An improved method for measuring soil $\text{N}_2\text{O}$ fluxes using a quantum cascade laser with a dynamic chamber

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Summary

A dynamic chamber method was developed to measure fluxes of N$_2$O from soils with greater accuracy than previously possible, through the use of a quantum cascade laser (QCL). The dynamic method was compared with the conventional static chamber method, where samples are analysed subsequently on a gas chromatograph. Results suggest that the dynamic method is capable of measuring soil N$_2$O fluxes with an uncertainty of typically less than 1–2 µg N$_2$O-N m$^{-2}$ hour$^{-1}$ (0.24–0.48 g N$_2$O-N ha$^{-1}$ day$^{-1}$), much less than the conventional static chamber method, because of the greater precision and temporal resolution of the QCL. The continuous record of N$_2$O and CO$_2$ concentration at 1 Hz during chamber closure provides an insight into the effects that enclosure time and the use of different regression methods may introduce when employed with static chamber systems similar in design. Results suggest that long enclosure times can contribute significantly to uncertainty in chamber flux measurements. Nonlinear models are less influenced by effects of long enclosure time, but even these do not always adequately describe the observed concentrations when enclosure time exceeds 10 minutes, especially with large fluxes.
Introduction

Nitrous oxide (N$_2$O) is a potent greenhouse gas (GHG) and the single largest contributor to global stratospheric ozone depletion (Ravishankara et al., 2009). The majority of N$_2$O is released into the atmosphere by the natural microbial processes of nitrification and denitrification (Davidson et al., 2000), but human activities (such as the wide scale use of nitrogen fertilizers) have resulted in a significant increase in global N$_2$O emissions since pre-industrial times (IPCC, 2007). Global N$_2$O fluxes have large uncertainties associated with them (55–75 %) (IPCC, 2007) because of the large temporal and spatial variability of N$_2$O fluxes, and the uncertainty inherent in the methodology predominantly used to measure them (Folorunso & Rolston, 1985; Velthof et al., 1996).

Almost all measurements use the closed, non-steady-state (or ‘static’) chamber method (Hutchinson & Mosier, 1981), because of its simplicity and small cost (de Klein & Harvey, 2013). In this method, gas samples are extracted from a chamber sealed on the soil surface during a 30–60 minute incubation period, and later analysed using a gas chromatograph (GC) instrument. The flux is inferred from the rate of change in gas concentration within the chamber. Because of the constraints imposed by the logistics of extracting samples and subsequent laboratory analysis, the sample size is typically limited to 2–4 samples per chamber closure. Consequently the fluxes calculated by any regression model are poorly constrained (Pedersen et al., 2010). Furthermore, data can be noisy, and it is not always clear which regression model is the most appropriate for fitting to the data (Levy et al., 2011). The resolution of GC instruments tends to be poor (>10 nmol mol$^{-1}$ for N$_2$O), meaning that small fluxes may not be clearly detectable.

Previous attempts to improve the precision of N$_2$O flux measurements, using infrared spectroscopy to measure concentration changes of N$_2$O within chambers, were limited by the
poor resolution of the instruments available (Yamulki & Jarvis, 1999; Laville et al., 2011), the logistical constraints of operation, and cost (Hensen et al., 2006; Hensen et al., 2013). However, advances in infrared laser technology have recently produced fast-response (> 10 Hz) N₂O analysers with improved sensitivity (< 5 nmol mol⁻¹), capable of operating in the field (Laville et al., 1999; Jones et al., 2011). In this study, we used a commercially-available infrared continuous wave quantum cascade laser (QCL) with a resolution of 30 pmol mol⁻¹. Pulsed QCL instruments (resolution of 1.5 nmol mol⁻¹) have been used successfully to measure N₂O fluxes using the eddy covariance method (Eugster et al., 2007; Kroon et al., 2007; Kort et al., 2011). The objective of this work was to incorporate this instrument into a dynamic non-steady-state chamber design, which allows for significantly improved accuracy and precision when measuring N₂O fluxes. This method would also then be able to verify measurements made with less precise methodologies such as static chambers. In this paper we describe the system design, the analysis of the high-resolution data obtained, and comparison with conventional static chamber measurements. Costs and benefits of the dynamic chamber/QCL system are compared with the conventional static chamber system.

Materials and methods

We constructed a non-steady-state flow-through (or dynamic) chamber system (Livingston & Hutchinson, 1995; Hensen et al., 2006) hereafter referred to as the dynamic chamber method, in which a closed volume of air was circulated between a chamber and the QCL gas analyser via a pump (Figure 1). A compact continuous wave quantum cascade laser (CW-QC-TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA, USA) was used to measure gas
concentrations within the chamber. This instrument uses tuneable infrared differential absorption spectroscopy (Zahniser et al., 2009), with a 0.5-litre multi-pass absorption cell, with an optical path length of 76 metres. The laser source requires a very stable temperature to operate, and a solid-state cooling system (Thermocube, SS cooling systems, New York, USA) kept the system at a constant temperature of 10˚C by pumping a cooled solution of water and ethanol (20%). The cell was kept at a constant low pressure (approximately 45 Torr) using a dry-scroll vacuum pump (SH-110, Varian Vacuum Technologies, Lexington MA, USA). The inlet of the QCL was fitted with a manual ball valve and a needle valve to control the air flow rate and cell pressure, as well as a safety valve attached to the pump to prevent back-flow. A 0.45-micron particle filter was attached to the inlet of the absorption cell.

The chamber consisted of a cylindrical polyvinyl chloride (PVC) plastic pipe of 38-cm inner diameter (ID) and 22-cm height. The chamber had PVC flanges fitted at the top and bottom. A 3-mm thick square aluminium metal lid was fitted to the top of the tube and sealed with epoxy resin and silica sealant. A 1-cm layer of closed cell neoprene sponge was fitted around the bottom flange. The chamber was placed onto a collar which could be inserted several cm into the soil (on average 5 cm). The collar consisted of a PVC flange attached to a stainless steel ring (2-mm thickness, 6-cm height). The closed cell neoprene sponge attached to the underside of the chamber formed an airtight seal with the collar.

The chamber was fitted with an internal fan (3000 rpm, Delta Electronics Inc., Taipei, Taiwan) and air temperature probe (CS109, Campbell Scientific, Logan, UT, USA). A pressure sensor (CS100, Campbell Scientific, UT, USA) fitted to the lid of the chamber measured the internal air pressure. All fittings on the lid of the chamber were sealed with silicone sealant to avoid gas leakage. The temperature and pressure sensors were connected to a data logger (CR1000, Campbell Scientific, UT, USA) which stored data every second. The
chamber was fitted with a rubber flap (1-mm thickness, 6-cm width) which could be rolled
down to shield the seal formed between the neoprene sponge and the base of the collar or
chamber from wind.

Two 30-m lengths of 9.5 mm ID Tygon® tubing were attached to both the inlet of the
QCL and the outlet of the pump. This provided a 30-m radius from the QCL in which the
chamber could be placed. Tygon® tubing was used as it allowed flexibility in the movement
of the chamber and does not interact with N₂O. A flow rate of approximately 6 to 7 l minute⁻¹
was used between the QCL and the chamber. There was a lag time of approximately 20
seconds between gas leaving the chamber and entering the analyser. Prior to each
measurement, the chamber was purged with ambient air for one minute, and the data for the
first minute following closure was discarded. The chamber volume was estimated after each
measurement by recording depth from the chamber top to the soil surface at ten points. The
typical volume of the enclosed system was 0.03 m³ with a cross sectional area of 0.12 m².

To investigate the effect that circulating air through the chamber had on internal
pressure, we made measurements in the lab with the chamber sealed on an impermeable
metal base. Care was taken to ensure that the chamber was completely sealed by using strong
clamps and bolts to seal between the neoprene layer and the metal base. In these
measurements, the chamber was fitted with a very sensitive differential pressure sensor
(PX654, Omega Engineering Inc., Stamford, CT, US) with a precision of 0.1 Pa. A flow rate
of 6 l minute⁻¹ reduced pressure in the chamber by approximately 3 Pa (because of the drop in
static pressure with fluid speed). This drop in pressure was considered to be considered
negligible when compared to the natural variation in air pressure caused by wind and
temperature variation (> 100 Pa).

Field measurements were made at two locations. Firstly, we measured on grass turf at
our institute (near Penicuik, Scotland, 55° 51' 42.827"N, 3° 12' 21.6393"W), where we
enhanced N$_2$O fluxes by applying 50 g of ammonium nitrate dissolved in 5 litres of water and spread over 10 m$^2$ (17.5 kg N ha$^{-1}$). Four collar rings were inserted into the treated area and one collar ring was inserted into an untreated area as a control. Measurements were made from each of the five chambers on four separate days, each lasting approximately one hour. Secondly, we made measurements in a grazed field using both chamber methods from the same collars at Crichton near Dumfries, SW Scotland (55° 2' 31.3238"N, 3° 35' 16.4393"W) where different fertilizer types (synthetic urine, cattle urine, cattle urine mixed with dicyandiamide (DCD) and cattle dung) had been applied at rates of 425, 435, 435 and 720 kg N ha$^{-1}$ respectively.

Fluxes of N$_2$O were calculated using linear and non-linear asymptotic regression methods (Equations (1)–(4)) using the HMR package for the statistical software R (Pedersen et al., 2010). The regression method that provided the best fit for the time series of concentration was chosen for each individual measurement, using goodness-of-fit statistics and visual inspection.

(i) Linear regression. Fluxes are calculated using the standard line of best fit through the data:

$$C_t = a + b \times t,$$

where $C_t$ is the gas concentration at time $t$, and $dC/dt$ is:

$$\frac{dc}{dt_0} = b .$$

(ii) HM model. This is a commonly used non-linear model derived by Hutchinson & Mosier (1981) with a negative exponential form of curvature. The change in $C$ with $t$ is given by:

$$C_t = C_{\text{max}} - (C_{\text{max}} - C_0) \exp(-kt),$$

where $C_0$ is the initial concentration, $C_{\text{max}}$ is the value at equilibrium and $k$ is a constant, and calculates $dC/dt_0$ as:

$$\frac{dc}{dt_0} = k(C_{\text{max}} - C_0) .$$
Once the rate of change in concentration of a particular gas is known it can then be used to calculate soil flux for each measurement (See Equation (5)). The flux can then be converted to the appropriate units by simple unit conversion factors.

\[ F = \frac{dc}{dt_0} \cdot \frac{\rho V}{A} \]  

(5)

where \( F \) is gas flux from the soil (nmol m\(^{-2}\) s\(^{-1}\)), \( \frac{dc}{dt_0} \) is the initial rate of change in concentration with time in nmol mol\(^{-1}\) s\(^{-1}\), \( \rho \) 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\(^2\).

Static chamber measurements were made at the Crichton site using identical chambers, following an existing protocol (see www.GHGPlatform.org.uk). Chambers were sealed for 40 minutes, then a single sample taken via a three-way tap in the lid. All gas samples were collected with a 20-ml syringe and stored in evacuated 20-ml glass vials. Rather than sampling gas concentration at the time of closure, this was estimated from 10 samples of ambient air collected during the measurement day. All of the samples were analysed on a 7890A GC System fitted with an ECD and FID detector (Agilent Technologies, Santa Clara, CA, USA) at SRUC. The concentration change inside the static chambers was calculated by subtracting the concentration of N\(_2\)O measured within the chamber (at \( t = 40 \) minutes) from the daily average ambient N\(_2\)O concentration. Using Equation (5), the flux of N\(_2\)O from each chamber was calculated assuming that the concentration change within the chamber was linear. The static and dynamic chamber methods were compared by measuring on the same collars on the same day or within 24 hours. Static chamber measurements were carried out in the early morning, and then dynamic chamber measurements were made throughout the day.
Results and discussion

Effects of wind

In initial tests, strong gusts of wind (> 10 m s⁻¹) did have a clear influence on the observed concentrations within the chamber, presumably by inducing air flow between the neoprene gasket and the collar (Figure 2). To counter this, a ring of rubber made from a bicycle inner-tube was used to form a skirt which could be rolled to cover the seal between the chamber and the collar. Subsequent to fitting this skirt, no further effects of wind on the concentrations within the chamber were observed, and the concentration pattern was as shown in Figure 3. Effects of wind were only observable with the high frequency concentration measurements from the QCL, and would not be detected in conventional static chambers, where concentration measurements are made at much lower time frequency (> 600 seconds).

The influence of enclosure time on calculated flux

Figure 4 shows the concentration increase within the chamber over the course of twenty one hour-long measurements made on metal collars inserted into fertilized grassland soil. The plots are ranked in order of magnitude of flux calculated using linear regression, increasing top-left to bottom-right (labelled 1 to 20 in sequential measurement order). The plots show that there is little noise in the measurements, and the clear pattern in concentration with time, irrespective of the magnitude of the flux. Almost all of the concentration changes appear to be close to linear with time, with only a few exceptions. The fluxes calculated from the chambers over a 60-minute measurement period using linear and non-linear regression are shown in Table 1. The $R^2$ values for both linear and non-linear fits exceed 0.99 for most of the
measurements; however, there are significant differences in the flux calculated using the
different regression methods. Flux calculated using linear regression is smaller than those
calculated using non-linear regression for all 20 measurements. The 95% confidence intervals
estimated from the fitted regressions are also shown in Table 1.

Figure 5 shows the fluxes calculated from these data over a range of possible
enclosure times, and with both linear and non-linear fitted models. Despite the appearance of
linearity in Figure 4, the calculated fluxes for the different time periods deviate from the flux
calculated after three minutes, and this deviation generally increases with the magnitude of
the flux (note that the fluxes are all shown on the same absolute scale.) At the extreme, this
can be approximately 1.5 nmol m\(^{-2}\) s\(^{-1}\) or 40% of the flux. Although a non-linear model
should be much less sensitive to enclosure time, even this progressively deviates from the flux
calculated after three minutes. In two cases, the non-linear model deviates more than the
linear one (measurements 12 & 16), but in these instances, the curves are slightly convex, and
non-linear fitting to these data would usually be rejected.

We would conclude from these results that fluxes should be calculated using chamber
enclosure times of considerably less than one hour. Whilst an effect of enclosure time might
be expected if using a linear model whenever there is any degree of curvature in the rate of
change in concentration, this is not expected when using a non-linear model. In principle, a
non-linear model should account for the effects of feedbacks which change the rate of change
in concentration over time (most obviously, the build-up of N\(_2\)O within the chamber slows the
rate of diffusion from the soil, and increases the loss of N\(_2\)O to ambient air through any leaks
present). Our empirical results show that the variation in the rate of change in concentration
over time is not always well represented by any model. For example, while the curvature in
measurements 9, 13 & 18 is accounted for well, there are changes in curvature in
measurements 11 & 15 which are not captured by the model. Presumably this arises because
of some artefact of the chamber, measuring environment or instrument which changes over time.

On the basis of these results, we would suggest that the safest approach is to use a short enclosure time, typically less than five minutes, where model assumptions are best met. This seems to provide a sufficiently long-enough data-run to establish a good fit, and be short enough to reduce any measurement artefacts which may change over time. One might attempt to find an optimal enclosure time by assessing the marginal increase in information with change in goodness-of-fit as enclosure time increases. More simply, the model residuals can be plotted against enclosure time, and the longest enclosure time chosen where no trend is present in the residuals.

The choice of regression model used to calculate fluxes from chamber measurements is recognised as one of the largest sources of uncertainty (Kroon et al., 2008; Pedersen et al., 2010; Parkin et al., 2012). We would also conclude that a non-linear model fit needs to be included whenever enclosure times are long, as they are more robust than the linear model to any artefact of enclosure time. It should be noted that statistical null-hypothesis testing of linear versus non-linear model fits is not pertinent, and failure to detect a statistical difference can be misconstrued as equivalence. For example, in measurement number 11, fluxes calculated by linear and non-linear models differ by 20%, but no statistically significant difference can be detected. With only three to five points as conventionally available from GC-based methods, there would be no chance of detecting any such statistical difference.

Comparison of dynamic and static chamber methods

Comparison of static and dynamic chambers at identical locations showed under-estimation in the flux measured with the static chamber measurements than from the dynamic chamber ($R^2$
value of 0.71); however this relationship is dominated by a small number of measurements
with much influence (Figure 6). A bias towards smaller flux measurements using the static
chamber method may arise because of the implicit assumption of linearity over the 40-minute
enclosure time (there was only one sample taken, and an estimate of initial concentration).
The lack of agreement between individual measurements using both methods in this
experiment is probably caused by the large uncertainty in the static chamber method.
Although there was inevitably some delay between measurements at the same locations by the
two methods (typically one to five hours, but as much as 24 hours in a few cases), the time
delay did not explain any of the difference in the measured fluxes. Nor was any pattern
related to diurnal temperature change apparent in the differences.

Background fluxes measured in the non-fertilized control plots of the field experiment
using the static chamber method ranged between -32 to 44 µg N₂O-N m⁻² hour⁻¹. In
comparison, fluxes measured from the same locations using the dynamic QCL method were
consistently below 10 µg N₂O-N m⁻² hour⁻¹, with calculated uncertainty of approximately 1
µg N₂O-N m⁻² hour⁻¹. The mean flux values calculated from all control plot measurements
from the dynamic and static chamber methods are 2.5 and 5.4 µg N₂O-N m⁻² hour⁻¹,
respectively, using linear regression. Both methods report similar mean flux values for the
control plots; however the range of flux measurements from the control plots varies
significantly between the methods (Figure 7). The small range of fluxes measured with the
dynamic chamber suggests that the method is able to provide measurements of small N₂O
flux with greater consistency and precision than the static chamber is able to.

Uncertainty calculation
For each measurement, we estimated the uncertainty associated with each of the terms in Equation (5), and propagated these to estimate the total uncertainty in the flux. Uncertainty in dC/dt was obtained from the 95% confidence interval in the regression slope parameter. Uncertainty in the chamber volume could be estimated by taking several measurements of height in each chamber, and taking the 95% confidence interval in the calculated chamber volume. Including estimates of the volume of vegetation, this gave values of approximately 10% of the total volume. Uncertainty in the air density term (ρ) arises from uncertainties in the temperature and pressure measurements. The 95% confidence interval for the mean temperature and pressure was calculated from the 1 Hz data, and added to the instrumental precision of the temperature probe (0.4°C) and pressure sensor (50 Pa). For the static chambers measurements, it was not possible to calculate regression uncertainty as concentration during chamber closure was only measured once. However, a previous study has estimated that the realistic confidence intervals based on uncertainty arising from instrumental errors and poor fitting to the model are typically of an order of 20% that of the measured flux, although this can vary substantially (Levy et al., 2011).

The results of the one-hour long and the comparison measurements suggest that the uncertainty in flux due to dC/dt can be large (minimum of approximately 20 µg N₂O-N m⁻² hour⁻¹) using the static chamber method, but is reduced to typically < 10 µg N₂O-N m⁻² hour⁻¹ in the dynamic QCL chamber method. Uncertainties from the temperature and pressure measurements are small and should apply to both methods (ranging from 0 to 2.83 µg N₂O-N m⁻² hour⁻¹). In the dynamic chamber method, only the volume term remains as a significant source of error; this is because errors in volume scale linearly with flux. Only occasionally does the uncertainty in dC/dt contribute significantly, where there is not a good relationship with concentration measurements (Figure 8).
The dynamic chamber used with the QCL provides more data than the static chamber method from which uncertainties from individual chamber measurements can be confidently estimated. This allows a detailed investigation of how to improve flux measurements as well as providing a clearer picture of the true spatial variability of N$_2$O fluxes from soils. The largest source of error in static chambers comes from estimating $dC/dt$ (Levy et al., 2011). This uncertainty is not as large using the dynamic chamber method. The largest source of error which could be eliminated from the dynamic chamber method is that of volume. The volume uncertainty can be difficult to address on non-uniform soils. Paying more attention to measuring the volume of vegetation and measuring the soil microtopography would be ways to improve the chamber volume estimation, as simple steps to increase the accuracy of chamber methods.

Advantages and disadvantages

The dynamic chamber method is adaptable and able to work with a variety of instruments and chamber designs. A significant advantage of this particular arrangement is that the high-precision laser instrument can be used for both micrometeorological measurements and chambers alternately. The biggest advantage of linking this laser to a dynamic chamber over conventional static chambers is the large resolution of N$_2$O concentration measurements. Uncertainty calculated in the smallest flux measurements was typically less than 2 µg N$_2$O-N m$^{-2}$ hour$^{-1}$, defined as the 95% confidence interval in the estimate of the flux, and this may be interpreted as a limit of detection for the measurement system (sensu Parkin et al., 2012), although definitions in the literature vary. The development of these methods is important to improving the accuracy of GHG measurements which can then provide reliable information on the efficacy of mitigation of N$_2$O from a variety of agricultural sources.
Currently the biggest drawbacks of using the QCL system are the initial setup cost and the power requirements of the system. The mobility of the instrumentation is limited as a mains power supply or generator is required, thus limiting the spatial coverage of the system. To avoid long lag times we limited the tubing to 30 metres, which limited the distance accessible for measurements. However, the QCL instrument is relatively robust to vibrations and temperature changes and is capable of being mounted in an off-road vehicle without significantly altering the detection limit of the system. A mobile system such as this would allow a wide area to be sampled. There are difficulties in using the dynamic chamber methods to make a large number of simultaneous measurements often demanded by field experiments comparing different treatments. However, because each measurement is short and no further laboratory analysis is required, we estimate that a larger number of flux measurements can be made per hour of effort (Table 2). Combined with the greater precision of the measurements, this yields an estimate of the mean or total flux from the sampled domain with less uncertainty than when using conventional static chambers.

The main disadvantages of the method are the large capital cost and the technical complexity of the instrument. With current trends in laser-based gas analysers, prices will decrease and ease-of-use will improve, and this gap between the methods will reduce.

Conclusions

Using precise, fast-response gas analysers such as a QCL in combination with chambers provides more reliable data than the conventional static chamber/GC approach. Fluxes and their associated physical and statistical uncertainties can be properly quantified, even when fluxes are very small (below 10 µg N$_2$O-N m$^{-2}$ hour$^{-1}$). It is important that errors and
uncertainties in these systems are understood, and the dynamic chamber methodology gives us insights that were previously unavailable. The enhanced precision, ability to measure several gases including isotopologues will advance our understanding of soil processes and associated emissions of N$_2$O and CH$_4$. Dynamic and static chamber methods can deliver roughly the same number of flux measurements in the field (up to ten) within one hour, assuming four samples are withdrawn from static chambers within this one hour, but the dynamic chamber method has no subsequent laboratory sample analysis stage, which can take several days. Currently high costs, power consumption, weight and lack of portability limit the use of fast dynamic chamber approaches to measure N$_2$O or CH$_4$ fluxes. In time, these restrictions will be lessened, as developments in lower power laser technology become available.

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References


Figure Captions

**Figure 1** Schematic diagram of the dynamic chamber used for more detail.

**Figure 2** Example of N$_2$O concentration measurements affected by wind over a 30-minute period without the use of the wind-blocking skirt. Concentration changes within the chamber should look close to linear (as in Figure 3), but an influence of gusts is apparent. The effect is more obvious when greater gas concentrations are present within the chamber. Measurement made on mown grass with added ammonium nitrate, at CEH Edinburgh, UK, March 2012.

**Figure 3** Example of N$_2$O and CO$_2$ concentration measurements recorded at 1 Hz by a QCL during three chamber measurements using the dynamic chamber from three different nearby locations within close range. Fluxes are calculated from the change in concentration over time. Each measurement lasts approximately 180 seconds of which the first 60 seconds are discarded from the regression analysis. Measurements were made on multiple grassland plots with synthetic urine fertiliser applied. (Crichton, Dumfries, SW Scotland, November 2012)

**Figure 4** Concentration increase over time within the chamber over the course of 20 hour-long measurements. The plots are ranked in order of magnitude of flux, increasing top-left (#13) to bottom-right (#20), labelled by an arbitrary measurement number. Measurement made on mown grass with added ammonium nitrate on 16 of the 20 plots (see Table 1): CEH Edinburgh, March 2012.
Figure 5 Fluxes calculated from the hour-long measurements (from Figure 4) over a range of possible enclosure times, and with both linear and nonlinear fitted models. Note that the fluxes are all shown on the same absolute scale.

Figure 6 A direct comparison of N$_2$O flux measurements made using the dynamic and static chamber methods at a SRUC field site in Dumfries (October to November 2012). The dashed line represents the 1:1 relationship. The dotted line is the line of least-squares best fit through all data points.

Figure 7 A comparison of N$_2$O fluxes measured from untreated control plots using both dynamic and static chamber methods. The box plot represents the 25th and 75th percentile ranges. The ability of the dynamic chamber method to measure background flux precisely is highlighted by the small range of uncertainty.

Figure 8 A representation of all of the calculated uncertainties made using the dynamic chamber method at the Crichton field site. The estimated uncertainty in dC/dt in static chambers (20%) is added as a comparison with literature estimates (Levy et al., 2011). The results demonstrate the improved ability to measure dC/dt precisely using the dynamic chamber method.
Table 1 A comparison of N$_2$O fluxes ($\mu$g N$_2$O-N m$^{-2}$ hour$^{-1}$) calculated using linear and non-linear regression from hour long measurements using the dynamic chamber method. The table is arranged in order of increasing flux.

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<th>Linear Flux</th>
<th>95% confidence interval</th>
<th>$R^2$</th>
<th>Non-linear Flux</th>
<th>95% confidence interval</th>
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Table 2  Cost-benefit analysis of QCL dynamic chamber and GC static chamber methods.

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<tr>
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<th>QCL Dynamic Chamber</th>
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<td>Capital cost</td>
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<td>Flux measurement time (minutes)</td>
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<td>60</td>
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<td>Number of simultaneous</td>
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<td>measurements</td>
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<tr>
<td>Laboratory analysis time</td>
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<td>Number of measurements per hour of effort</td>
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<td>5</td>
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<tr>
<td>Uncertainty (95 % CI) (µg N₂O-N m⁻² hour⁻¹)</td>
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