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Characterisation of Analytical Uncertainty in Chamber Soil Flux Measurements

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ABSTRACT

Flux chamber methodologies are used at the global scale to measure the exchange of trace gases between terrestrial surfaces (soils) and the atmosphere. These methods evolved as a simplistic necessity to measure gas fluxes from a time when gas analysers were limited in capability and costs were prohibitively high, since which thousands of studies have deployed a wide variety of chamber methodologies to build vast datasets of soil fluxes. However, analytical limitations of the methods are often overlooked and are poorly understood by the flux community, leading to confusion and misreporting of observations in some cases. In recent years, the number of commercial suppliers of gas analysers claiming to be capable of measuring trace gas fluxes from chambers has drastically increased, with a myriad of analysers (and low-cost sensors) now on offer with a wide variety of capabilities. While chamber designs and the capabilities of analysers vary by orders of magnitude, the rudimentary analytical uncertainties of individual flux measurements can still be standardised for direct comparison of methods. This study aims to serve as a guide to calculate the analytical uncertainty of chamber flux methodologies in a standardised way for direct comparisons. We provide comparisons of a variety of chamber measurement methodologies (closed static and dynamic chamber methods) to highlight the impact of analytical noise, chamber size, enclosure time and number of gas samples. With the associated tools, researchers, commercial suppliers and other stakeholders in the flux community can easily estimate the limitations of a particular methodology to establish and tailor the suitability of particular chambers and instruments to experimental requirements.

1 | Introduction

One of the most common methods deployed by researchers to measure trace gas emissions in the field is the use of static gas flux chambers (Maier et al. 2022). Flux chambers operate under the relatively simple principle that a known surface area is enclosed within a known volume of air, and the change in concentration of a trace gas within that volume allows us to infer the rate of emission or uptake of that trace gas species. These chambers are popular due to their robustness and ease of deployment, which allows for the collection of flux data from almost any environment and does not require the complex needs and assumptions of micrometeorological flux measurements or electricity in the field (e.g., Zaman et al. 2021). A diverse assortment of flux chamber designs has been developed over decades to measure a variety of gas exchange rates in the environment and are popular with researchers who investigate greenhouse gas fluxes (GHGs) in soils (Lundegårdh 1927; Hutchinson and Mosier 1981; Pumpanen et al. 2004) and volatile organic compounds (VOCs) emissions from plants and soil (Eklund 1992; Drewer, Leduning, Purser, et al. 2021). Until quite recently, the measurement of most trace gases (other than CO_2) depended on analysis by gas chromatography (GC), meaning that a small number of samples (2–6) were manually

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Summary

- This study serves as a guide to calculate analytical uncertainty of chamber flux methodologies.
- A tool is provided to help non-experts understand the analytical uncertainty of flux measurements.
- Comparisons of analytical uncertainty in flux chambers are provided.

extracted during a chamber measurement to be analysed in the lab (Collier et al. 2014). The development of fast-response infrared (IR) laser analysers in the last decade means that samples can be measured at high frequency in real time in a closed chamber system (e.g., Hensen et al. 2006; Cowan, Famulari, Levy, et al. 2014) and so many more samples can be obtained.

The estimation of the surface flux from the change in concentration is formally an inverse problem, most commonly solved by linear regression (Levy et al. 2011). However, due to interactions between trace gases and the sources from which they are emitted (soils, plants and material surfaces) the assumption of linear change in gas concentration is not always realistic, in which case other functions can be used to determine dC/dt in the chamber (Pedersen et al. 2010; Silva et al. 2015; Hüppi et al. 2018). Regardless of the regression model used to determine gas flux, each method is prone to analytical uncertainty from the instrument used in gas analysis. While the analytical noise (σ) of commercially available gas analyser instruments is reported in the specification provided by suppliers, this does not equate with the analytical uncertainty in flux measurements. Often, the impact of this analytical noise on flux uncertainty is ignored in studies, and total uncertainty is not propagated through experimental data. When sample sizes are low (e.g., $n<10$) and the analytical noise is relatively high, if errors are not propagated, fluxes and their response to drivers can be misinterpreted. This lack of understanding has resulted in confusion, such as the misinterpretation of negative fluxes, as highlighted in Cowan, Famulari, Levy, Anderson, et al. (2014). It also inhibits those without in-depth expertise from proper assessment of methodology and transparency of statistical significance of results in academic reviews (such as peer review or proposal reviews) as there is no straightforward procedure to check the limitations of different methodologies for the 'non-expert'.

To assess the instrumentation and chamber design appropriate for effective experiments, there is a requirement that researchers understand the limitations of their measurement methodology in the planning stages of any research proposal. The analytical uncertainty—taking into account the gas analyser and chamber physical configuration—can be easily calculated before any measurements take place, and its suitability can be compared to the expected magnitude of fluxes. This study provides a standardised method which researchers can apply. To make this method accessible to all, this study also provides an open-access tool (https://connect-apps.ceh.ac.uk/chamberuncertaintytool/) by which non-experts can easily determine the lower bound on uncertainty in any flux chamber method for planning experiments and deciding on appropriate equipment. By clearly outlining protocols to determine the limitations in flux chamber methodology, we can assess the strengths and weaknesses and highlight best operating procedures for future experimental efforts.

2 | Methods

2.1 | Calculation of Gas Flux

All non-steady-state chamber methods rely on the same basic formula to calculate fluxes:

$$F = \frac{dC}{dt} \times \frac{\rho V}{A} \tag{1}$$

where F is the gas flux from the soil (nmol $m^{-2} s^{-1}$), dC/dt is the rate of change in the concentration in time in nmol $mol^{-1} s^{-1}$, usually estimated by linear regression, ρ is the density of air in mol m^{-3}, V is the volume of the chamber in m^3 and A is the ground area enclosed by the chamber in m^2. In our examples, we assume a temperature of 10°C (283.15 K) and air pressure of 101.3 kPa, though the sensitivities to these variables are small (e.g., errors of 3°C or 1 kPa result in a relative error of approximately 1%). Thus, ρ remains approximately constant at 43.04 mol m^{-3} for the purposes of Equation (1).

2.2 | Calculation of Analytical Uncertainty

We use the 95% confidence interval (95% CI) as our measure of uncertainty, provided by the standard formula for linear regression, but with an additional multiplier to convert the regression slope into flux units:

$$\mathrm{CI}_{\beta}^{95} = \beta \pm \sqrt{\frac{\sigma^2}{n-1 \quad \sum (t_i - \bar{t})^2}} \times T \times \frac{\rho V}{A} \tag{2}$$

where β is the estimate of dC/dt, σ is the residual standard deviation in the gas concentration (i.e., instrumental noise; formally, precision $= 1/\sigma^2$), n is the number of data points in the regression, $\sum(t_i - \bar{t})^2$ is the variance in the time variable, and T represents the t statistic for the 95% CI, reaching a value of 1.96 as sample size approaches infinity. This equation multiplies the uncertainty in the dC/dt component with the air density and chamber height to convert it into flux units, so it is a function of the characteristics of the chamber and analyser.

In the following examples, we use variables that would be typical for the measurement of fluxes of the greenhouse gas nitrous oxide (N_2O) from soils, but the same principles apply to all gas flux measurements. While it is possible to automate static chambers, these measurements are typically carried out by hand. To calculate fluxes and measurement uncertainty, at least three gas concentrations are required. Due to logistical constraints when manually sampling gases for analysis using a GC, the number of samples rarely exceeds 4 per chamber, though we include a range of 3–7 measurements per chamber for comparison (calculating uncertainty with two concentration measurement points is not feasible). The dynamic chamber method is used commonly for

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manual and auto-chamber methods, and measurements typically last 3–10 min. As IR analysers are often able to provide measurements at 1 Hz, this means a single chamber measurement can have several hundred concentration points, and enclosure times are typically reduced. Sample intervals of 1, 5, 15, 30 and 60 s are typical for a variety of IR instruments.

As dC is proportional to chamber height, this is a critical dimension. Most chambers are either cuboid or cylindrical in shape, so height is equivalent to V/A; where chambers are more complex shapes, the actual V/A ratio is required (also known as the effective height). Chamber heights vary depending on the vegetation present, for example, with taller chambers needed for experiments where cereal crops are enclosed. Effective heights of chambers used in the simulation in this study are 0.1, 0.3 and 0.6 m, which covers the range of those described in the majority of published studies.

We collated data on the typical operational precision of GC and IR laser instrumentation used to measure nitrous oxide (N_2O) by the research community (Table 1). IR analysers integrate a signal over a given period of time, and this can be varied to provide fewer data points with lower noise if required. Several factors may degrade the precision of GC and IR analysers, such as age, temperature stability and degradation of parts such as GC columns or cell mirrors, so instrumental noise should be assessed on a case-by-case basis rather than relying on the manufacturer's specification (Henson et al. 2013). In this study, we encompass a wide variety of equipment and conditions. GC instrumental noise is set to 1, 2, 3, 5, 10 or 20 ppb and IR instrumental noise is set to 0.03, 0.1, 0.2, 0.4, 5 and 20 ppb based on commercially available instruments (Table 1).

2.3 | Example Flux Data

We calculated the analytical uncertainty in gas analyser—chamber configurations from a variety of past N_2O flux measurement campaigns carried out by the authors. We compared this with the actual observed uncertainty, that is, using the observed value of σ from the linear regression of C against t for each measurement, rather than the manufacturer's estimate of σ (the standard deviation in the actual fitted regression for the measured data). Here, as well as noise introduced by instrumental analysis, the magnitude of σ is influenced by real-world interferences, such as pressure fluctuations, leaks or poor mixing of air in chambers. Data included dynamic chamber measurements using a high-precision QCL, and static chamber measurements using a more typical GC instrument. The former were from a variety of farm soils at Easter Bush Farm (Midlothian, UK) as reported in Cowan, Famulari, Levy, Anderson, et al. (2014) (1054 flux measurements) and are available as an open-access dataset (Cowan, Levy, and Skiba 2019). The static chamber data came from a range of experiments across the UK and Ireland (6823 flux measurements), but mainly focussed on grasslands in central Scotland and Ireland, as reported in Cowan, Levy, Moring, et al. (2019) and Maire et al. (2020), though some are unpublished. Because N_2O data typically span multiple orders of magnitude, we limited our analysis to values $< 2\,\text{nmol}\,\text{m}^{-2}\,\text{s}^{-1}$ for the purpose of comparing analytical uncertainties.

3 | Results

3.1 | Effect of Measurement System Parameters on Uncertainty

The impact that each system parameter has on the overall analytical uncertainty of a chamber method is shown in Figure 1 for an example system. Analytical uncertainty increases linearly with instrumental noise and chamber height (V/A ratio). By contrast, analytical uncertainty decreases with enclosure time and sample rate according to an inverse-square function. Where $n < 20$, the most effective way to reduce analytical uncertainty is to increase the sample rate or enclosure time of the

TABLE 1 | Examples of instrumental noise σ for a range of commercially available instruments capable of measuring N_2O fluxes.

Instrument type	Instrument ID	σ for N_2O (ppb)	References
GC	Hewlett Packard 5890 series II	33	Jones et al. (2011)
GC	Intersmat IGC-120 DFL	20	Thijsse (1978)
GC	Agilent GC7890B	5.0	Drewer, Leduning, Griffiths, et al. (2021)
GC	Varian Model 3800	3.0	Zafonte et al. (2010)
GC	Agilent 6890 N	0.25	Schmidt et al. (2014)
IR	Picarro G2508	25 (1 s) 0.4 (5 min)	Brannon et al. (2016)
IR	DFB-QCL	6 (1 s)	Jahjah et al. (2014)
IR	Aerodyne QCL	0.3 (1 s)	Nelson et al. (2004)
IR	Custom Portable QCL	0.2 (lab) 8.0 (portable)	Stiefvater et al. (2023)
IR	Aerodyne QCL (compact)	0.03 (1 s)	McManus et al. (2015)

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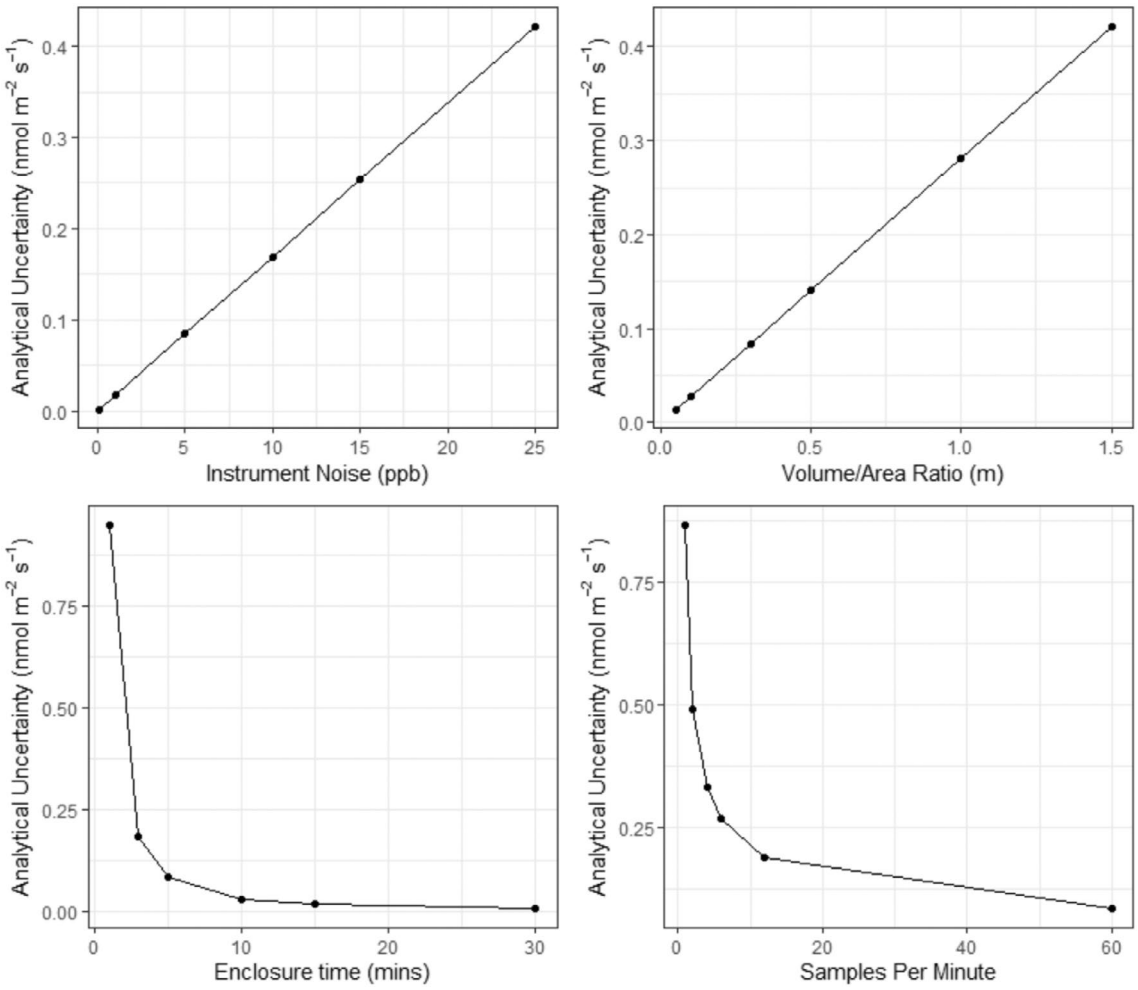

FIGURE 1 | The effect of each measurement system parameter on analytical uncertainty in an example system. In each panel, values for all other variables were held constant at $\sigma = 5$, sampling interval = 1 s, enclosure time = 5 min and $V/A = 0.3$ m, except for that shown on the x axis.

measurement. Where $n > 20$, reducing the instrumental noise and chamber V/A ratio becomes more effective. Clearly, the marginal impact of any parameter depends on the values of the other parameters in the system.

3.2 | Predicting Analytical Uncertainty for Typical Systems

For a variety of typical N_2O flux measurement systems (Figures 2 and 3), the analytical uncertainty ranges over several orders of magnitude from 6×10^{-5} to 51.56 nmol m^{-2} s^{-1} depending on the different methodological factors. This range highlights the impact that instrumental noise, enclosure time, the number of samples and chamber height can have (Figures 2 and 3). The range demonstrates the importance of considering factors other than instrumental precision. The analytical uncertainty is proportional to chamber height and inversely proportional to enclosure time, but the latter relationship is non-linear. The combination of a short enclosure time, large chamber height and relatively high instrumental noise gives the largest analytical uncertainties.

3.3 | Comparison of Analytical Versus Measured Uncertainty

We compare the theoretical analytical uncertainty with the actual measured uncertainty of gas flux for two chamber flux methods (as outlined in Section 2). The QCL-based dynamic chamber system had a calculated analytical uncertainty of 0.001 nmol m^{-2} s^{-1}. The mean and median observed uncertainties were 0.004 and 0.002 nmol m^{-2} s^{-1}, respectively, so much larger in relative terms, but still very small in both absolute terms—around two orders of magnitude less than the mean fluxes (0.26 nmol m^{-2} s^{-1}) (Figure 4). The GC-based static chamber systems had analytical uncertainties that varied only with chamber height (0.14–0.28 m), ranging from 0.061 to 0.125 (mean 0.111) nmol m^{-2} s^{-1}. The mean and median observed uncertainties were 0.215 and 0.163 nmol m^{-2} s^{-1}, respectively, again approximately double the analytical uncertainty, but also large in absolute terms, larger than the mean observed flux (0.15 nmol m^{-2} s^{-1}) (Figure 3). Thus, in both systems, there are considerable additional uncertainties in the gas sampling process that are of similar or greater magnitude than the calculated analytical uncertainty. For the QCL-based dynamic chamber

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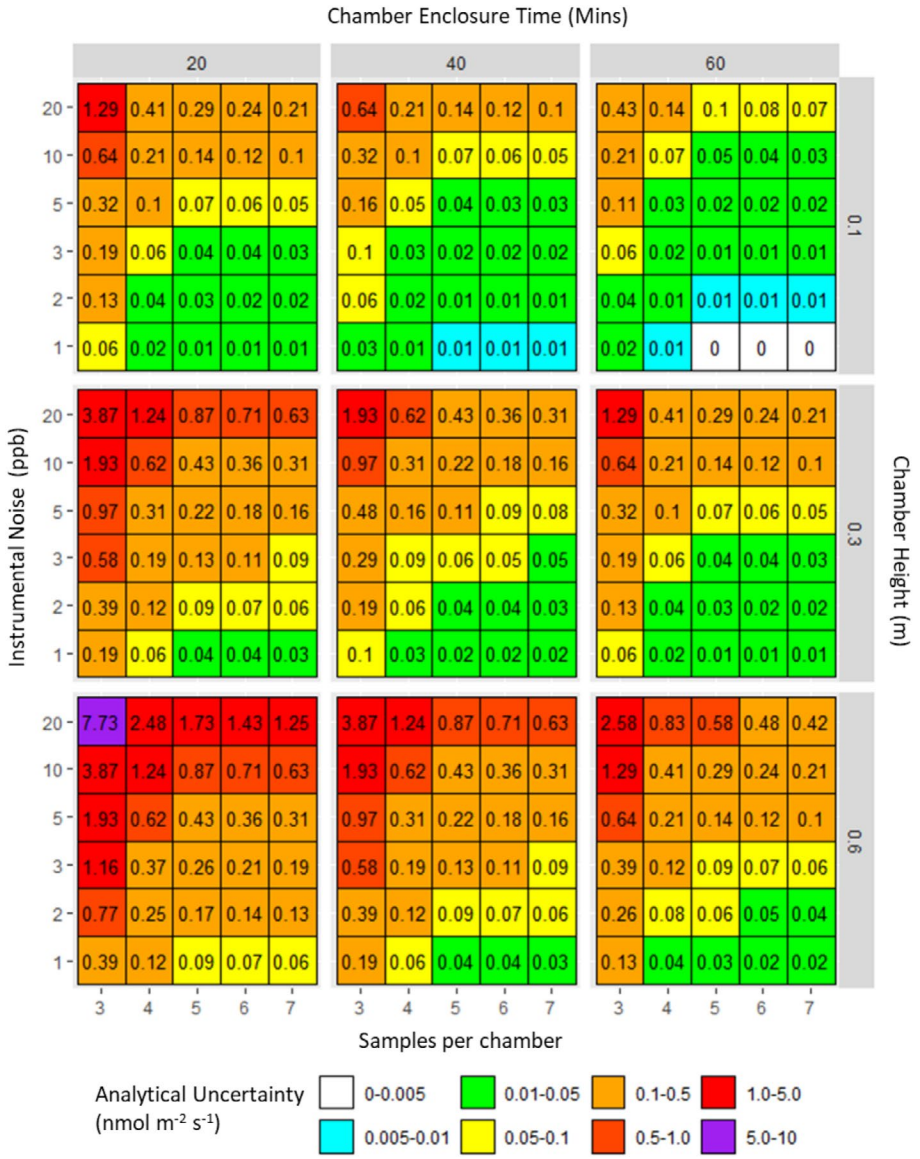

FIGURE 2 | Analytical uncertainty (95% CI) representative of GC-based methodology as a function of: The instrumental noise, number of gas samples taken per flux measurement, length of enclosure time (20, 40 and 60 min) and chamber height (0.1, 0.3 and 0.6 m assuming cuboid or cylindrical shape) as calculated by Equation (2).

system, the analytical uncertainty was larger than the magnitude of the flux in only 1.1% of cases (Figure 3b). By contrast, in the GC-based static chamber system, the analytical uncertainty was larger than the magnitude of the flux in 63% of cases, and the observed uncertainty was larger than the magnitude of the flux in 68% of cases (Figure 4c,d).

4 | Discussion

Without considering the accompanying statistical challenges, researchers can face difficult decisions when purchasing expensive instrumentation for trace gas flux measurements. The number of commercially available IR gas analysers has increased drastically over the past two decades, with dozens of options available for the most commonly measured species (e.g., Rannik et al. 2015; Twigg et al. 2022). The rise in availability of 'low-cost' sensors has also complicated decisions. Low-cost sensors typically apply less sensitive technology, which may be able to achieve sufficient precision if operated correctly under certain conditions (e.g., Bastviken et al. 2020; Zawilski and Bustillo 2024). However, there have been occasions where instrumentation designed for industrial uses (e.g., high concentrations associated with stacks) has been marketed optimistically toward environmental scientists, without knowledge of the more precise requirements of the soil flux community. As a result, not all instruments meet the required specifications to detect, for example, small treatment differences in environmental fluxes, despite commercial claims. When choosing to procure an instrument to carry out chamber flux measurements, we highly recommend that researchers investigate the trade-offs between the cost of instrumentation and the instrumental capabilities and features of chamber and experimental design to minimise analytical uncertainty. In this way, they can establish

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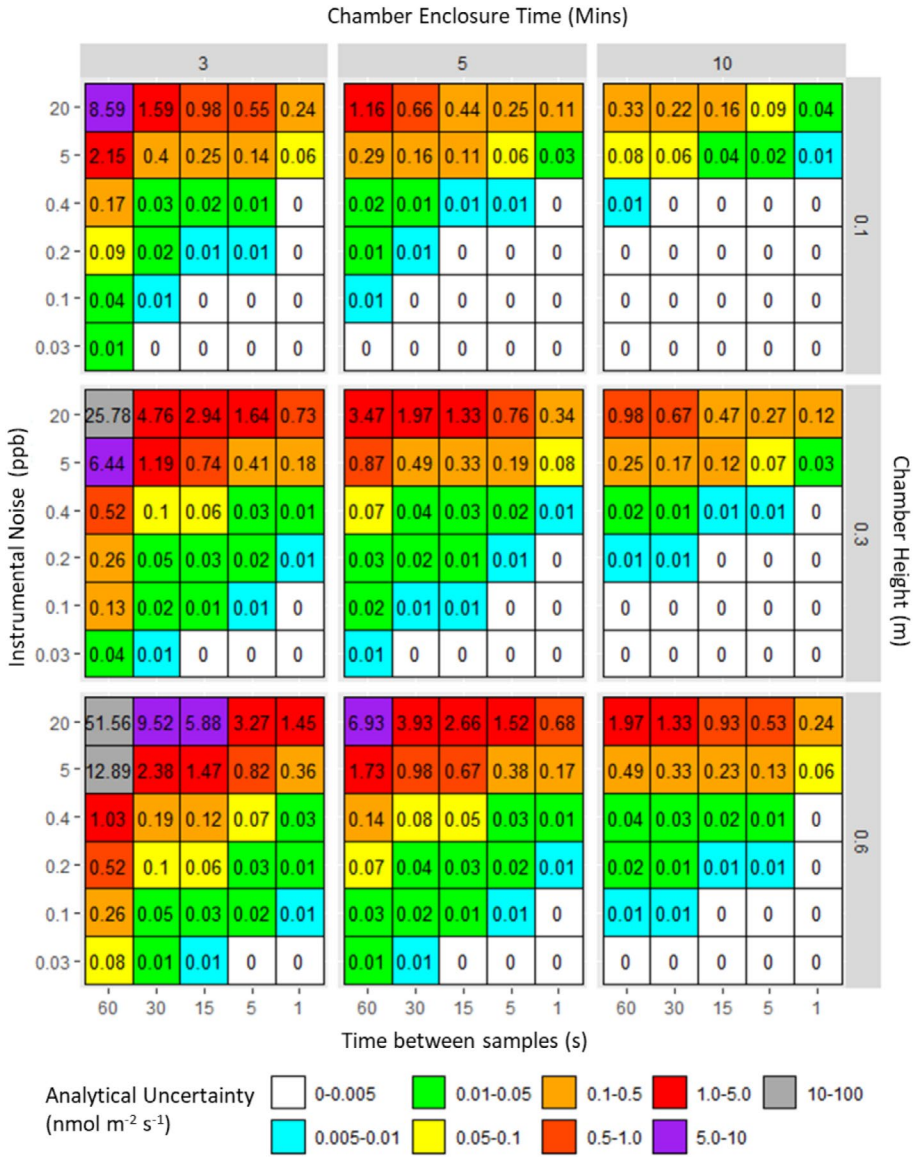

FIGURE 3 | Analytical uncertainty (95% CI) in representative of IR-laser-based methodology as a function of: The instrumental noise, the time between concentration samples, length of enclosure time (3, 5 and 10 min) and chamber height (0.1, 0.3 and 0.6 m assuming cuboid or cylindrical shape) as calculated in Equation (2). Analytical uncertainty below 0.005 nmol m^{-2} s^{-1} rounded to 0 in figure.

the optimal chamber methodology for an experiment, given the budget.

While fast, high-precision analysers can provide individual flux measurements with extremely low statistical uncertainty over short periods of time (e.g., 1–3 min per flux chamber measurement), a slightly less precise or slower (and cheaper) analyser may be able to match the analytical precision if enclosure time is increased and/or chamber volume is decreased in relative terms. Our analysis highlights that traditional static chamber flux measurements using GC analysis can outperform some dynamic chamber methods with low precision analysers, in terms of individual measurement uncertainty (see Figures 2 and 3). As such, we stress that the use of portable or low-cost analysers (which tend to be a bit noisier) to carry out fast measurements in the field is not always better than the application of basic static chamber methodology in terms of individual measurement uncertainty depending on factors such as the number of measurements made and the experimental aims of measurements (e.g., identifying treatment or environmental effects). Extending enclosure time comes at a cost if it results in fewer measurements per day, or if the assumption of linearity breaks down (e.g., wind can cause leaks, or temperature can change within the chamber over time), so that more parameters need to be estimated (with additional uncertainty). Where environmental drivers such as temperature and moisture are being investigated in terms of gas fluxes in soils, the influence that these drivers have may be an order of magnitude lower than the analytical uncertainty of a methodology. However, under circumstances of high fluxes (e.g., N_2O emissions immediately after application of nitrogen fertilisers, or CH_4 emissions from manure heaps), analytical uncertainty may be insignificant compared to the spatial variability. The equations (and accessible tool, https://connect-apps.ceh.ac.uk/chamberuncertaintytool/) provided by this study will allow for improved decision making and reporting of methodology applied in chamber flux research.

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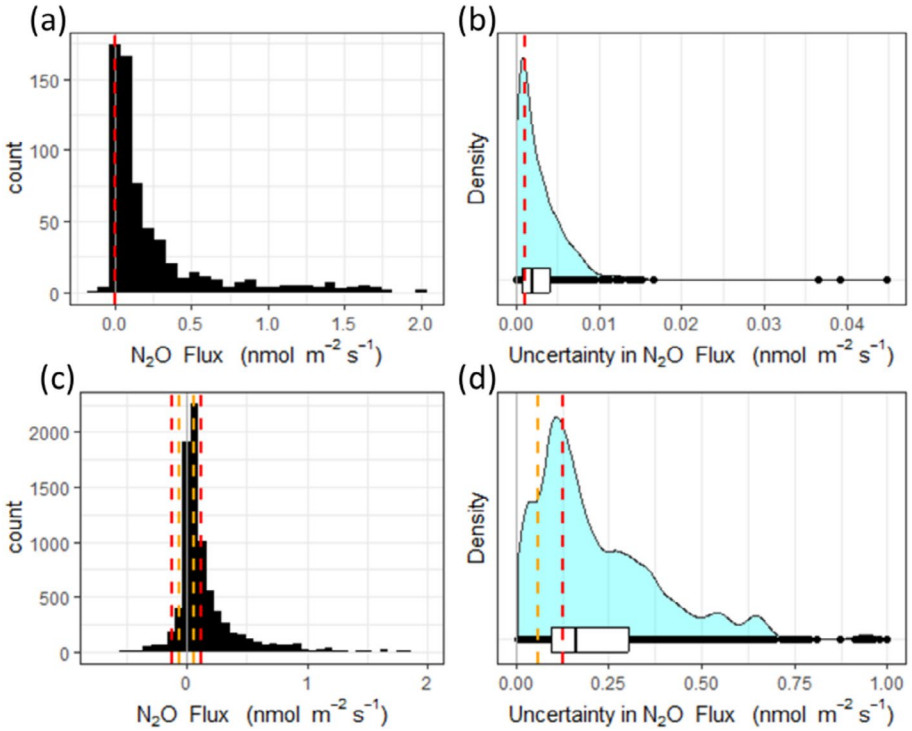

FIGURE 4 | Chamber flux data measured in the field and associated measured uncertainty are shown for (a, b) QCL-based measurements of N_2O from farm soils, and (c, d) GC-based measurements of N_2O from grasslands. The analytical uncertainties are shown (red, with orange for smaller chamber volume setup). Box and whisker plots represent the median and 25th and 75th percentiles of the uncertainty in measured flux uncertainty.

Historically, our understanding of the magnitude of soil gas fluxes has been limited by the methods at our disposal. Without extremely high-precision flux methodology, it is often difficult to determine the difference between instrumental noise and the true natural variability of soil fluxes. However, with modern high-precision analysers, we now have data that allow us to discern these differences. As an example, extensive research has shown that the vast majority of fluxes of N_2O in the UK are consistently below $0.5\,nmol\,m^{-2}\,s^{-1}$ (Cowan, Famulari, Levy, Anderson, et al. 2014; Cowan et al. 2020). Thus, if experimentation aims to assess the drivers of fluxes of this magnitude, either the analytical uncertainty in the measurement methodology should be an order of magnitude smaller than these emissions, or the number of replicates needs to be drastically increased. Historically, due to the lack of high-precision instruments, the latter has been the only option. This strategy is more justifiable when the gas in question has high temporal or spatial variability, and thus the uncertainty in the individual measurements is small relative to the large uncertainty in interpolating in space and time (Chadwick et al. 2014; Vargas and Le 2023). While only one chamber can be sampled at a time when using the dynamic chamber method, if this process can be automated, the number of measurements can be increased significantly in comparison to manual static chamber methods, thus greatly decreasing temporal uncertainty in comparison to manual measurements (Grace et al. 2020). Where gas fluxes follow a Gaussian distribution, simple statistics can be applied to optimise sampling strategies where the variance in flux measurements is known. However, this is not the case for gas fluxes such as N_2O, which are known to follow a highly skewed distribution in both time and space, and thus uncertainty analysis becomes significantly more complicated (Levy et al. 2017). Optimising sampling strategies and the trade-offs of methodology for these gases is beyond the scope of this study, but this would be the next step in assessing the suitability of any chamber flux methodology for a given experiment.

Our method is a simple extension of the statistics of regression; some other methods to estimate uncertainty in chamber studies have been ad hoc and inconsistent. The minimum detectable flux (MDF) method for flux chambers reported in Christiansen et al. (2015) does not include sample size in its calculation, thus the calculated MDF for a measurement with two samples ($n = 2$) is erroneously the same as a measurement with $n > 1000$. The analytical uncertainty (as calculated using Equation 2) represents the lower bound on the possible uncertainty in flux measurements from a given system. The actual uncertainty associated with a measurement includes uncertainty from a number of other sources. The analyser may show additional variability when run in field conditions, compared with the stable lab conditions in which precision is usually assessed, and may show higher noise when subject to fluctuations in temperature and water vapour. Probably more important is the additional variability introduced by the process of extracting gas samples, which is prone to leaks in syringes, taps and vials, as well as the pressure effects of removing gas from the chamber. Poor mixing of air within the chamber adds further sampling variability, and there is always scope for simple human error (such as errors in labelling and ordering vials on a GC). These phenomena lead to the measured uncertainty being substantially larger than the analytical uncertainty and affect GC-based measurements more than in-line IR-based measurements according to our results. This additional uncertainty needs to be considered when planning experimental work.

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The 95% CI analytical uncertainty calculated using Equation (2) represents the expectation for that interval, given the system parameters. However, for any given individual flux, the measured uncertainty can be lower than this, if by chance the samples all fall close to the best-fit line. Where analytical uncertainty is very large and the true flux near zero, a significant proportion of the best-fit lines may have negative slope, even if an uptake flux is not plausible (Cowan, Famulari, Levy, Anderson, et al. 2014). When processing flux data using linear regression, it is not good practice to filter out measurements based on low R^2, or to remove negative values from the dataset where calculated flux is below the analytical uncertainty of the method. Applying quality controls to data that is essentially 'noise around zero' isn't statistically justifiable and would lead to a systematic bias in the dataset.

In addition to the above, there are many other sources of uncertainty in chamber measurements which are often unquantifiable without taking additional measures. While measurements of ammonia (NH_3) fluxes have been attempted using chamber methods (e.g., di Scotto Perta et al. 2020; Kamp et al. 2024), it is not possible to directly observe fluxes of NH_3 from the soil using chambers due to the strong physical interactions of the gas with moisture and the surfaces of all chamber-system materials. In such cases, there are additional sources and sinks within the system not included in the standard equations, and the soil flux is very poorly constrained (uncertainties can be orders of magnitude higher). Vegetation in chambers and uneven surfaces can introduce uncertainty in the internal volume, and this propagates proportionally into the flux. That is, an uncertainty of 10% in the effective height of a chamber contributes a further 10% uncertainty to the measured flux, in combination with the analytical uncertainty described in this study (scaling relative to flux magnitude). The effect of enclosure with a chamber is to remove the normal pressure fluctuations caused by wind, and there is an extensive literature on the importance of this as a bias in the measured flux (e.g., Xu et al. 2006). Arguably, chambers can never be truly representative of the ambient environment, and so the true flux from soils is essentially unobservable using chambers, and the systematic uncertainties can only be estimated by combining data with alternative measurement techniques, for example, micrometeorological methods such as eddy covariance.

4.1 | Use as a Decision-Making Tool

When developing a chamber flux method for scientific studies, many considerations need to be taken into account (e.g., logistics and economical constraints). The analytical uncertainty in individual flux measurements is only one of these factors. However, the data generated by any chamber method will have predictable characteristics in terms of analytical uncertainty, which may be limiting in terms of the usefulness of generated flux data. The importance of the analytical uncertainty varies depending on the scope of any given measurement activities. The analytical uncertainty is less important where the number of flux measurements is large or the signal to noise ratio is small (e.g., CO_2 chamber fluxes or GHG fluxes from large sources such as manure heaps). However, where the analytical uncertainty is close to or larger than the magnitude of the measured fluxes, this warrants more caution in the analysis and interpretation of measured data. We cannot provide exact guidelines for what analytical uncertainty should be acceptable for any particular gas, as its significance will vary by experimental aims and design. However, below we provide examples where analytical uncertainty is a significant term.

Most soil N_2O flux measurements fall below 0.5 nmol m^{-2} s^{-1} (as described in Figure 4, e.g., Cowan, Levy, and Skiba 2019) and a large fraction of these fall below 0.2 nmol m^{-2} s^{-1}. In developing countries, the static chamber method is still widely used as the primary N_2O flux measurement method. An enclosure time of 60 min, where 3–4 samples are extracted from a chamber, is typical (e.g., Bhatia et al. 2023; Drewer, Leduning, Griffiths, et al. 2021). In these circumstances, we would expect an analytical uncertainty in the region of 0.1–1.0 nmol m^{-2} s^{-1} depending on the exact particulars of the methodology (see Figure 2 and tool). For crops, chambers often need to accommodate the height of the plants (which may be > 1 m in height) (e.g., Chaichana et al. 2018; Reba et al. 2020) which will significantly increase the analytical uncertainty of a chamber flux method. Consider an example using a GC with instrumental noise of 10 ppb for N_2O and the chamber height is 1 m. With these parameters, a static chamber method which samples 3 times from the chamber over 40 min will exceed an analytical uncertainty of 3.1 nmol m^{-2} s^{-1}; thus, the majority of the flux data would contain analytical uncertainty an order of magnitude larger than the actual N_2O flux. By increasing the enclosure time to 80 min and increasing the number of samples taken to 10, the analytical uncertainty is reduced to 0.2 nmol m^{-2} $s,^{-1}$ which may or may not be suitable depending on the aims of the experiment. However, if achieving this sampling regime is logistically impossible due to cost restraints of analysis, then the experimental setup must be reconsidered.

The same considerations apply to dynamic chamber methods which deploy IR instruments capable of measuring gas concentrations at much faster rates (e.g., 1 Hz). Consider an example where an IR instrument with instrumental noise of 10 ppb (at 1 Hz) for N_2O is available and the chamber height is 1 m, as in the above example. If the measurement is carried out over 3 min, the analytical uncertainty exceeds 1.1 nmol m^{-2} s^{-1}. In order to achieve an analytical uncertainty below 0.1 nmol m^{-2} s^{-1}, the enclosure time must be at least 15.5 min long per chamber. With the use of Equation (2) (and the accompanying tool) researchers can plan the desired efficiencies of equipment such as auto-chamber setups where the precision of individual measurements can be balanced with the total number of chamber measurements that a single instrument can carry out via switching between chambers. These calculations provide guidelines which can be applied to optimise any specific experiment and provide the means to improve decision making.

5 | Conclusions

This study provides a guide that allows researchers and instrument providers to establish the analytical uncertainty in gas flux chamber methodology. Our study provides a method by which the theoretical limits of the precision of flux measurements from different chamber systems can be compared. We highlight in our demonstrations that variations in chamber design and

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methodology can have significantly more impact on the uncertainty of the fluxes reported than the instrumental precision, which is only one part of the equation. Our recommendation is that researchers check and include the analytical uncertainty of their flux methodology in publications and research proposals so that the reader can understand the limitations of the measurements and data gathered. This study aims to serve as a reference for those unfamiliar with the statistics used to estimate this value and to provide a reference for the accompanying open-access calculation tool (https://connect-apps.ceh.ac.uk/chamberuncertaintytool/).

Author Contributions

Nicholas Cowan: conceptualization, investigation, writing – original draft, methodology, visualization, writing – review and editing, formal analysis, project administration, data curation, resources. **Pete Levy:** conceptualization, investigation, writing – original draft, methodology, writing – review and editing, visualization, software, formal analysis, data curation, supervision. **Maddalena Tigli:** methodology, validation, visualization, writing – review and editing, software, data curation. **Galina Toteva:** conceptualization, investigation, writing – review and editing, methodology, formal analysis, data curation, resources. **Julia Drewer:** conceptualization, funding acquisition, investigation, methodology, validation, writing – review and editing, project administration, supervision, resources.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are openly available in eidc.ac.uk at https://doi.org/10.5285/54EDBDCF-086E-40A7-B2CC-C1E4FCBFBBBC.

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