quantified as in Venterea et al. (2020) by calculating the N_2O fluxes of the subset of chambers where four or more headspace samples were taken using the most appropriate nonlinear scheme and comparing them with fluxes calculated from the same chambers using only three headspace sampling points and linear regressions.

5.3.1 | First air sample (t_0)

Estimation of unbiased fluxes requires the change in chamber headspace N_2O concentrations over time (dC/dt) to be determined within the chamber, so the initial (t_0) chamber headspace N_2O concentration should be sampled immediately after deployment. However, there is some evidence that for typical field flux measurements, individual chamber t_0 N_2O concentrations are indistinguishable from ambient air concentrations (or indeed one another), and ambient air samples taken at mid-chamber height can be used instead of individual t_0 samples (Chadwick et al., 2014). In addition, Chadwick et al. (2014) found that across eight sites, where t_0 and ambient N_2O concen-

trations were significantly different, this strongly affected resulting fluxes (calculated by linear regression) at only two of the eight sites (with three sites showing small but significant differences and the final three showing no significant differences). Underlying reasons for the different effects at these sites were not investigated.

Indeed, further investigation is required to better ascertain why (and therefore when) ambient N_2O concentrations will be significantly different from t_0 concentrations. Consistency may be challenged by weather conditions that prevent N_2O produced in the soil from mixing with the atmosphere. In the absence of wind to remove N_2O accumulating at or immediately below the soil surface, the t_0 headspace sample may be above ambient N_2O concentrations, especially if the chamber contains a fan promoting headspace mixing. An example of such accumulation during nighttime is shown in Figure 1 for a 24-h measurement period with automated chambers (data from Petersen, Well, Taghizadeh-Toosi, & Clough, 2020). According to Figure 1, the t_0 samples were in fact near ambient level around midmorning, when manual static chamber gas sampling typically takes place (Section 4.2). Interestingly, wind velocities at 2-m height remained at $0\text{--}2\text{ m s}^{-1}$ also during the day, whereas air temperature fluctuated between 3 and 16.6°C . It suggests that cooling can contribute to the development of a layer of (heavier) stagnant air at the soil surface where N_2O may be trapped.

Reprioritization of resources to better capture spatial and temporal variability may be effective in reducing the overall uncertainty of N_2O emission estimates. However,

several precautions are necessary: (a) the N_2O concentration above the soil may be influenced by the soil N_2O fluxes, so ambient air samples from above each plot should only be used as t_0 estimates for chambers placed on that plot; (b) permanently inserted bases should be low so they do not restrict lateral air flow and mixing of air in the chamber area; (c) similarly, growing vegetation may reduce ambient air mixing; and (d) sampling time of day to approximate daily mean N_2O emissions should also consider the impact of time of day on t_0 (compared with ambient air N_2O concentrations); and (e) ideally, adequate testing should be conducted to show there is no significant difference between individual chamber t_0 N_2O concentrations and ambient air samples, noting that this difference may vary with weather conditions. If individual chamber headspace t_0 concentrations are proportional to N_2O fluxes, however, using a single ambient air N_2O concentration for a group of chambers will produce an underestimate of lower fluxes, and an overestimate of higher fluxes.

5.4 | Ancillary measurements

The need for additional measurements depends upon the experiment objective(s). Recommended best practice for the calculation of N_2O fluxes from individual chambers requires measurements of soil moisture, bulk density, and temperature to allow for application of the chamber bias correction (CBC) method (Venterea et al., 2020). The CBC method has the potential to improve flux estimate accuracy and precision depending on other factors, and its potential performance can be assessed using methods described by Venterea et al. (2020). If the aim is to generate new N_2O EFs, soil mineral N contents are usually recorded but may not be necessary (López-Aizpún et al., 2020). A recommended minimum set of ancillary measurements for N_2O EF studies would improve the potential for subsequent meta-analyses (de Klein, Alfaro, et al., 2020; López-Aizpún et al., 2020). If the goal is to understand temporal patterns in N_2O emissions, or for model development or verification, then a wider range of (frequent) ancillary measurements are necessary (de Klein, Alfaro, et al., 2020; Dorich et al., 2020; Giltrap et al., 2020).

Soil N_2O production, reduction, and transport depend on the availability of C and N substrates (Loick et al., 2017), gas diffusivity (Bateman & Baggs, 2005), and redox potential (Rubol, Silver, & Bellin, 2012). To understand and predict N_2O net production processes and emission rates, these controlling parameters should be monitored during soil N_2O flux studies. However, different ancillary measurements will be required at different frequencies. Soil bulk density, pH, organic C, and total N content usually only need to be measured infrequently (e.g., once

per experiment, once per season, or after an expected significant change, such as cultivation). Average soil and air temperature and rainfall should be measured on a daily or hourly basis, and soil WFPS should be measured at daily or weekly intervals—as often as needed to provide a representative estimate of the chamber soil conditions on each gas sampling occasion. Automated sensors placed in each chamber are advantageous in providing high-frequency and -resolution data, and the use of sensors for air and soil temperature and soil moisture is recommended (Pavelka et al., 2018). Soil mineral N measurements are needed as often as resources allow, especially during the first 30 d after fertilizer, manure, or urine application (and will inevitably include soil moisture content determinations).

The spatial scale of variation of each ancillary variable will also differ, and samples representative of conditions for each chamber should ideally be collected (i.e., some variables may be consistent across the block scale, whereas others may vary at the within-plot scale). Care should be taken to ensure that destructive sampling areas (often near chambers for comparable data) are large enough for the required number of samples to be taken, without the structure or hydraulic properties of the soil near the NSS chamber being altered (Section 4.4 and 5.1). The use of small nondestructive soil moisture, temperature, and nitrate sensors or samplers inserted within chambers represents an advantage in this respect, as well as providing chamber-specific, high-frequency ancillary data (Supplemental Section 6). Intermittent spot checking or validation of sensor data via established destructive methods may be worthwhile. Table 1 summarizes our recommendations for best practice chamber installation and sampling protocols to minimizing the introduction of further uncertainty.

6 | CONCLUSION

Obtaining accurate and precise soil N_2O emission estimates using small static chambers is challenging due to the high spatial variability and episodic nature of soil N_2O fluxes. Experimental design and chamber deployment protocols must consider all sources of uncertainty (spatial, temporal, and experimental) associated with N_2O fluxes and prioritize resources effectively to minimize overall uncertainty based on the experiment objectives (Supplemental Section 7). For some small-scale experiments, this may mean focusing resources on determining individual chamber N_2O emission estimates, whereas for spatial variability assessments and integrations, a greater number of chambers, better capturing spatial variability and sampled less intensively over a longer period with a simpler individual chamber protocol (Chadwick et al., 2014), could be more appropriate.


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CONFLICT OF INTEREST

The authors confirm that there are no conflicts of interest.

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SUPPORTING INFORMATION

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

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