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1 **An improved method for measuring soil N₂O fluxes using a quantum**
2 **cascade laser with a dynamic chamber**

3

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13 *Running title: Dynamic chamber method.*

14

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16 **Summary**

17

18 A dynamic chamber method was developed to measure fluxes of N₂O from soils with greater
19 accuracy than previously possible, through the use of a quantum cascade laser (QCL). The
20 dynamic method was compared with the conventional static chamber method, where samples
21 are analysed subsequently on a gas chromatograph. Results suggest that the dynamic method
22 is capable of measuring soil N₂O fluxes with an uncertainty of typically less than 1–2 μg
23 N₂O-N m⁻² hour⁻¹ (0.24–0.48 g N₂O-N ha⁻¹ day⁻¹), much less than the conventional static
24 chamber method, because of the greater precision and temporal resolution of the QCL. The
25 continuous record of N₂O and CO₂ concentration at 1 Hz during chamber closure provides an
26 insight into the effects that enclosure time and the use of different regression methods may
27 introduce when employed with static chamber systems similar in design. Results suggest that
28 long enclosure times can contribute significantly to uncertainty in chamber flux
29 measurements. Nonlinear models are less influenced by effects of long enclosure time, but
30 even these do not always adequately describe the observed concentrations when enclosure
31 time exceeds 10 minutes, especially with large fluxes.

32

33 **Introduction**

34

35 Nitrous oxide (N₂O) is a potent greenhouse gas (GHG) and the single largest contributor to
36 global stratospheric ozone depletion (Ravishankara *et al.*, 2009). The majority of N₂O is
37 released into the atmosphere by the natural microbial processes of nitrification and
38 denitrification (Davidson *et al.*, 2000), but human activities (such as the wide scale use of
39 nitrogen fertilizers) have resulted in a significant increase in global N₂O emissions since pre-
40 industrial times (IPCC, 2007). Global N₂O fluxes have large uncertainties associated with
41 them (55–75 %) (IPCC, 2007) because of the large temporal and spatial variability of N₂O
42 fluxes, and the uncertainty inherent in the methodology predominantly used to measure them
43 (Folorunso & Rolston, 1985; Velthof *et al.*, 1996).

44 Almost all measurements use the closed, non-steady-state (or ‘static’) chamber
45 method (Hutchinson & Mosier, 1981), because of its simplicity and small cost (de Klein &
46 Harvey, 2013). In this method, gas samples are extracted from a chamber sealed on the soil
47 surface during a 30–60 minute incubation period, and later analysed using a gas
48 chromatograph (GC) instrument. The flux is inferred from the rate of change in gas
49 concentration within the chamber. Because of the constraints imposed by the logistics of
50 extracting samples and subsequent laboratory analysis, the sample size is typically limited to
51 2–4 samples per chamber closure. Consequently the fluxes calculated by any regression
52 model are poorly constrained (Pedersen *et al.*, 2010). Furthermore, data can be noisy, and it is
53 not always clear which regression model is the most appropriate for fitting to the data (Levy
54 *et al.*, 2011). The resolution of GC instruments tends to be poor (>10 nmol mol⁻¹ for N₂O),
55 meaning that small fluxes may not be clearly detectable.

56 Previous attempts to improve the precision of N₂O flux measurements, using infrared
57 spectroscopy to measure concentration changes of N₂O within chambers, were limited by the

58 poor resolution of the instruments available (Yamulki & Jarvis, 1999; Laville *et al.*, 2011),
59 the logistical constraints of operation, and cost (Hensen *et al.*, 2006; Hensen *et al.*, 2013).
60 However, advances in infrared laser technology have recently produced fast-response (> 10
61 Hz) N₂O analysers with improved sensitivity ($< 5 \text{ nmol mol}^{-1}$), capable of operating in the
62 field (Laville *et al.*, 1999; Jones *et al.*, 2011). In this study, we used a commercially-
63 available infrared continuous wave quantum cascade laser (QCL) with a resolution of 30
64 pmol mol⁻¹. Pulsed QCL instruments (resolution of 1.5 nmol mol⁻¹) have been used
65 successfully to measure N₂O fluxes using the eddy covariance method (Eugster *et al.*, 2007;
66 Kroon *et al.*, 2007; Kort *et al.*, 2011). The objective of this work was to incorporate this
67 instrument into a dynamic non-steady-state chamber design, which allows for significantly
68 improved accuracy and precision when measuring N₂O fluxes. This method would also then
69 be able to verify measurements made with less precise methodologies such as static
70 chambers. In this paper we describe the system design, the analysis of the high-resolution
71 data obtained, and comparison with conventional static chamber measurements. Costs and
72 benefits of the dynamic chamber/QCL system are compared with the conventional static
73 chamber system.

74

75

76 **Materials and methods**

77

78 We constructed a non-steady-state flow-through (or dynamic) chamber system (Livingston &
79 Hutchinson, 1995; Hensen *et al.*, 2006) hereafter referred to as the dynamic chamber method,
80 in which a closed volume of air was circulated between a chamber and the QCL gas analyser
81 *via* a pump (Figure 1). A compact continuous wave quantum cascade laser (CW-QC-
82 TILDAS-76-CS, Aerodyne Research Inc., Billerica, MA, USA) was used to measure gas

83 concentrations within the chamber. This instrument uses tuneable infrared differential
84 absorption spectroscopy (Zahniser *et al.*, 2009), with a 0.5-litre multi-pass absorption cell,
85 with an optical path length of 76 metres. The laser source requires a very stable temperature
86 to operate, and a solid-state cooling system (Thermocube, SS cooling systems, New York,
87 USA) kept the system at a constant temperature of 10° C by pumping a cooled solution of
88 water and ethanol (20%). The cell was kept at a constant low pressure (approximately 45
89 Torr) using a dry-scroll vacuum pump (SH-110, Varian Vacuum Technologies, Lexington
90 MA, USA). The inlet of the QCL was fitted with a manual ball valve and a needle valve to
91 control the air flow rate and cell pressure, as well as a safety valve attached to the pump to
92 prevent back-flow. A 0.45-micron particle filter was attached to the inlet of the absorption
93 cell.

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

102 The chamber was fitted with an internal fan (3000 rpm, Delta Electronics Inc., Taipei,
103 Taiwan) and air temperature probe (CS109, Campbell Scientific, Logan, UT, USA). A
104 pressure sensor (CS100, Campbell Scientific, UT, USA) fitted to the lid of the chamber
105 measured the internal air pressure. All fittings on the lid of the chamber were sealed with
106 silicone sealant to avoid gas leakage. The temperature and pressure sensors were connected to
107 a data logger (CR1000, Campbell Scientific, UT, USA) which stored data every second. The

108 chamber was fitted with a rubber flap (1-mm thickness, 6-cm width) which could be rolled
109 down to shield the seal formed between the neoprene sponge and the base of the collar or
110 chamber from wind.

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

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

131 Field measurements were made at two locations. Firstly, we measured on grass turf at
132 our institute (near Penicuik, Scotland, 55° 51' 42.827"N, 3° 12' 21.6393"W), where we

133 enhanced N₂O fluxes by applying 50 g of ammonium nitrate dissolved in 5 litres of water and
 134 spread over 10 m² (17.5 kg N ha⁻¹). Four collar rings were inserted into the treated area and
 135 one collar ring was inserted into an untreated area as a control. Measurements were made
 136 from each of the five chambers on four separate days, each lasting approximately one hour.
 137 Secondly, we made measurements in a grazed field using both chamber methods from the
 138 same collars at Crichton near Dumfries, SW Scotland (55° 2' 31.3238"N, 3° 35' 16.4393"W)
 139 where different fertilizer types (synthetic urine, cattle urine, cattle urine mixed with
 140 dicyandiamide (DCD) and cattle dung) had been applied at rates of 425, 435, 435 and 720 kg
 141 N ha⁻¹ respectively.

142 Fluxes of N₂O were calculated using linear and non-linear asymptotic regression
 143 methods (Equations (1)–(4)) using the HMR package for the statistical software R (Pedersen
 144 *et al.*, 2010). The regression method that provided the best fit for the time series of
 145 concentration was chosen for each individual measurement, using goodness-of-fit statistics
 146 and visual inspection.

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

$$148 \quad C_t = a + b \times t, \quad (1)$$

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

$$150 \quad \frac{dC}{dt_0} = b . \quad (2)$$

151 (ii) HM model. This is a commonly used non-linear model derived by Hutchinson & Mosier
 152 (1981) with a negative exponential form of curvature. The change in C with t is given by:

$$153 \quad C_t = C_{max} - (C_{max} - C_0) \exp(-kt), \quad (3)$$

154 where C₀ is the initial concentration, C_{max} is the value at equilibrium and k is a constant, and
 155 calculates dC/dt₀ as:

$$156 \quad \frac{dC}{dt_0} = k(C_{max} - C_0) . \quad (4)$$

157

158 Once the rate of change in concentration of a particular gas is known it can then be
159 used to calculate soil flux for each measurement (See Equation (5)). The flux can then be
160 converted to the appropriate units by simple unit conversion factors.

161
$$F = \frac{dC}{dt_0} \cdot \frac{\rho V}{A}, \quad (5)$$

162 where F is gas flux from the soil ($\text{nmol m}^{-2} \text{s}^{-1}$), dC/dt_0 is the initial rate of change in
163 concentration with time in $\text{nmol mol}^{-1} \text{s}^{-1}$, ρ is the density of air in mol m^{-3} , V is the volume
164 of the chamber in m^3 and A is the ground area enclosed by the chamber in m^2 .

165 Static chamber measurements were made at the Crichton site using identical
166 chambers, following an existing protocol (see www.GHGPlatform.org.uk). Chambers were
167 sealed for 40 minutes, then a single sample taken *via* a three-way tap in the lid. All gas
168 samples were collected with a 20-ml syringe and stored in evacuated 20-ml glass vials.
169 Rather than sampling gas concentration at the time of closure, this was estimated from 10
170 samples of ambient air collected during the measurement day. All of the samples were
171 analysed on a 7890A GC System fitted with an ECD and FID detector (Agilent Technologies,
172 Santa Clara, CA, USA) at SRUC. The concentration change inside the static chambers was
173 calculated by subtracting the concentration of N_2O measured within the chamber (at $t = 40$
174 minutes) from the daily average ambient N_2O concentration. Using Equation (5), the flux of
175 N_2O from each chamber was calculated assuming that the concentration change within the
176 chamber was linear. The static and dynamic chamber methods were compared by measuring
177 on the same collars on the same day or within 24 hours. Static chamber measurements were
178 carried out in the early morning, and then dynamic chamber measurements were made
179 throughout the day.

180

181 **Results and discussion**

182

183 *Effects of wind*

184

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

195

196 *The influence of enclosure time on calculated flux*

197 Figure 4 shows the concentration increase within the chamber over the course of twenty one
198 hour-long measurements made on metal collars inserted into fertilized grassland soil. The
199 plots are ranked in order of magnitude of flux calculated using linear regression, increasing
200 top-left to bottom-right (labelled 1 to 20 in sequential measurement order). The plots show
201 that there is little noise in the measurements, and the clear pattern in concentration with time,
202 irrespective of the magnitude of the flux. Almost all of the concentration changes appear to
203 be close to linear with time, with only a few exceptions. The fluxes calculated from the
204 chambers over a 60-minute measurement period using linear and non-linear regression are
205 shown in Table 1. The R^2 values for both linear and non-linear fits exceed 0.99 for most of the

206 measurements; however, there are significant differences in the flux calculated using the
207 different regression methods. Flux calculated using linear regression is smaller than those
208 calculated using non-linear regression for all 20 measurements. The 95% confidence intervals
209 estimated from the fitted regressions are also shown in Table 1.

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

220 We would conclude from these results that fluxes should be calculated using chamber
221 enclosure times of considerably less than one hour. Whilst an effect of enclosure time might
222 be expected if using a linear model whenever there is any degree of curvature in the rate of
223 change in concentration, this is not expected when using a non-linear model. In principle, a
224 non-linear model should account for the effects of feedbacks which change the rate of change
225 in concentration over time (most obviously, the build-up of N_2O within the chamber slows the
226 rate of diffusion from the soil, and increases the loss of N_2O to ambient air through any leaks
227 present). Our empirical results show that the variation in the rate of change in concentration
228 over time is not always well represented by any model. For example, while the curvature in
229 measurements 9, 13 & 18 is accounted for well, there are changes in curvature in
230 measurements 11 & 15 which are not captured by the model. Presumably this arises because

231 of some artefact of the chamber, measuring environment or instrument which changes over
232 time.

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

241 The choice of regression model used to calculate fluxes from chamber measurements
242 is recognised as one of the largest sources of uncertainty (Kroon *et al.*, 2008; Pedersen *et al.*,
243 2010; Parkin *et al.*, 2012). We would also conclude that a non-linear model fit needs to be
244 included whenever enclosure times are long, as they are more robust than the linear model to
245 any artefact of enclosure time. It should be noted that statistical null-hypothesis testing of
246 linear versus non-linear model fits is not pertinent, and failure to detect a statistical difference
247 can be misconstrued as equivalence. For example, in measurement number 11, fluxes
248 calculated by linear and non-linear models differ by 20%, but no statistically significant
249 difference can be detected. With only three to five points as conventionally available from
250 GC-based methods, there would be no chance of detecting any such statistical difference.

251

252 *Comparison of dynamic and static chamber methods*

253

254 Comparison of static and dynamic chambers at identical locations showed under-estimation in
255 the flux measured with the static chamber measurements than from the dynamic chamber (R^2

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

266 Background fluxes measured in the non-fertilized control plots of the field experiment
267 using the static chamber method ranged between -32 to 44 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$. In
268 comparison, fluxes measured from the same locations using the dynamic QCL method were
269 consistently below 10 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$, with calculated uncertainty of approximately 1
270 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$. The mean flux values calculated from all control plot measurements
271 from the dynamic and static chamber methods are 2.5 and 5.4 $\mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$,
272 respectively, using linear regression. Both methods report similar mean flux values for the
273 control plots; however the range of flux measurements from the control plots varies
274 significantly between the methods (Figure 7). The small range of fluxes measured with the
275 dynamic chamber suggests that the method is able to provide measurements of small N_2O
276 flux with greater consistency and precision than the static chamber is able to.

277

278 *Uncertainty calculation*

279

280 For each measurement, we estimated the uncertainty associated with each of the terms in
281 Equation (5), and propagated these to estimate the total uncertainty in the flux. Uncertainty in
282 dC/dt was obtained from the 95% confidence interval in the regression slope parameter.
283 Uncertainty in the chamber volume could be estimated by taking several measurements of
284 height in each chamber, and taking the 95% confidence interval in the calculated chamber
285 volume. Including estimates of the volume of vegetation, this gave values of approximately
286 10% of the total volume. Uncertainty in the air density term (ρ) arises from uncertainties in
287 the temperature and pressure measurements. The 95% confidence interval for the mean
288 temperature and pressure was calculated from the 1 Hz data, and added to the instrumental
289 precision of the temperature probe (0.4°C) and pressure sensor (50 Pa). For the static
290 chambers measurements, it was not possible to calculate regression uncertainty as
291 concentration during chamber closure was only measured once. However, a previous study
292 has estimated that the realistic confidence intervals based on uncertainty arising from
293 instrumental errors and poor fitting to the model are typically of an order of 20% that of the
294 measured flux, although this can vary substantially (Levy *et al.*, 2011).

295 The results of the one-hour long and the comparison measurements suggest that the
296 uncertainty in flux due to dC/dt can be large (minimum of approximately $20 \mu\text{g N}_2\text{O-N m}^{-2}$
297 hour^{-1}) using the static chamber method, but is reduced to typically $< 10 \mu\text{g N}_2\text{O-N m}^{-2} \text{hour}^{-1}$
298 in the dynamic QCL chamber method. Uncertainties from the temperature and pressure
299 measurements are small and should apply to both methods (ranging from 0 to $2.83 \mu\text{g N}_2\text{O-N}$
300 $\text{m}^{-2} \text{hour}^{-1}$). In the dynamic chamber method, only the volume term remains as a significant
301 source of error; this is because errors in volume scale linearly with flux. Only occasionally
302 does the uncertainty in dC/dt contribute significantly, where there is not a good relationship
303 with concentration measurements (Figure 8).

304 The dynamic chamber used with the QCL provides more data than the static chamber
305 method from which uncertainties from individual chamber measurements can be confidently
306 estimated. This allows a detailed investigation of how to improve flux measurements as well
307 as providing a clearer picture of the true spatial variability of N₂O fluxes from soils. The
308 largest source of error in static chambers comes from estimating dC/dt (Levy *et al.*, 2011).
309 This uncertainty is not as large using the dynamic chamber method. The largest source of
310 error which could be eliminated from the dynamic chamber method is that of volume. The
311 volume uncertainty can be difficult to address on non-uniform soils. Paying more attention to
312 measuring the volume of vegetation and measuring the soil microtopography would be ways
313 to improve the chamber volume estimation, as simple steps to increase the accuracy of
314 chamber methods.

315

316 *Advantages and disadvantages*

317 The dynamic chamber method is adaptable and able to work with a variety of instruments and
318 chamber designs. A significant advantage of this particular arrangement is that the high-
319 precision laser instrument can be used for both micrometeorological measurements and
320 chambers alternately. The biggest advantage of linking this laser to a dynamic chamber over
321 conventional static chambers is the large resolution of N₂O concentration measurements.
322 Uncertainty calculated in the smallest flux measurements was typically less than 2 μg N₂O-N
323 m⁻² hour⁻¹, defined as the 95% confidence interval in the estimate of the flux, and this may be
324 interpreted as a limit of detection for the measurement system (*sensu* Parkin *et al.*, 2012),
325 although definitions in the literature vary. The development of these methods is important to
326 improving the accuracy of GHG measurements which can then provide reliable information
327 on the efficacy of mitigation of N₂O from a variety of agricultural sources.

328 Currently the biggest drawbacks of using the QCL system are the initial setup cost and
329 the power requirements of the system. The mobility of the instrumentation is limited as a
330 mains power supply or generator is required, thus limiting the spatial coverage of the system.
331 To avoid long lag times we limited the tubing to 30 metres, which limited the distance
332 accessible for measurements. However, the QCL instrument is relatively robust to vibrations
333 and temperature changes and is capable of being mounted in an off-road vehicle without
334 significantly altering the detection limit of the system. A mobile system such as this would
335 allow a wide area to be sampled. There are difficulties in using the dynamic chamber methods
336 to make a large number of simultaneous measurements often demanded by field experiments
337 comparing different treatments. However, because each measurement is short and no further
338 laboratory analysis is required, we estimate that a larger number of flux measurements can be
339 made per hour of effort (Table 2). Combined with the greater precision of the measurements,
340 this yields an estimate of the mean or total flux from the sampled domain with less
341 uncertainty than when using conventional static chambers.

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

345

346

347 **Conclusions**

348

349 Using precise, fast-response gas analysers such as a QCL in combination with chambers
350 provides more reliable data than the conventional static chamber/GC approach. Fluxes and
351 their associated physical and statistical uncertainties can be properly quantified, even when
352 fluxes are very small (below $10 \mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$). It is important that errors and

353 uncertainties in these systems are understood, and the dynamic chamber methodology gives
354 us insights that were previously unavailable. The enhanced precision, ability to measure
355 several gases including isotopologues will advance our understanding of soil processes and
356 associated emissions of N₂O and CH₄. Dynamic and static chamber methods can deliver
357 roughly the same number of flux measurements in the field (up to ten) within one hour,
358 assuming four samples are withdrawn from static chambers within this one hour, but the
359 dynamic chamber method has no subsequent laboratory sample analysis stage, which can take
360 several days. Currently high costs, power consumption, weight and lack of portability limit
361 the use of fast dynamic chamber approaches to measure N₂O or CH₄ fluxes. In time, these
362 restrictions will be lessened, as developments in lower power laser technology become
363 available.

364

365

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367

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372

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438

439 **Figure Captions**

440

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

442

443 **Figure 2** Example of N₂O concentration measurements affected by wind over a 30-minute
444 period without the use of the wind-blocking skirt. Concentration changes within the chamber
445 should look close to linear (as in Figure 3), but an influence of gusts is apparent. The effect is
446 more obvious when greater gas concentrations are present within the chamber. Measurement
447 made on mown grass with added ammonium nitrate, at CEH Edinburgh, UK, March 2012.

448

449 **Figure 3** Example of N₂O and CO₂ concentration measurements recorded at 1 Hz by a QCL
450 during three chamber measurements using the dynamic chamber from three different nearby
451 locations within close range. Fluxes are calculated from the change in concentration over
452 time. Each measurement lasts approximately 180 seconds of which the first 60 seconds are
453 discarded from the regression analysis. Measurements were made on multiple grassland plots
454 with synthetic urine fertiliser applied. (Crichton, Dumfries, SW Scotland, November 2012)

455

456 **Figure 4** Concentration increase over time within the chamber over the course of 20 hour-
457 long measurements. The plots are ranked in order of magnitude of flux, increasing top-left
458 (#13) to bottom-right (#20), labelled by an arbitrary measurement number. Measurement
459 made on mown grass with added ammonium nitrate on 16 of the 20 plots (see Table 1): CEH
460 Edinburgh, March 2012.

461

462 **Figure 5** Fluxes calculated from the hour-long measurements (from Figure 4) over a range of
463 possible enclosure times, and with both linear and nonlinear fitted models. Note that the
464 fluxes are all shown on the same absolute scale.

465 **Figure 6** A direct comparison of N₂O flux measurements made using the dynamic and static
466 chamber methods at a SRUC field site in Dumfries (October to November 2012). The dashed
467 line represents the 1:1 relationship. The dotted line is the line of least-squares best fit through
468 all data points.

469

470 **Figure 7** A comparison of N₂O fluxes measured from untreated control plots using both
471 dynamic and static chamber methods. The box plot represents the 25th and 75th percentile
472 ranges. The ability of the dynamic chamber method to measure background flux precisely is
473 highlighted by the small range of uncertainty.

474

475 **Figure 8** A representation of all of the calculated uncertainties made using the dynamic
476 chamber method at the Crichton field site. The estimated uncertainty in dC/dt in static
477 chambers (20%) is added as a comparison with literature estimates (Levy *et al.*, 2011). The
478 results demonstrate the improved ability to measure dC/dt precisely using the dynamic
479 chamber method.

480 **Table 1** A comparison of N₂O fluxes ($\mu\text{g N}_2\text{O-N m}^{-2} \text{ hour}^{-1}$) calculated using linear and non-
 481 linear regression from hour long measurements using the dynamic chamber method. The table
 482 is arranged in order of increasing flux.

Plot number	Added N Treatment	Linear			Non-linear		
		Flux	95% confidence interval	R^2	Flux	95% confidence interval	R^2
13	N	3.9	124.5	0.84	17.4	1.3	0.98
3	N	8.7	13.5	0.99	10.2	0.2	0.99
8	N	12.9	14.1	0.99	14.9	0.6	0.99
18	N	15.7	69.5	0.95	35.4	2.0	0.99
2	Y	52.9	13.9	0.99	62.3	0.3	0.99
10	Y	204.3	20.1	0.99	230.2	3.0	0.99
7	Y	219.7	9.6	0.99	248.3	0.3	0.99
9	Y	298.1	31.8	0.99	424.7	1.3	0.99
5	Y	362.5	0.5	0.99	405.2	0.0	0.99
11	Y	627.5	12.3	0.99	718.9	0.4	0.99
4	Y	705.1	21.4	0.99	905.7	0.5	0.99
14	Y	780.6	6.0	0.99	881.8	0.7	0.99
1	Y	1202.9	19.5	0.99	1508.9	0.5	0.99
6	Y	1277.4	8.8	0.99	1443.7	0.3	0.99
12	Y	1440.3	2.0	0.99	1626.4	1.1	0.99
15	Y	3048.6	9.6	0.99	3445.4	0.6	0.99
19	Y	3419.8	3.2	0.99	3861.6	1.1	0.99
16	Y	3707.8	6.6	0.99	4184.4	1.6	0.99
17	Y	3849.8	11.9	0.99	4427.8	0.2	0.99
20	Y	3922.9	6.7	0.99	4432.7	0.4	0.99

483

484 Table 2 Cost-benefit analysis of QCL dynamic chamber and GC static chamber methods.

	QCL Dynamic Chamber	GC Static Chamber
Capital cost	€120 k	€18 k
Flux measurement time (minutes)	5	60
Number of simultaneous measurements	1	up to 10
Laboratory analysis time (minutes)	0	60
Number of measurements per hour of effort	12	5
Uncertainty (95 % CI) ($\mu\text{g N}_2\text{O-N m}^{-2}\text{ hour}^{-1}$)	2	20

485















