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Comparison of CO_2, CH_4 and N_2O soil-atmosphere exchange measured in static chambers with cavity ring-down spectroscopy and gas chromatography

Jesper Riis Christiansen [a,*], Josh Outhwaite [b], Sean M. Smukler [b]

[a] Department of Forest and Conservation Sciences, Faculty of Forestry, University of British Columbia, 2424 Main Mall, Vancouver, British Columbia V6T 1Z4, Canada
[b] Faculty of Land and Food Systems, University of British Columbia, 2357 Main Mall, Vancouver, British Columbia V6T 1Z4, Canada

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ABSTRACT

A laboratory and field experiment compared fluxes of CO_2, CH_4 and N_2O measured with cavity ring-down spectroscopy (CRDS) and gas chromatography (GC). The comparison between CRDS and GC showed that average CO_2 fluxes were significantly higher for CRDS in both the laboratory and field, but the same experimental treatments effects were detected for both techniques. Compared to CRDS, the GC technique was severely limited in detecting CH_4 fluxes in both the laboratory and field. Thus, only 16% of measured GC fluxes were detectable in the laboratory and none in the field whereas CRDS could detect 65% and 97% of the CH_4 fluxes in the laboratory and field. In contrast, N_2O fluxes measured with CRDS and GC were not different for both the laboratory and field. It was observed that a lower proportion of N_2O fluxes could be detected with CRDS (73%) than GC (92%) in the laboratory and similar recovery (65% and 68%) for the field. Thus, the same treatment effects were observed for both CRDS and GC. Furthermore, the comparison between CRDS and GC showed that enclosure times as short as 600 s for our field study site are suitable to estimate the same treatment effects, but not necessarily flux magnitude. We conclude that CRDS and GC can provide the same level of information regarding treatment effects in both laboratory and field experiments for CO_2 and N_2O, but not for CH_4 and it is possible to reduce enclosure time without comprising comparability between the two techniques.

1. Introduction

Soil-atmosphere exchange of the greenhouse gases (GHG) carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are commonly measured with closed static chambers (Pihlatie et al., 2013) or in laboratory incubations in combination with off-site gas chromatographic (GC) methods. In recent years the development of cavity ring-down spectroscopy (CRDS) and other online techniques for GHGs, such as tunable diode laser (TDL) or quantum cascade laser (QCL) promises to reach an unprecedented level of detail and precision for estimating the exchange of GHGs between the soil and the atmosphere (Cowan et al., 2014; Hensen et al., 2013). Laser technologies like CRDS, TDL or QCL have a superior detection limit and higher precision compared to GC (Christiansen et al., 2015; Hensen et al., 2013). However, these rapid real-time techniques are however expensive, require a stable power supply and can be difficult to transport which constrains their use for many research groups and limits their utility for analysis in remote areas. Also, CRDS instruments are currently limited by only one inlet line. This implies that the same machine has to be used for each chamber or incubation vessel individually either by manually moving the machine around between chambers or having it connected in an automated chamber setup with a distribution manifold (Jassal et al., 2005). State-of-the-art autochamber systems have been developed that can measure GHG fluxes from up to sixteen chambers using the CRDS technology (Picarro Inc., 2013). However, this level of replication still severely limits the capabilities to capture the spatial variability of GHG fluxes within an ecosystem. It was recently shown that CO_2, CH_4 and N_2O fluxes measured with automatic chamber with CRDS and mobile chambers with GC were comparable and that spatial variability could surpass the differences in measurement techniques (Ruan et al., 2014). Thus, it was suggested

* Corresponding author. Present address: Department of Geoscience and Natural Resource Management, Faculty of Science, University of Copenhagen, Rolighedsvej 23, DK-1958 Frederiksberg C, Denmark.
E-mail address: jrc@ign.ku.dk (J.R. Christiansen).

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that using a GC based static chambers to capture spatial variability in combination with an automated CRDS system working at high temporal resolution would result in a more accurate spatiotemporal assessment of the GHG exchange within an ecosystem, field or experimental unit (Ruan et al., 2014) than using either technique in isolation.

However, even if a distribution manifold enables automated sampling of chambers (Jassal et al., 2005) in the field or incubation chambers in the laboratory, sample numbers can still be limited by enclosure times. As sampling is done sequentially, long enclosure times that are usually employed in studies of CH_4 and N_2O subject treatments to large temporal variability (e.g., 30 min would only enable 2 samples per hour per chamber). Alternatively, sampling using the GC method, simultaneous or near simultaneous sampling can be achieved with discrete sampling points (e.g., taking multiple samples sequentially or simultaneously using multiple people). Thus, despite often needing enclosure times of ≥30 min (depending on chamber design) to achieve accurate quantification of GHG fluxes there are strategies to use GC sampling methods to capture spatial variability while minimizing the time between samplings within a specific treatment. Alternatively, if the CRDS were made mobile (i.e., no manifold) to capture spatially variability in the field by sampling chambers similar to those used for GC measurements sample numbers would still be limited by enclosure times. The higher frequency and higher precision of concentration measurement achieved by CRDS could however substantially shorten enclosure time and help to avoid or minimize the negative impact of the closed static chamber on the soil-atmosphere gas gradient that can lead to considerable underestimation of the pre-deployment flux (Creelman et al., 2013). Despite the superior analytic capabilities of modern techniques, such as CRDS and other fast methodologies, there is a lack of quantitative information of the relative performance of laser based and GC based techniques to measure GHG fluxes under the same experimental conditions (see Cowan et al. (2014) and Grossel et al. (2014) for recent comparisons between GC and QCL).

Our objectives of this study were therefore, (1) to compare the magnitude and temporal variability of CO_2, CH_4 and N_2O flux rates estimated with CRDS and GC techniques in laboratory and field experiments and (2) compare the flux rate of CO_2, CH_4 and N_2O and relative error measured with CRDS and GC techniques to identify optimal enclosure time for field experiments combining CRDS and GC techniques. The study was conducted using state-of-the-art CRDS and GC systems. The CO_2, CH_4 and N_2O fluxes measured with the two techniques were compared in a laboratory setup where soil moisture and nitrogen (N) levels were manipulated for intact cores from three different land use types as well as in a field experiment where the effect on GHG was evaluated at two levels of aboveground biomass incorporation in to the soil to mimic two N addition levels.

2. Materials and methods

2.1. Laboratory experiment

Twelve 316 cm^3 intact core soil samples were collected from a 2 m^2 permanent plot within each of the three land uses (forest, agriculture and wetland) at the University of British Columbia (UBC) Farm in Vancouver, Canada in February 2014. Before collection, soil moisture was examined using a decagon 5TM moisture meter (Decagon Devices, Pullman, WA, USA) to ensure treatment samples varied by no more than 5% moisture by volume. Because of the small plot size and limited moisture variation, soil physical and chemical properties were assumed to have a high degree of similarity within treatments. Cores were stored under refrigeration before moisture and N application. The incubation was divided into two 2-week experiments to test the effect of two levels of soil moisture (water filled pore space (WFPS)) (called "75% WFPS" and "35% WFPS"). It was assumed that at sampling the water content of the cores were equal to the field capacity of the cores to be used in the second round of testing at the lower moisture level. The cores were stored at 3 °C refrigeration with no manipulation to moisture or nitrogen content.

2.1.1. Treatment manipulation

The porosity of each habitat's soil was first determined by destructively oven drying five excess, fully saturated soil cores at 105 °C for 48 h for each habitat type. Averages of these values were then assumed to represent the overall habitat soil porosity to estimate water additions/removal required to establish two discrete target moisture treatments of 35 and 75% WFPS. Following the two weeks of emissions analysis, actual moisture levels were determined again by oven drying. Agricultural treatments were found to range from 69 to 82% WFPS in treatment one and 36–38% WFPS in treatment two; forest habitat treatments ranged from 22 to 28% and 26–41% WFPS in treatments one and two, respectively; and wetland habitat treatments ranged from 73 to 94% and 32–44% WFPS in the two respective treatments.

To achieve the high moisture level treatment deionized water was added to soils by syringe, ensuring even distribution. Before moisture levels were adjusted, KNO_3 solutions were applied to N-amended treatments, again by syringe. Nitrogen treatment levels were set at 100 kg KNO_3–N ha^{-1}, therefore stock solutions of 100 mL deionized water to 1.88 g KNO_3 were created, and 15 mL of solution added to each core sample. For some cores water needed to be removed to achieve the lower moisture content. After N addition these cores were air dried to the correct weight. After soil moisture manipulation the levels were held constant throughout the two weeks of experimentation by adding deionized water with a syringe to compensate for water loss through evaporation. Following moisture and KNO_3 addition, samples were left to pre-incubate for 48 h in lightly covered containers at room temperature prior to flux measurements.

To measure the fluxes of CO_2, CH_4 and N_2O the cores were placed in a 1 L jar and closed with a screw lid for 30 min. The threading of the jar was covered by layers of teflon tape to achieve a gas tight seal between the jar and the lid. The CRDS was connected to the jar through a combined inlet and outlet, where the outlet tube extended to the bottom of the jar and the inlet tube only extended a couple of centimeters in to the jar from the lid. The CRDS measured continuously for the closure time of the jar by recirculating the air between the jar and the analyzer. Four headspace samples for GC analysis, each of 10 mL of headspace (less than 4% of total headspace of jar + CRDS tubes, pump and cavity), were manually sampled at 0, 10, 20 and 30 min through a butyl rubber septum in the lid and transferred to an evacuated 6 mL Labco exetainer (Labco Limited, Ceredigion, UK) for subsequent GC analyses.

2.2. Field experiment

The field experiment was performed at the UBC Farm. The field experiment started May 14th, 2014 and ended June 2nd, 2014 and the fluxes were measured from eight chamber on four occasions giving a total of 32 chamber enclosures.

Two treatments were compared in the experiment, cover crop (CC) and no cover crop (No CC), to mimic different levels of carbon (C) and N additions to the soil. Two rates of C and N inputs were intended to stimulate the microbial community variably and result in broad differences in fluxes of CO_2, CH_4 and N_2O thus providing a better dataset on which to compare the performance of CRDS and GC.

The cover crop consisted of Hairy Vetch (*Vicia villosa* Roth) and Fall Rye (*Secale cereale*). The field was divided in to eight equally sized plots and randomly assigned with or without aboveground cover crop. Prior to the field experiment the cover crop was harvested in four of the eight plots and chamber collars 20 cm in diameter were installed immediately after the harvesting and left one week before flux measurements prior to plowing, providing the pre-treatment flux estimation.

Collars were inserted 7–8 cm in to the soil leaving 6–11 cm above the soil surface. The chamber volumes ranged from 2.5 to 2.9 L. Following the first flux measurement at May 14th, the collars were taken out of the soil. The cover crop was then mowed and all plots were plowed. Immediately after the plowing the collars were reinserted at approximately the same locations and adjusted to the same chamber height. When measuring the flux an opaque lid was fitted on top of the collar to seal of the headspace. Inside each chamber air was circulated in a horizontal direction by a fan powered by a 9 V battery. Enclosure time was 30 min where the CRDS measured continuously by recirculating the air between the chamber and analyzer. Five headspace samples each of 12 mL (less than 2% of total headspace of chamber + CRDS tubes, pump and cavity) for GC analysis were taken at 0, 3, 10, 20 and 30 min after closure. GC samples were sampled through a 1 mm tube fitted with a luer-lock 3-way stopcock and 10 mL transferred to an evacuated 6 mL Labco exetainer.

2.3. Cavity ring-down spectroscopy

A CRDS analyzer, Picarro G2508 Greenhouse Gas Analyzer (Picarro Inc., Santa Clara, CA, USA), was used in this study. The default company settings were used throughout the laboratory and field experiments (Fleck et al., 2013). Data output from the G2508 was on average every 2 s as dry mole fraction in ppm. The flow rate between the G2508 and incubation vessel and chamber was 250 mL min^{-1} using a low-leak external vacuum pump. Data was retrieved from the G2508 hard drive after each day of flux measurements. For technical details on the CRDS technology the reader is referred to Fleck et al. (2013).

2.4. Gas chromatography

The GC samples were analyzed on a Bruker 456 gas chromatograph (Bruker Corp., Billerica, MA, USA) equipped with a headspace Combi-pal auto sampler (CTC Analytics, Zwingen, Switzerland), a thermal conductivity detector (TCD), a flame ionization detector (FID), and an electron capture detector (ECD) for simultaneous analysis of CO_2, CH_4, and N_2O, respectively. The GC system was calibrated using Praxair certified standard gases (Low standard CO_2 = 350, CH_4 = 1.5, N_2O = 0.22 ppm; High standard CO_2 = 2025, CH_4 = 2.9, N_2O = 2.2 ppm; and 1 ppm N_2O (with N_2 balance gas)). Standard gas sample analyses were repeated and re-calibration performed if quality control standards, one standard for every 10 samples, showed > 5% deviance from expected concentration.

2.5. Flux calculation

Exponential development of headspace concentrations was consistently observed and thus considered when calculating the GHG flux. To account for non-linear development of headspace concentrations an exponential regression model was used (Hutchinson and Mosier, 1981; Pedersen et al., 2010; Pihlatie et al., 2013):

$$C(t) = C_\infty + (C_0 - C_\infty)e^{-\kappa t} \quad (1)$$

where $C(t)$ is the headspace concentration in ppm at time t, C_∞ is the assumed constant concentration in ppm at a given source depth below the surface, which the headspace concentration theoretically should approach with time, C_0 is the headspace concentration in ppm at $t = 0$ and κ is the concentration saturation rate (s^{-1}). The time derivative or slope (S_{exp}) of equation 1 at $t = 0$ is assumed to represent the pre-deployment flux in ppm s^{-1} and is given by:

$$S_{exp} = (C_\infty - C_0) \times \kappa \quad (2)$$

The flux at $t = 0$, F_0, for linear or exponential regression in mmol CO_2 m^{-2} h^{-1} or μmol CH_4/N_2O m^{-2} h^{-1} was calculated according to the equation:

$$F_0 = S\frac{V}{A \times R \times (273.15 + T)} \times 3600 \quad (3).$$

where S is the slope (ppm s^{-1}) of the regression line at $t = 0$, V is chamber volume in L, A is chamber area in m^2, R is the gas constant in L K^{-1} mol^{-1}, when it is assumed that the chamber pressure is equal to 1 atm. The factor of 3600 converts the flux to hourly values. For CO_2 the flux (F_0) was divided by 1000 to obtain the correct unit. Linear regression was also considered when comparing the effect of enclosure time on GHG fluxes as linear regression can been used as a substitute for non-linear models at short enclosure times.

Fluxes were filtered based on the regression analyses between headspace concentration and time. All regression (linear or exponential) fits were accepted if the relationship was significant ($p < 0.05$). Following regression and rate calculation all fluxes were rechecked to identify fluxes with flawed concentration measurements that could give abnormal high exchange rates.

An average minimum detectable flux (MDF) was calculated for both the CRDS and GC systems based on the analytic precision of the instruments. The MDF was defined as the flux equivalent to the analytic precision of raw output divided by enclosure time. The MDF was used in evaluation of the impact of enclosure time on the calculated flux. For CRDS the company specifications for the precision of the G2508 for the raw data output was 0.6, 0.01 and 0.025 ppm for CO_2, CH_4 and N_2O, respectively (Picarro Inc., 2013). For the GC system a certified "low" standard containing near ambient concentrations of CO_2 (342 ppm), CH_4 (1.74 ppm) and N_2O (0.23 ppm) was used. Fifteen samples were analyzed with the precision defined as the method quantification limit (MQL) (Corley, 2003) (standard deviation × 3 × $t_{99\%}$) where $t_{99\%}$ is the t value at the 99% confidence interval at df = 14 (2.977) giving a precision of 20.2 ppm for CO_2, 0.49 ppm for CH_4 and 0.058 ppm for N_2O. Using an average chamber volume and area of 2.7 L and 0.3 m^2, respectively, and an average air temperature of 22 °C during the field trial the theoretical MDF's at an enclosure time of 1800 s were calculated. For CRDS: MDF_{CO2} = ±0.004 mmol CO_2 m^{-2} h^{-1}, MDF_{CH4} = ±0.07 μmol CH_4 m^{-2} h^{-1}, MDF_{N2O} = ±0.18 μmol N_2O m^{-2} h^{-1}. For GC: MDF_{CO2} = ±0.14 mmol CO_2 m^{-2} h^{-1}, MDF_{CH4} = ±3.5 μmol CH_4 m^{-2} h^{-1}, MDF_{N2O} = ±0.41 μmol N_2O m^{-2} h^{-1}. The MDF's were scaled to enclosure times between 1 and 1800 s by multiplying the MDF at 1800 s with the fraction 1800/enclosure time in seconds.

2.6. Statistical analyses

For all statistical analyses SAS 9.4 (SAS Institute Inc., Cary, NC, USA) software was used. For all analyses p-values <0.05 were considered significant.

For curve fitting PROC NLIN was used for exponential regression with default settings of the software. To estimate the standard error of the slope at $t = 0$ (S_{exp}, Eq. (2)) the PROC HPNLMOD was used. The PROC HPNLMOD uses the Delta method to approximate the standard error of composite variables, which in this case was the first derivative (Eq. (2)) at $t = 0$ of Eq. (1). The standard error of the estimate for the slope at $t = 0$ was divided with the flux to provide a measure of the relative error in % for each enclosure time.

All data was checked for normality using PROC Univariate. Certified gas concentrations were normally distributed. Laboratory

and field fluxes were not normally distributed and were log transformed to obtain normality. N_2O fluxes measured in the laboratory were still not normally distributed after transformation.

For each certified gas standards paired Students *t*-tests were performed using PROC TTEST to assess whether the CRDS and GC concentrations of CO_2, CH_4 and N_2O were similar.

For the laboratory fluxes two statistical tests were performed for both CRDS and GC to test for experimental effects. The first was a *t*-test of the soil moisture effect for each N addition level for each habitat. The effect of N addition effect was also assessed with a *t*-test for each soil moisture treatment for each habitat. Thus, the analysis did not compare the habitats as our focus was to test if the same conclusions could be achieved with CRDS and GC for different soil conditions.

To assess whether CRDS and GC field fluxes of CO_2, CH_4 and N_2O would reflect the same temporal variability under the different C and N input treatments, CC and No CC, a repeated measures ANOVA was performed for both CRDS and GC fluxes for all three gases using the MIXED procedure. The treatment effect was the level of biomass incorporation (CC and No CC), the random factor in the model was the plot and the repeated factor was the date of measurement. To test the difference in flux magnitude between CRDS and GC a *t*-test was performed separately for each date of the field experiment, resulting in four different *t*-tests for CO_2, CH_4 and N_2O, respectively.

It was further tested how a shorter enclosure time would impact the calculated magnitude and uncertainty of the in situ flux estimates. Each time series of CO_2, CH_4 and N_2O measured during chamber enclosure in the field was sequentially reduced by 100 s for CRDS from enclosure times of 1800–100 s, and for GC from 1800 s to 600 s. This provided 18 estimates for each CRDS time series and three estimates for GC. The flux was averaged for all chambers and dates due to the low temporal and spatial variability of CO_2, CH_4 and N_2O.

3. Results and discussion

3.1. Calibration of cavity ring-down and gas chromatography

CRDS showed a more consistent linear response to increasing concentrations of CO_2 and CH_4 than GC, but not N_2O (Fig. 1). Thus, for CO_2, CRDS showed no deviation to certified concentrations whereas GC overestimated CO_2 concentrations more at higher concentrations (Fig. 1A). For CO_2 the absolute differences between CRDS and GC were substantial (58, 130 and 1357 ppm) relative to the certified concentration level for all standards, except for the blank (Fig. 1A). Thus, CRDS and GC concentrations were significantly different across the entire certified concentration range for CO_2. It is unlikely that the significantly higher CO_2 concentration above 2000 ppm are due to storage in the vials, as it would be expected that diffusion out of the vial would decrease concentrations compared to the certified standard. Instead, the deviation indicates that the TCD responds in non-linear fashion at concentrations above 2000 ppm, whereas the CRDS is linear across the entire concentration range.

For CH_4 the response of the CRDS was extremely linear over the entire certified concentration range (Fig 1B), even at sub-ambient concentrations, but GC showed an overestimation at sub-ambient concentrations below 1 ppm. This might be explained by a pollution of laboratory air with a higher CH_4 concentration of the sub-ambient samples. It is a challenge to measure sub-ambient CH_4 concentrations on GC systems as handling of samples and transfer of gas from vials to injection ports often happens in ambient concentrations and not in a closed loop as is the case with CRDS. The pollution issue becomes less critical at sample CH_4 concentration above the ambient level as it also observed in our case (Fig. 1B). The consistently higher CH_4 concentrations measured with GC at sub-ambient levels would theoretically lead to an underestimation of CH_4 uptake rates compared to CRDS (Fig. 1B). As for CO_2, CRDS and GC concentrations of CH_4 were significantly different across the entire range of tested concentrations, but relative differences were smaller than observed for CO_2 (Fig. 1B).

The N_2O concentrations measured with CRDS and GC were significantly different for concentrations below 3 ppm, but again absolute differences were small. Thus, the CRDS and GC showed the same response across the range of concentrations (Fig. 1C). Especially, at concentrations below 1 ppm the CRDS measurements coincided closely with certified concentrations, whereas GC overestimated the N_2O for the 1 ppm certified gas more than was the case for CRDS (difference of −0.03 ppm for CRDS vs +0.08 for GC) (Fig. 1C).

3.2. Comparison of cavity ring-down and gas chromatography fluxes

A direct comparison between CRDS and GC CO_2 fluxes showed consistently (except on three occasions) smaller GC fluxes compared to CRDS in both the laboratory (Fig. 2A) and field experiments (Fig. 2B), but generally there was a linear relationship between CRDS and GC indicating a systematic difference between the two techniques. Thus, the average GC flux (10.8 ± 0.6 mmol CO_2 $m^{-2}\,h^{-1}$) was significantly lower than measured with CRDS (13.0 ± 0.7 mmol CO_2 $m^{-2}\,h^{-1}$) in the laboratory. Similarly, the CO_2 fluxes measured with GC (21.5 ± 1.7 mmol CO_2 $m^{-2}\,h^{-1}$) were lower ($p < 0.0001$) than CRDS (26.7 ± 1.8 mmol CO_2 $m^{-2}\,h^{-1}$) in the field. For CH_4 there was no such relationship between CRDS and GC for either the laboratory (Fig. 2C) or the field experiment (Fig. 2D), and although CH_4 fluxes differed greatly between the two techniques the average GC fluxes (-1.78 ± 0.65 μmol CH_4 $m^{-2}\,h^{-1}$) were similar to average CRDS fluxes (-1.09 ± 0.2 μmol CH_4 $m^{-2}\,h^{-1}$) in the laboratory. The difference was highlighted in the field experiment where GC CH_4 fluxes displayed both positive and highly negative rates (−12–4 μmol CH_4 $m^{-2}\,h^{-1}$) compared to CRDS fluxes between −1.03 and −0.31 μmol CH_4 $m^{-2}\,h^{-1}$. Due to the extreme variability of GC CH_4 fluxes no significant difference between CRDS and GC was found. This indicates a much more uncertain flux estimation of CH_4 using GC than CRDS. For N_2O the comparison between CRDS and GC in the laboratory showed a high correspondence between the flux magnitudes across a wide range of fluxes (Fig. 2E) and average GC N_2O fluxes (6.9 ± 2.0 μmol N_2O $m^{-2}\,h^{-1}$) were thus similar to CRDS (7.1 ± 2.3 μmol N_2O $m^{-2}\,h^{-1}$). The comparison was somewhat similar for the field experiment although average GC N_2O fluxes (2.2 ± 0.4 μmol N_2O $m^{-2}\,h^{-1}$) were slightly higher than CRDS N_2O fluxes (1.7 ± 0.3 μmol N_2O $m^{-2}\,h^{-1}$) (Fig. 2F), but not significantly different. These findings correspond to a recent comparison between GC and QCL (Grossel et al., 2014) that showed similar average N_2O fluxes measured with the two techniques for low and high flux situations. This was also the case in Cowan et al. (2014), but static chamber fluxes (GC technology) were more variable than estimated with QCL due to a large uncertainty associated with headspace sampling (1 per enclosure) and flux calculation. We did not find a higher variability association with GC fluxes compared to CRDS which can be attributed to a smaller variation in flux magnitude during the field study and more GC sampling points per chamber enclosure providing a more robust flux estimate with GC.

3.3. Laboratory experiment – effect of nitrogen and soil moisture on GHG fluxes

For the forest samples a significant reduction in CO_2 respiration by N addition at 75% WFPS and 35% WFPS was observed by CRDS,

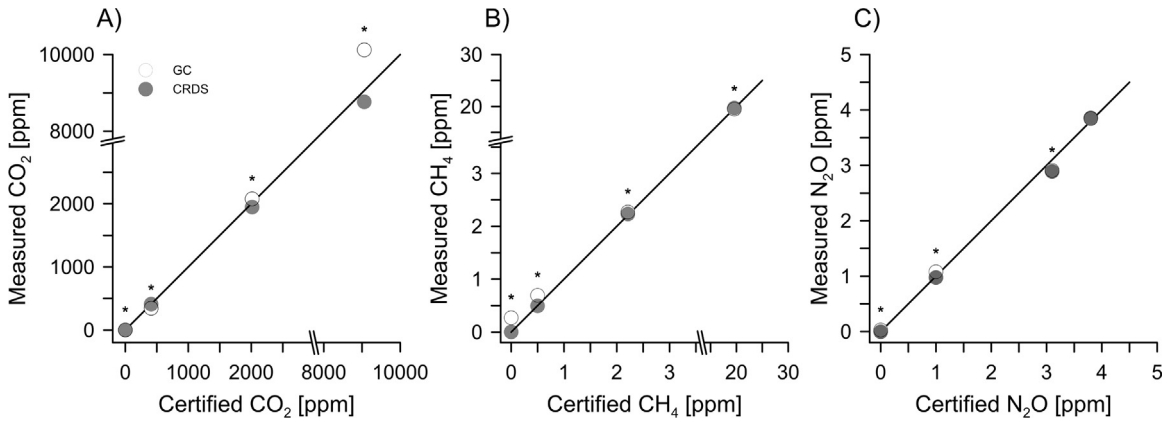

Fig. 1. Measured concentrations (ppm) of (A) CO_2, (B) CH_4 and (C) N_2O for cavity ring-down spectroscopy (CRDS) and gas chromatography (GC) compared to certified gas concentrations (ppm). An asterisk indicate significant ($p < 0.05$) difference between CRDS and GC concentration estimation.

indicating similar response to N under two different soil moisture regimes (Fig. 3A). For GC, the effect of N addition was only detected at 75% WFPS (not shown). As expected, respiration rates decreased when soils dried out, but only significantly for controls measured with both CRDS and GC (Fig. 3A). It should be noted that the soil cores for the 75% WFPS treatment did not achieve field capacity at rewetting and the response to soil moisture we observe might be due to a rapid increase in activity of the microbial community at rewetting, a so-called Birch effect. No treatment effects (H_2O or N) were observed for CRDS and GC CO_2 fluxes for the agriculture soils and rates were comparable across the entire range of treatments (Fig. 3B). For the wetland soils respiration rates measured with both CRDS and GC decreased significantly under N addition for FC, but rates were similar for the drier moisture treatment for both CRDS and GC (Fig. 3C). Fluxes measured with CRDS were significantly smaller for the lower moisture treatment compared to 75% WFPS for both control and N amended cores, but this was not detected with GC.

Overall there was a much smaller recovery of CH_4 fluxes measured with both techniques compared to CO_2 and N_2O. For GC eight out of 49 fluxes were significant compared to 32 out of 49 for CRDS, corresponding to a detection level of 16% and 65% of all CH_4 fluxes for GC and CRDS, respectively. Thus, on only four out of 12 experimental manipulations (four in each habitat) was it possible to perform the statistics to test for treatment effect on both the CRDS and GC results. The analyses showed that there was a

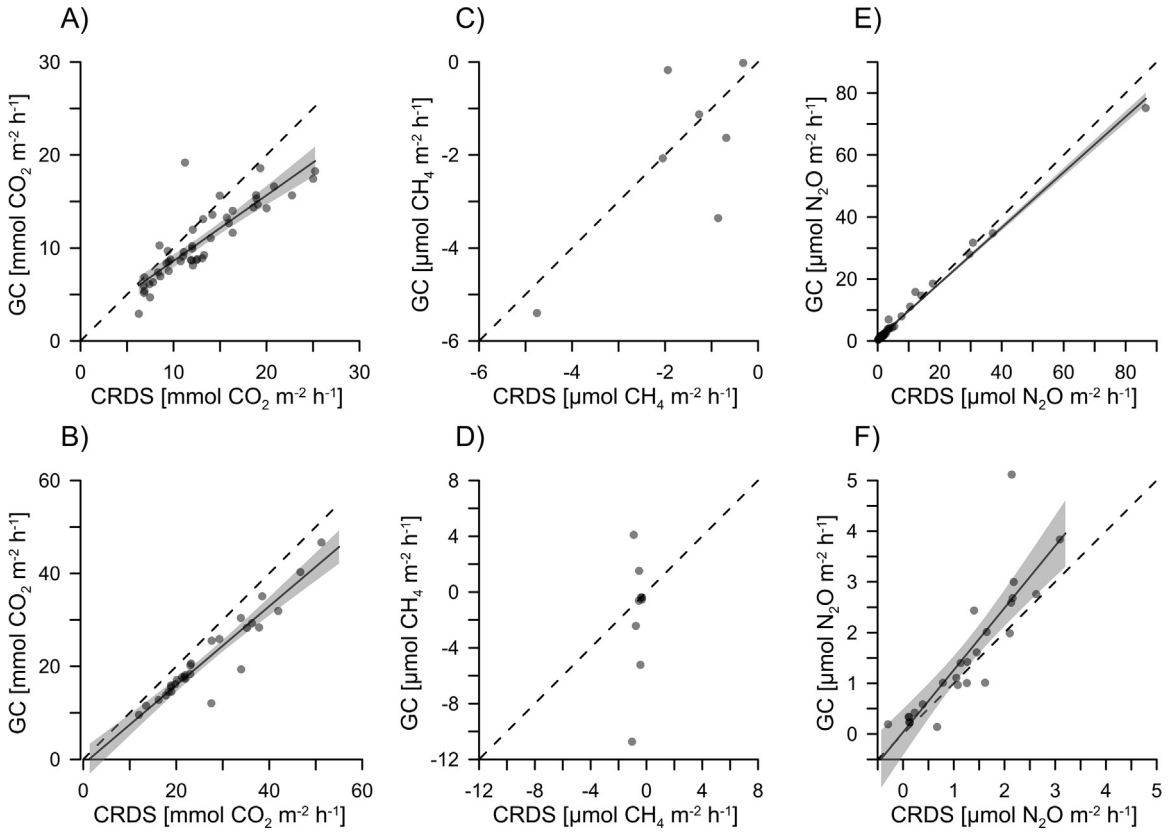

Fig. 2. Comparison between CO_2, CH_4 and N_2O fluxes measured with cavity ring-down spectroscopy (CRDS) and gas chromatography (GC). The 1:1 line is shown with a dashed line and linear regression fit with 95% confidence interval is shown with a solid line and grey are, respectively, (A) laboratory CO_2 fluxes, (B) field CO_2 fluxes, (C) laboratory CH_4 fluxes, (D) field CH_4 fluxes, (E) laboratory N_2O fluxes and (F) field N_2O fluxes.

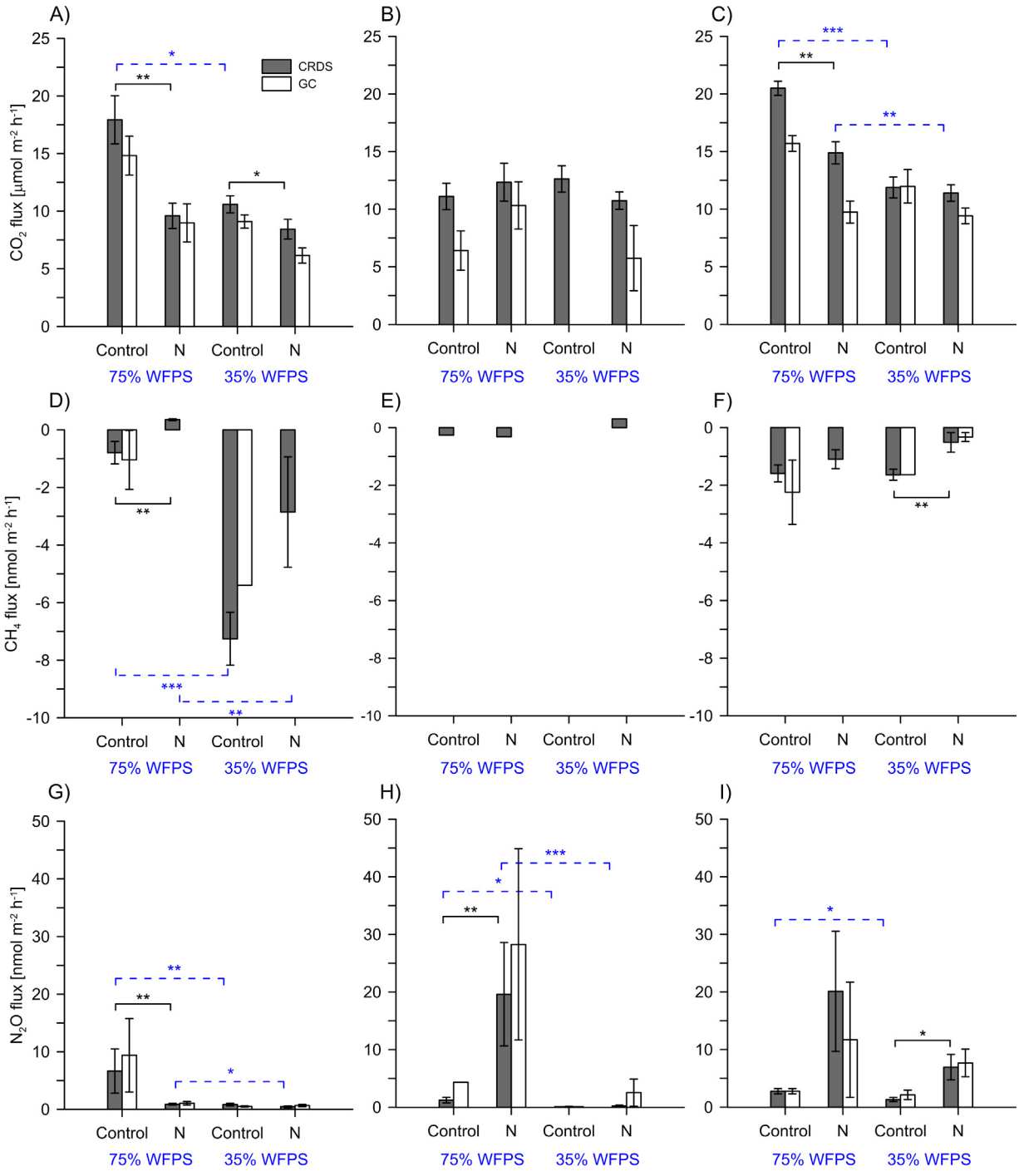

Fig. 3. Rates of CO_2 respiration for (A) forest, (B) agriculture and (C) wetland. Oxidation of CH_4 for (D) forest, (E) agriculture and (F) wetland. Emission of N_2O for (A) forest, (B) agriculture and (C) wetland. All rates are calculated with the exponential regression and are shown as the mean ± standard error of the mean for the entire incubation experiment (3 weeks). Treatments are control and N addition (100 kg NO_3–N ha^{-1}) for two levels of soil moisture: 75% water filled pore space (WFPS) and 35% WFPS. Gas fluxes measured with cavity ring-down spectroscopy (CRDS) and gas chromatography (GC) are shown in grey and white bars, respectively. Only statistical results for CRDS are shown. Asterisks denote significant effect of N addition (black solid horizontal lines) and soil moisture (blue dashed horizontal lines) where $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$. Bars without an error bar represent only one flux value for that specific experiment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

significant reduction in the CH_4 oxidation rate in forest soils under N addition (Fig. 3D) measured by the CRDS, but not GC. The average reduction from N addition was higher for the drier moisture treatment, but was more variable and not significant (Fig. 3D). Drying increased ($p < 0.01$) CH_4 oxidation rates under control and N amended conditions (Fig. 3D) measured with CRDS, but not GC. Of all the incubated cores, only three samples measured by the CRDS displayed CH_4 fluxes for the agricultural habitat at rates much lower than observed for forest or wetland soil samples (Fig. 3E). Accordingly, it was not possible to perform any statistical analyses on the data. Wetland samples displayed CH_4 oxidation, but at rates comparable to 75% WFPS control forest soil samples (Fig. 3F). Significant differences were detected between the control and N treatment at 35% of WFPS using the CRDS but not GC. As the incubation experi-

ment was designed to observe atmospheric CH_4 oxidation the lack of detection GC CH_4 fluxes falls in line with the fact that GC was not able to detect a linear decrease in CH_4 concentrations to the same degree as CRDS at sub-ambient concentrations as shown for the calibration test (Fig. 1B). Therefore, it would be associated with a higher degree of uncertainty to measure reduction of CH_4 concentration starting from ambient level using GC than CRDS.

Contrary to expectations, N addition resulted in a reduction ($p < 0.01$) of N_2O emissions in forest soil samples compared to controls at 75% WFPS (Fig. 3G), but only for CRDS fluxes. Also, N_2O fluxes for controls and N amended samples at 75% WFPS were higher ($p < 0.01$) than the drier moisture treatment as measured by CRDS but this effect was not detected with GC. Together this could indicate that rewetting of the control cores initiated a stimulation of N_2O production that was higher than was possible for the N treatment. However, for agriculture and wetland samples N addition did seem to have an effect on N_2O production at both 75% WFPS and 35% of WFPS, but the response was highly variable and not significantly different from controls, except for significantly higher N_2O fluxes for N amended cores at 75% WFPS measured with CRDS but not GC (Fig. 3H). Similar as observed for the forest soils N_2O emissions were higher ($p < 0.05$) at 75% WFPS for both control and N amended samples for CRDS, but not GC (Fig. 3H). The N_2O fluxes for the N amended wetland samples showed a highly variable response to the N treatment at 75% WFPS for both CRDS and GC, but were not different than controls. At the lower moisture treatment N_2O increased after N addition, but were not different from controls (Fig. 3I). Generally, soil moisture did not seem to impact N_2O fluxes in the wetland soils (Fig. 3I) although N_2O emission from control samples at 75% WFPS was higher ($p < 0.05$) than the drier cores (Fig. 3I). Similarly, to what was observed for CO_2, N_2O fluxes showed the same response for both CRDS and GC regardless of the treatment (Fig. 3G–I).

For 22 out of 36 possible treatments comparisons for the moisture and N manipulation there were enough CRDS and GC fluxes (CO_2, CH_4 and N_2O), respectively, to compare the ability of CRDS and GC techniques to capture the experimental treatments with ten comparisons for CO_2, three for CH_4 and nine for N_2O. Of the remaining 14 comparisons 10 could only be measured with CRDS and for the last four neither CRDS nor GC fluxes could be used to compare the techniques. For the 10 out of 22 actual comparisons between CRDS and GC the statistical analyses of the treatment gave the same result for CRDS and GC. However, the remaining 12 comparisons all showed a significant treatment effect measured with CRDS but not with GC for CO_2, CH_4 or N_2O.

3.4. Field experiment – Temporal variability of CO_2, CH_4 and N_2O

Soil respiration showed a similar temporal variability for the plots with and without cover crop, increasing immediately after plowing and showing a gradual decrease toward the end of the measurement period reaching similar magnitudes as before the plowing (Fig. 4A). The repeated measures ANOVA showed that for the two treatments the average CO_2 fluxes for CC plots were higher than fluxes in No CC for both the CRDS ($p = 0.007$) and the GC ($p = 0.032$). This was caused by the rapid increase of and significantly higher respiration rates right after plowing and on May 20th for the CC treatment. The *t*-tests for both CRDS and GC CO_2 fluxes showed that the treatment effect was mainly caused by differences between CC and No CC on May 14th and 20th (Fig. 4A).

There was no treatment effect on CH_4 fluxes in the field experiment measured by the CRDS, although it was observed that CH_4 uptake did decrease over time in the cover crop treatment, whereas CH_4 uptake for the No CC treatment increased. It was only before plowing that the CH_4 uptake measured with CRDS in the treatments differed significantly (Fig. 4B). Lack of significance may in part be due to the relatively small fluxes observed here. Skiba et al. (2009) for example, observed CH_4 uptake rates 10 times larger in European forested sites. It is noteworthy that only 9 out of the 32 possible GC flux measurement were measured, compared to 31 out of 32 for CRDS and a closer inspection of the GC data clearly showed that the concentration measurements were flawed resulting in abnormally high CH_4 exchange rates, both positive and negative. Thus, it was assessed that including these biased GC fluxes in the treatment test was irrelevant. This failure to capture CH_4 uptake in these soils with GC would have led to the wrong conclusion that CH_4 uptake is absent or CH_4 exchange highly variable in these agricultural soils, when on the contrary CH_4 uptake is consistent, albeit at small rates, as documented with CRDS. It has been suggested that agricultural operations disrupt CH_4 oxidation in the soil environment due to disturbance of the methanotrophic community (Priemé et al., 1997) and hence agricultural soils do not contribute to mitigating rising atmospheric concentration of CH_4. However, it has to be considered that chamber fluxes from agricultural soils most likely have been measured with GC that is sensitive to sub-ambient concentrations of CH_4 and that result in highly uncertain flux estimates as we also showed here. Using CRDS in agricultural settings will therefore likely change our current perception of the relationship of agricultural soils to atmospheric CH_4 uptake. The substantial deviation in performance of CRDS and GC in regards to CH_4 poses a challenge in assessing spatiotemporal dynamics that is not easily solved. Careful examination of the errors and elimination of these from gas sampling for use in GC in the field and laboratory, storage to analysis is obviously a pre-requisite to be able to minimize error of the concentration.

Similar to CH_4, no overall treatment effect was observed for N_2O fluxes using the repeated measures ANOVA for the two-week period of the experiment. However, the individual *t*-tests between treatments showed that on May 20th N_2O fluxes differed between the CC and No CC treatments (Fig. 4C). The similar temporal variability and magnitude of N_2O fluxes for CRDS and GC, illustrates the potential for scaling temporal variability of chamber fluxes to ecosystem level when automatic and manual chambers are used together.

In terms of comparison to other field chamber designs it has to be cautioned that our chamber was relatively small. Therefore the comparable fluxes of each CO_2 and N_2O (CH_4 was not detected in the field for GC) between CRDS and GC, respectively, might be a result of the GC system being able to detect the fluxes within the maximum 30 min. For larger chambers a longer enclosure time would be needed in order to detect the same flux which would disturb the soil-headspace gradient more and possibly lead to a higher degree of underestimation, especially for GC that require higher increase in signal than CRDS. Part of this underestimation can be overcome by using exponential regression that takes in to account the diminishing gradient between the soil and headspace (Pihlatie et al., 2013). However, using exponential regression requires that the number of chamber headspace samples is increased compared to linear regression. Furthermore, this test was only performed with a single GC system and it cannot be ruled out that other GC systems would produce different conclusions.

3.5. Relation between enclosure time and flux estimation

Generally, shorter chamber enclosure times resulted in increased estimates of CO_2 and N_2O emission for both CRDS and GC, and increased uptake rates of CH_4 (CRDS) for both exponential and linear regression (Fig. 5A–C). Also, it was evident that GC flux estimates calculated with linear regression were consistently smaller than exponential estimates for CO_2 which was also the case for CRDS linear fluxes (Fig. 5A). CRDS and GC flux estimates for N_2O were in better agreement across all three comparable enclosure

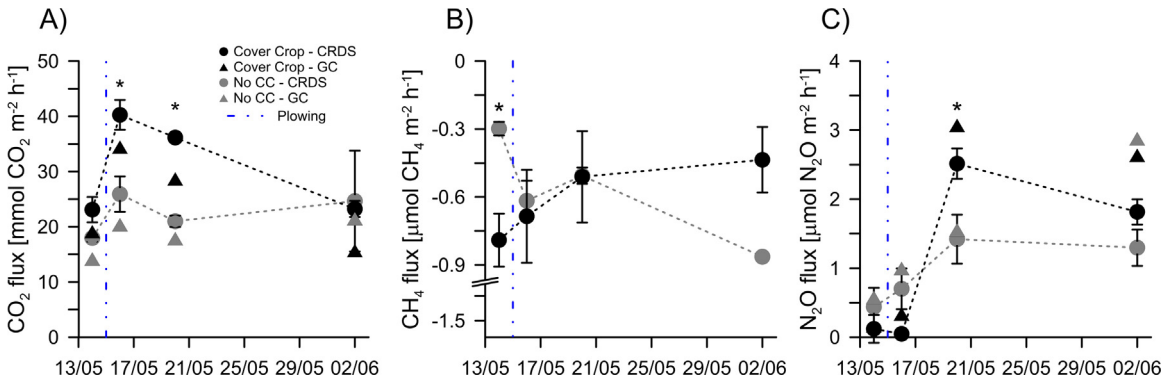

Fig. 4. Average greenhouse gas fluxes ± standard error of (A) CO_2, (B) CH_4 and (C) N_2O over time in a field experiment measured with cavity ring-down spectroscopy (CRDS) (circles) and gas chromatography (GC) (triangles). Some error bars are smaller than the symbol and cannot be seen. Error bars are only shown for CRDS fluxes for visual purposes. The fluxes were measured before and after plowing of plots with (cover crop) and without (no CC) aboveground cover crop. Asterisks represent significant ($p < 0.05$) differences between the cover crop and no CC treatments for both CRDS and GC, except for CH_4 where only CRDS fluxes were tested.

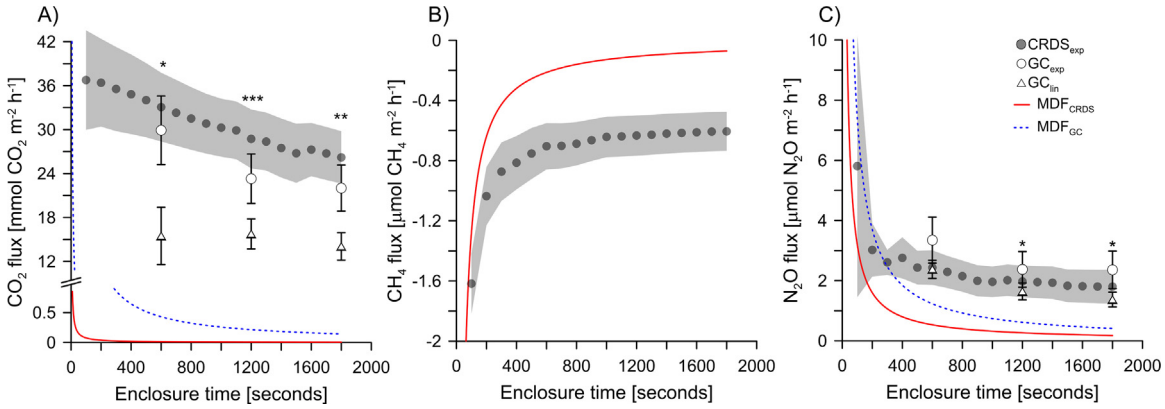

Fig. 5. The average flux rate ±95% confidence interval for the entire field trial period (May 14th–June 2nd) (A) CO_2, (B) CH_4 and (C) N_2O related to enclosure time for linear (triangles) and exponential (circles) regression CRDS (closed symbols) and for GC (open symbols). The solid (red) and dashed (blue) lines show the theoretic minimal detectable flux (MDF) for CRDS and GC, respectively, for an average chamber volume and area of 2.7 L and 0.3 m^2 and an average chamber headspace temperature of 22 °C. Asterisks denote significant differences between CRDS and GC fluxes calculated with exponential regression where $^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

times (Fig. 5C) although GC N_2O fluxes estimated with exponential regression were larger ($p < 0.05$) than CRDS fluxes at enclosure times of 1200 s and 1800 s. This is in accordance with the flux data from the field experiment (Fig. 4C). A similar finding was observed in (Cowan et al., 2014) for N_2O fluxes and attributed to unknown chamber artefacts that influence the rate of concentration change over time that cannot be captured by existing non-linear flux calculation models (Kroon et al., 2008; Pedersen et al., 2010).

The uncertainty (95% confidence interval) of average CRDS and GC CO_2 fluxes increased from ±3.6 to ±6.8 mmol CO_2 m^{-2} h^{-1}, ±0.13 to ±0.20 µmol CH_4 m^{-2} h^{-1} and ±0.56 to ±0.87 µmol N_2O m^{-2} h^{-1} (with an outlier of ±4.36 at 100 s) (Fig. 5A–C).

The fact the flux estimates increase with shorter enclosure time underlines that the chamber fluxes can only be considered as approximations of the true pre-deployment flux. However, bearing in mind that the longer the enclosure time the more distorted the soil–atmosphere gas gradient will be and hence lead to strong non-linear development that cannot be captured by the regression models in use. Accordingly, a shorter enclosure time will lead to less disturbance of the soil gas–atmosphere gradient and presumably result in flux estimates closer to the pre-deployment flux (Venterea and Baker, 2008). Therefore, in this case the increasing flux estimates reflect that the exponential equation (Eq. (1)) obtains a better fit of the portion of the chamber enclosure right after chamber deployment and hence reflect a better approximation of the pre-deployment flux (Cowan et al., 2014).

Whereas shorter enclosure time reduces the chamber disturbance to the soil system the flux calculation may also be associated with higher uncertainty of the regression because the fitted equations have fewer sample points. Furthermore, the relative flux error (error of the slope of the regression line at $t = 0$ divided by the flux) for CRDS CO_2 flux estimates were generally less than 1% for enclosure times between 100 and 1800 s (Fig. 6A). At enclosure times less than 400 s the relative flux error varied between 0 and 6%. For the GC CO_2 fluxes the relative flux error was both higher and lower compared to CRDS at enclosure times of 1200 and 1800 s, respectively. This indicates that the fewer sampling points may give rise to a higher uncertainty of the flux estimate. For CH_4 the relative flux error of CRDS (GC not detected) ranged between 0 to almost 2000% of the flux (Fig. 6B). However, for 93% of the flux estimates across the different enclosure times the relative error was less than 10% and for these the relative flux error increased exponentially with shorter enclosure time (Fig. 6B). The very high relative flux errors are related to the small CH_4 fluxes we observed. As discussed above, the fluxes reported here are generally in the lower end of what is often observed in field studies, e.g., 10 times lower than observed in forests. Hence, this will give rise to a higher statistical uncertainty of regression analyses when the flux is low. Similar to the observation for CH_4, the relative flux error for N_2O increased exponentially with shorter enclosure time from around 2% at 1800 s to 12–25% at 100 s (Fig. 6C). The relative flux errors for the GC N_2O fluxes were in the same range as for CRDS at enclosure times of

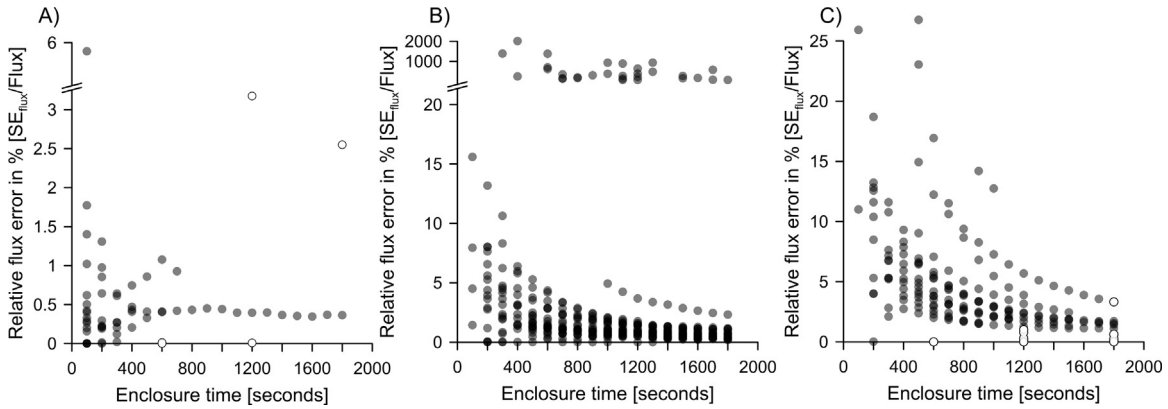

Fig. 6. Relative flux error (%) (SE_{Flux}/Flux) for (A) CO_2, (B) CH_4 and (C) N_2O related to enclosure time for the field experiment. Filled grey circler represent CRDS and filled white circles represent GC.

1200 and 1800 s, respectively, but on some occasions close to zero for all three enclosure times between 600 and 1800 s (Fig. 6C).

A counterintuitive result was that the relative flux errors for GC CO_2 and N_2O fluxes were close to zero (Fig. 6A and C). We attribute this to the flexibility of the exponential regression equation in obtaining a perfect fit between the sampling points during the enclosure. However, using this relative error to assess the performance of the exponential regression for GC may be problematic as the numbers of model parameters compared to time points in the model is high and thus the degrees of freedom are low.

Identifying an optimal enclosure time for all three gases is dependent both on the specific chamber design as well as the sensitivity of the gas analytic technique, but our results demonstrate that the relative flux error can be kept under 5% of the flux for the majority of flux measurements at enclosure times at or above 600 s for the CRDS we used (Fig. 6A–C) and well above the MDF for our chamber setup (Fig. 5A–C). At short enclosure time and low fluxes random instrument noise and chamber artefacts may lead to occasionally very high relative errors for all gases which should be avoided. Reducing the enclosure time for GC samples generally lead to same conclusions as for CRDS, but in most cases fluxes were significantly different compared to CRDS which could lead to biased conclusions of the absolute flux magnitude (Fig. 5A and C). Generally, it is accepted that shorter enclosure times reduce the systematic errors encountered with the use of closed chambers (Cowan et al., 2014; Creelman et al., 2013; Venterea and Baker, 2008) which is in line with our findings. However, the limit to which the chamber enclosure time can be reduced depends on the interaction between the flux magnitudes, chamber design and instrument precision where under higher fluxes the enclosure time can be reduced substantially without compromising flux uncertainty, but under lower fluxes instrument precision will constrain the enclosure time with the same chamber design. The role of chamber design was exemplified in (Laville et al., 2011) where increasing the chamber volume to accommodate plant growth but maintaining the same enclosure time (15 min) as for a smaller chamber resulted in fluxes below the detection limit of the QCL instrument for the larger chamber. This highlights the complexity in choosing the correct enclosure time especially under highly variable fluxes, such as N_2O.

4. Conclusions

We compared the performance of the GHG analytic techniques of cavity ring-down CRDS and GC in laboratory and field experiments to assess how well these different techniques estimated the same flux dynamics of CO_2, CH_4 and N_2O. It was shown that CRDS performed better when measuring a concentration range of certified gas concentrations for CO_2 (0–9000 ppm) and CH_4 (0–20 ppm), but performance was similar for N_2O (0–4 ppm). For the laboratory experiment CRDS performed better than GC considering all three gases, but in terms of identifying relative treatment effects of N addition and moisture manipulation the same results could be obtained with GC for CO_2, except for the wetland land use, and N_2O, but not for CH_4 where GC was severely limited. In the field experiment CRDS and GC also showed a consistent significant difference of CO_2 fluxes, but N_2O fluxes were similar. However, both CRDS and GC displayed the same temporal trend and treatment effects between cover crop and no cover crop treatments for CO_2 and N_2O. We conclude that the CRDS and GC systems we used can provide the same level of information regarding treatment effects in both laboratory and field experiments for CO_2 and N_2O, but not for CH_4. However, the significant different CO_2 fluxes between CRDS and GC and the substantial deviation we observed for both CH_4 and N_2O shows that it is imperative that the analytic instruments, chamber designs and sampling protocols are intercalibrated if used together in ecosystems studies of GHG balances to scale fluxes to ecosystem level.

The CRDS clearly outperformed the GC in terms of estimating CH_4 fluxes in the field. No fluxes could be detected above the background of the GC instrument while the CRDS detected nearly all of the fluxes. Using the CRDS or other high precision flux measurement methodologies, like TDL and QCL, could substantially change our understanding the relationship of agricultural soils to atmospheric CH_4.

In our study enclosure times as short as 600 s are suitable to estimate the same flux magnitude and treatment effects as longer enclosure time for CRDS and GC fluxes of CO_2 and N_2O. We realize our study represents a low flux environment, probably due to dry conditions during the experiment. Under higher fluxes enclosure times may be reduced even further and still provide the same level of information regarding flux magnitude and treatment effect. However, giving a universal minimum enclosure time is difficult since this is highly dependent on chamber design and analytic precision of the instrument used. For example, larger chambers will need longer enclosure times. So although our results suggest the CRDS can be used with short enclosure times to enable effective spatio-temporal sampling it is still recommended that the chamber design is tested prior to experiments and the volume-to-area ratio kept low to minimize enclosure times.

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