Biogeosciences Discuss., 10, 18277–18308, 2013
www.biogeosciences-discuss.net/10/18277/2013/
doi:10.5194/bgd-10-18277-2013

Biogeosciences Discussions
Open Access

High temporal frequency measurements of greenhouse gas emissions from soils

K. Savage[1], **R. Phillips**[2], **and E. Davidson**[1]

[1]The Woods Hole Research Center, 149 Woods Hole Rd, Falmouth, MA 02540, USA
[2]Landcare Research, Riddett Road, Massey University, Palmerston North, 4472, New Zealand

Received: 18 October 2013 – Accepted: 4 November 2013 – Published: 25 November 2013

Correspondence to: K. Savage (savage@whrc.org)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the most important anthropogenic greenhouse gases. Variation in soil moisture can be very dynamic, and it is one of the dominant factors controlling the net exchange of these three greenhouse gases (GHG). Although technologies for high frequency, precise measurements of CO_2 have been available for years, methods for measuring soil fluxes of CH_4 and N_2O at high temporal frequency have been hampered by lack of appropriate technology for in situ real-time measurements. A previously developed automated chamber system for measuring CO_2 flux from soils was configured to run in-line with a new quantum cascade laser (QCLAS) instrument that measures N_2O and CH_4. Here we present data from a forested wetland in Maine and an agricultural field in North Dakota, which provided examples of both net uptake and production for N_2O and CH_4. The objective was to provide a range of conditions in which to run the new system and to compare results to a traditional manual static chamber method.

The high precision and more than ten-times lower minimum detectable flux of the QCLAS system, compared to the manual system, provided confidence in measurements of small N_2O uptake in the forested wetland. At the agricultural field, the greatest difference between the automated and manual sampling systems came from the effect of the relatively infrequent manual sampling of the high spatial variation, or "hot spots", in GHG fluxes. "Hot spots" greatly influenced the seasonal estimates, particularly for N_2O, over one 74 day alfalfa crop cycle. The high temporal frequency of the automated system clearly characterized the transient response of all three GHG's to precipitation and demonstrated a clear diel pattern related to temperature for GHG's. A combination of high frequency automated, and spatially distributed chambers would be ideal for characterizing "hot spots" and "hot moments" of GHG fluxes.

BGD
10, 18277–18308, 2013

1 Introduction

The production and transport of CO_2, CH_4, and N_2O in soils is strongly affected by changes in soil temperature and moisture through diel cycles, wet-up and dry-down events, management practices, seasonal patterns, and interannual variation in climate (Davidson and Schimel 1995; Borken et al., 2006; Davidson et al., 2006). Microbial decomposition of soil organic matter and root respiration are the dominant sources of CO_2 production. The microbial processes of nitrification and denitrification are the dominant sources of N_2O (Firestone and Davidson, 1989), and these soil microbial processes are subject to rapid responses to wetting and thawing events (Davidson, 1992). There is growing evidence of an occasional net sink of N_2O in soils (Chapuis-Lardy et al., 2007; Schlesinger 2013), but elucidation of this process has been hampered, in part, by lack of sufficient sensitivity and frequency of N_2O flux measurements. Methane is produced under anaerobic conditions by methanogenic bacteria and consumed under aerobic conditions by methanotrophic bacteria (Davidson and Schimel, 1995). Hence the balance between release and uptake of CH_4 from soils is dependent largely on soil moisture status, which can change rapidly with precipitation events. Fluxes associated with precipitation events are difficult to study if humans must be present to make measurements immediately before, during, and after storms.

Reliable and continuous automated systems are needed for measuring fluxes of CH_4 and N_2O to determine how short-term variation in moisture, temperature, and rhizosphere activity, as well as human management practices such as tillage and fertilization, influence production, consumption, and transport of these soil gases. The static chamber technique involves manual collection of gas data over a time course (< 1 h) using vials that are subsequently analyzed by gas chromatography in the laboratory (Verchot et al., 1999, 2000; Davidson et al., 2008; Phillips et al., 2009) and can be labor-intensive and time-consuming. Manual fluxes are typically measured once per day, week, or month and often only during daylight hours. While the manual chamber technique for GHG flux measurement is widely accepted, the lack of diurnal data, par-

BGD
10, 18277–18308, 2013

ticularly for CH_4 and N_2O fluxes, may compromise emission estimates. Estimates of annual fluxes from soils may also be subject to error if short-term responses to climatic variation and management interventions are inadequately sampled by infrequent manual measurements (Savage et al., 2008). Opportunities for mitigation efforts to reduce emissions of CO_2, CH_4 and N_2O could be missed due to lack of understanding of transient spikes in emissions of these gases in response to rapidly changing environmental conditions.

With manual sampling using GC, it is usually necessary to leave a chamber over the soil for 20 min or more in order to detect a significant change in CH_4 or N_2O concentration in the chamber headspace. Leaving a chamber in place for this long can affect concentration gradients of these gases within the soil profile under the chamber, thus causing a bias in the estimated flux (Davidson et al., 2002). In the case of CO_2, the availability of fast-response, portable infrared gas analyzers allows in situ methods for measuring soil CO_2 flux, with the chamber over the soil for only 5 min or less (Davidson and Trumbore, 1995), thus minimizing the artifact of altering diffusion gradients. Current generation of newly available laser technology, which can measure CH_4 and N_2O at up to 10 Hz, now provide an opportunity to make quicker measurements of these two important greenhouse gases at the surface of soils at high temporal frequencies.

We had previously developed an automated system for measuring soil respiration at high temporal frequency (every 30 min) using an Infrared Gas Analyzers (Savage and Davidson, 2003; Savage et al., 2008). These high frequency measurements provided valuable insight into transient responses of soil respiration to precipitation events, which maybe missed using a manual approach (Savage et al., 2009). Here we describe the technical details and methodologies to integrate an automated soil respiration system with a newly available quantum cascade laser (QCLAS), which measures N_2O, CH_4 and H_2O at 10 Hz (Aerodyne Research Inc., Billerica, MA). This automated method will enable continual, high frequency, simultaneous measurements of the three most important greenhouse gases from soils. Since this system was previously tested for

BGD
10, 18277–18308, 2013

CO_2 flux (Savage et al., 2008), this manuscript will focus primarily on the integration, and precision of the QCLAS to measure N_2O and CH_4 fluxes at the soil surface.

The system was deployed in early autumn at a forested wetland site in Howland (ME). The following spring, the system was moved to an alfalfa agricultural site near Mandan (ND). Our purpose is not to compare forested wetland vs. agricultural sites per se, but rather to provide a range of conditions in which to run the automated QCLAS chamber system through sensitivity tests. We then compare fluxes using the automated QCLAS with fluxes using manual static chambers for a full alfalfa crop cycle at the ND agricultural site.

2 Materials and methods

2.1 Study sites

2.1.1 Howland Forest wetland

The Howland Forest research site is located about 35 miles north of Bangor, Maine (45.20407° N, 68.74020° W). The forest is owned by the Northeast Wilderness Trust, which has dedicated the site to conservation and scientific research. Stands in this forest consist primarily of red spruce (*Picea rubens* Sarg.) and eastern hemlock (*Tsuga canadensis* (L.) Carr.). This stand was selectively logged (not clear-cut) early in the 1900s, but has been minimally disturbed since that time. Soils range from well drained to very poorly drained over relatively small areas (Levine et al., 1994). Physical and chemical data on the soil are provided by Fernandez et al. (1993). Mean annual temperature is +5.5 °C, and mean annual precipitation is about 1000 mm.

The sampling location was in a forested wetland approximately 80 m from a climate controlled instrument hut where the equipment was housed. This system was deployed at this location from mid September to early November 2011 and consisted of four automated soil gas flux sampling chambers, each measured hourly. Chambers were

BGD
10, 18277–18308, 2013

placed in a forested wetland dominated by *sphagnum* and peat. Peat depths were approximately 1 m in the area these chambers were placed. The water table was a few cm below the *sphagnum* surface over the course of this sample period. Soil temperature was measured at 10 cm depth (Type-T thermocouple). Soil moisture was measured using the Campbell Scientific CS616 water content reflectometer probes, placed at 10 cm depth. Soil temperature and moisture were measured hourly and data stored on a Campbell Scientific CR10X datalogger (Campbell Scientific, Logan UT). Precipitation data are from the Howland Forest Ameriflux eddy covariance tower (Dave Hollinger US Forest Service pers. comm).

2.1.2 North Dakota Alfalfa Field

The agricultural site is located near Mandan, ND, USA (46°46′ N, 100°55′ W). Soils are classified as Temvik–Wilton silt loam (Fine-silty, mixed, superactive, frigid Typic and Pachic Haplustolls, Soil Survey Staff, 2008). Climate at the study site is semiarid with mean annual temperature of 10 °C and mean annual precipitation of 412 mm. The study site was managed for annual grain production for over 50 yr and was seeded to alfalfa (*Medicago sativa*, L) in 2009 using a no-till drill (8 kg seed ha^{-1}). The alfalfa crop is harvested for silage approximately two times per year, and the time period from re-growth to harvest is considered one crop cycle. Management input is limited to 6.7 kg N ha^{-1} and 33 kg P ha^{-1} as granular monoammonium phosphate in mid-March each year. Soil properties measured in fall 2008 indicated C, N, and pH were 24.0 g kg^{-1}, 2.3 g kg^{-1}, and 5.7 (Phillips et al., 2009).

The automated chamber system was installed at the ND site and measurements commenced on 19 March 2012, ten days following soil thaw, and continued for one full alfalfa crop cycle (74 d). Five automated chambers were set up in a semi-circle, approximately 3 m apart. The gas analyzing equipment (IRGA and QCLAS) were housed in a climate controlled building approximately 15 m from chambers. A static chamber of similar shape and volume (~ 400 cm^3) to the automated chamber was located within 1 m of each automated chamber in a similar configuration. The site was also instru-

BGD
10, 18277–18308, 2013

mented with a rain gauge (TR-525), a soil temperature probe (T105) placed 2 cm below the soil surface, an air temperature probe (FW05) located at the soil surface, and three soil moisture probes (CS615) placed horizontally 4 cm below the surface (Campbell Scientific, Logan, UT).

2.2 Automated sampling system

A schematic diagram of the automated system is shown in Fig. 1, which is similar to a previously developed automated system for measuring soil respiration (Savage and Davidson, 2003). For simplicity, Fig. 1 shows only 3 chambers and is not to scale. The chamber design is based upon that of Tim Savas (Marine Biology Laboratory, Woods Hole MA). Briefly, chamber tops are 30.5 cm diameter schedule 80 PVC piping cut to 12.7 cm lengths. A 0.13 cm thick schedule 80 PVC sheet is cut to 30.5 circular diameter and fixed using PVC cement to one side of the cut piping. This creates the chamber top. Collars are also made of the same schedule 80 PVC pipe, cut to 5.1 cm lengths and beveled on one site at about 0.13 cm from the end. This end of the collar is inserted into the soil surface. Chamber tops are raised and lowered via a pneumatic piston (Minuteman Controls, Wakefield MA). T-slot aluminum bar (MSC Industrial Supply, Melville NY) is used to make the chamber structures which support the chambertop while being lifted or lowered onto the collar.

Flow from each of the chambers is controlled by two sets of manifold mounted solenoid valves (Minuteman Controls, Wakefield MA). One set of solenoids controls the flow from the closed chamber to the analyzers and the other set controls the return flow from the analyzers to the closed chamber. Chambers are lifted and lowered via pneumatic pistons. An air compressor supplies the pressurized air to a set of slider valves (Minuteman Controls, Wakefield MA). The compressor is set to supply 40 psi of pressure, such that when the chamber top is in the down position, there is downward pressure sealing the chambertop to the collar. The timing of each of the chambers and the lifting and lowering of the chamber tops is controlled by a relay driver (Campbell Scientific, Logan, UT), such that when one chamber is activated, the relay driver turns

BGD
10, 18277–18308, 2013

on the flow control solenoids and activates the piston control solenoids to lower the chamber top onto the collar. A CR1000 datalogger (Campbell Scientific, Logan, UT) is used to control the timing of the relay driver, sending it a signal to turn on or off a chamber at a particular interval over a one hour period.

The chamber air flows from the closed chamber first to the Licor 6252 IRGA (Licor, Lincoln NE) for CO_2 measurement and then to the QCLAS for measurement of CH_4, N_2O and H_2O. For a complete description of the QCLAS instrument, see Nelson et al., 2004. Briefly, the QCLAS is thermoelectrically cooled, uses a 76 m pathlength, 0.5 L volume, and multiple pass absorption cell for sampling. The laser frequency for the QCLAS is 1271 cm^{-1} for each of CH_4 and N_2O. The laser is thermoelectrically cooled (Thermocube) to 32 °C. The QCLAS operates at below ambient pressure (40 Torr) and for this reason needs to be downstream of the IRGA, which operates at ambient pressure. A dual head diaphragm pump (KNF Neuberger, Trenton NJ) maintains a steady flow rate of 0.8 L min^{-1} from chambers to the QCLAS. A datalogger (Campbell Scientific CR1000) records IRGA and QCLAS data at 1 Hz. Analog output is sent from the IRGA to the logger and QCLAS data is sent to the logger through an RS232 cable. Calibration gases were automatically run through the IRGA and QCLAS using the QCLAS built in solenoid valve system. Flow from a calibration gas is toggled on and allowed to flow for 2 min through the IRGA and the QCLAS and outflow is vented to the atmosphere.

At both Howland Forest and North Dakota, each of the chambers was sampled once per hour. Each chamber was active for 10 min with 2 min to flush the tubing lines and 8 min when the chamber top was down over the collar. Gas concentrations were corrected for water vapor interference using the QCLAS H_2O concentration data. Automated fluxes were calculated using measurements collected over a 4 min time period, beginning 60 s after the chamber top closed to 300 s into the run. Fluxes were calculated from a linear regression of change in headspace concentration over time and were scaled to the collar area, corrected for atmospheric pressure and temperature.

BGD
10, 18277–18308, 2013

2.3 Manual sampling technique

Manual chamber flux data were collected three times per week between 09:00 and 12:00 CST, from March through June 2012, in conjunction with the automated chamber flux data. Details of this technique are described in detail by Phillips et al. (2009). Briefly, four headspace samples (15 mL) were sampled every 6 min (total time 18 min), and were then immediately injected into evacuated, 12 mL exetainers (Labco Unlimited, Buckinghamshire, UK). These samples were analyzed for CO_2, N_2O and CH_4 with a Varian (Varian Inc., Walnut Creek, CA), Model 3800 Gas Chromatograph and Combi-Pal auto-sampler (Phillips et al., 2009). Manual fluxes were calculated using 4 measurements collected over an 18 min time period. Fluxes were calculated from the change in chamber headspace concentration over time in the same manner as those from the automated system.

2.4 Instrument accuracy and precision

According to QCLAS factory specifications, the range for N_2O measurements is 0.3 to 3000 ppb at 10 Hz, with a sensitivity of 0.3 ppb. The range for CH_4 measurements is 0.5 to 5000 ppb at 10 Hz, with a sensitivity of 0.5 ppb. Specifically for our purposes of measuring GHG flux from soils, we configured the QCLAS to sample at a 1 Hz frequency. Two tanks of high precision NOAA standards (NOAA/ESRL/GMD, Boulder, CO) were used to determine QCLAS precision and accuracy for N_2O and CH_4 (Table 1). The absolute N_2O concentrations measured at the QCLAS were within 1 % of the NOAA standard for concentrations above and below ambient. The absolute CH_4 concentrations measured at the QCLAS were 7 % greater than the NOAA standard for concentrations above and below ambient. CH_4 and N_2O concentrations were corrected for this measurements difference post data processing. The absolute concentration difference for CH_4 standards may be indicative of peak interpretation within the QCLAS as the instrument is trained on interpreting the N_2O gas peak. Precision (relative standard deviation) for N_2O was 0.04 ppb at both concentrations (Table 1). The precision

BGD
10, 18277–18308, 2013

for CH_4 was 0.31 ppb at 2116.27 ppb and 0.26 ppb at 1764.63 ppb (Table 1). Levels of precision higher than factory specifications were likely achieved by the lower QCLAS sampling frequency (1 Hz).

The precision of GC analysis, expressed as a coefficient of variation for 10 replicate injections of a low concentration standard (2000 ppb for CH_4 and 363.7 ppb N_2O) and a high concentration standard (10 000 ppb for CH_4 and 1682.1 ppb N_2O) was consistently < 2 % for both gases.

2.5 Diel trends in GHG's

Diel trends in GHG fluxes were examined specifically in the ND dataset as it comprised a full growing alfalfa crop cycle. Diel patterns of GHGs were modeled using a sinewave function (see Savage et al., 2013):

$$R = \mathrm{yo} + A \cdot sine\left(\left(\frac{2 \cdot \pi \cdot \mathrm{TOD}}{2400}\right) + c\right) \quad (1)$$

Where, yo represents the mean flux over the time period modeled, A is diel amplitude, c corresponds to the shift of minimum and maximum diel peaks (radians) and TOD is time of day in hundreds. Units for yo and A are the same as the flux units for the GHG modeled. Bootstrapping 1000 model fits (R 2.7.1) was used to determine 95 % confidence intervals around model parameters.

3 Results and discussion

The high temporal frequency automated measurements of GHGs from a forested wetland in Howland ME and an agricultural site in Mandan, ND, provided a range of conditions in which to run the automated QCLAS chamber system through sensitivity tests and compare these with fluxes measured using the manual static chamber GC technique.

BGD
10, 18277–18308, 2013

3.1 Minimum detectable fluxes of N_2O and CH_4

Calculations of minimum detectable fluxes of N_2O and CH_4 for chamber-based measurements were made following the methodologies developed by Parkin et al. (2012). Automated chambers at Howland Forest collected ambient air for three minutes (n = 180) every hour, and these data were used to determine the mean and coefficient of variation (CV) for N_2O and CH_4. The minimum detectable flux for the automated system using the QCLAS for N_2O averaged ±0.01 µg N_2O-N $m^{-2} hr^{-1}$ and for CH_4 was ±0.03 µg CH_4-C $m^{-2} hr^{-1}$. Similarly for the study site in ND, the minimum detectable fluxes using the automated QCLAS system were ±0.05 µg N_2O-N $m^{-2} hr^{-1}$ and ±0.180 µg CH_4-C $m^{-2} hr^{-1}$. It is likely that the higher minimum detectable fluxes calculated from ambient air samples at the ND site compared to the Howland Forest site may be indicative of the air quality, where the location in ND is industrial/agricultural, whereas in Howland Maine the surrounding area is primarily forest.

The Parkin method was also used to calculate the minimum detectable fluxes for the manual static chambers. Ten ambient air samples were taken in the same method as gas flux samples. Minimum detectable fluxes were ±0.70 µg N_2O-N m^{-2} $hr^{-1}$for N_2O and ±3.32 µg CH_4-C $m^{-2} hr^{-1}$ for CH_4.

The high precision of the QCLAS instrument gives greater confidence in measurement of very low fluxes of both N_2O and CH_4 compared to the manual method.

3.2 Frequency distribution of N_2O and CH_4 fluxes

The purpose of using an automated sampling system is the ability to measure fluxes at high temporal frequencies without supervision. The drawback to this is determining if the automated system is functioning correctly unsupervised e.g., are the chambers closing properly over the collar? Our previous extensive measurements of CO_2 flux from soils (Savage et al., 2008) gives us confidence that there is a strong CO_2 flux, characterized by a linear increase in Δ [CO_2] in the chamber headspace. In contrast,

BGD
10, 18277–18308, 2013

N_2O and CH_4 fluxes are often small positive or negative values that are difficult to distinguish from a zero flux. The R^2 value of the linearly increasing Δ [CO_2] was used as an indicator that the system was functioning correctly. When the Δ [CO_2] R^2 value was ≥ 0.90, we have confidence that the system was operating correctly and hence we also have confidence in the fluxes of N_2O and CH_4 measured concurrent to CO_2. We assigned an R^2 of < 0.90 for Δ [CO_2] as an indication that there may have been an issue with the chamber closing and sealing correctly or other unknown problem, and we use this indicator of unreliable CO_2 flux measurement to identify which N_2O and CH_4 concurrently measured fluxes were also unreliable.

The frequency distribution of N_2O and CH_4 fluxes, at the Howland Forest wetland site and the North Dakota agricultural site (Fig. 2) are plotted separately for those fluxes that met the $R^2 \geq 0.90$ criteria and those that did not meet that criteria ($R^2 < 0.90$) for Δ [CO_2]. N_2O and CH_4 flux measurements that fell into the $\Delta[CO_2]R^2 < 0.90$ category were normally distributed near zero, which would be expected for random error due to improper closing of the chamber. For this small percentage of fluxes that did not meet the $\Delta[CO_2]R^2 \geq 0.90$ criteria, we considered all three GHG measurements suspect and did not use them in subsequent analysis.

At the Howland Forest wetland, for 96 % of fluxes measured, we have confidence that the system was working correctly based on the $\Delta[CO_2]R^2 \geq 0.90$. Of that 96 %, approximately 9 % of those fluxes fell below the minimum detectable range (see Sect. 3.1) for either N_2O or CH_4 fluxes (Fig. 2). In ND, 90 % of fluxes measured met the Δ [CO_2] $R^2 \geq 0.90$ criteria for confidence. Of those 90 %, 12 % fell below the minimum detectable range for either N_2O or CH_4 (Fig. 2). The 9–12 % of N_2O and CH_4 measurements at each site that met the concurrent Δ [CO_2] $R^2 \geq 0.90$ criterion but were below the minimum detectable N_2O or CH_4 flux were considered reliable N_2O and CH_4 flux measurements that were not statistically significantly different from zero. We did not change the values to zero, so as to avoid introducing bias in the population distribution of measurements, but we consider them equivalent to zero net flux. The populations of N_2O and CH_4 fluxes that met our reliability criterion were not normally distributed.

BGD
10, 18277–18308, 2013

Since the manual measurements require supervision, it was assumed that the manual chamber was always properly sealed during each measurement, therefore no minimum linear criteria for Δ [CO_2] was used as an indicator for proper chamber sealing as was used for the automated system flux data. For the manual measurements at the ND site, of the 190 samples measured over the 74 day period, 5 % of N_2O and 1 % of CH_4 fluxes were below the minimum detectable flux (see Sect. 3.1). All manually measured fluxes were used for subsequent analysis at their measured values, similarly to the automated fluxes.

3.3 Forested wetland in Howland Forest

High precision measurements of the QCLAS system enabled the quantification of very small and sporadic production of N_2O from these soils, however the consumption of N_2O dominated the soil atmosphere exchange in the wetland at the Howland Forest (Fig. 3a). Since the minimum detectable flux for N_2O was ± 0.01 µg N_2O-N $m^{-2} hr^{-1}$, this provides confidence that the small N_2O uptake (primarily in the -0.5 to -1.5 µg N_2O-N $m^{-2} hr^{-1}$ range) is a real phenomenon and not random variation within the detection limit of the system. These soils are nitrogen limited (Fernandez et al., 1993); hence low N_2O fluxes were expected. Consumption of N_2O by soils, has previously been observed (Chapuis-Lardy et al., 2007), but is often either doubted as not significantly different from zero or ignored. However, recent studies addressing this issue have found N_2O consumption related to soil moisture and thick soil organic layers (Fraiser et al., 2010; Ullah and Moore, 2011; Schlesinger, 2013). The wetland site has both a thick organic layer and wet conditions. However, it should be cautioned that this was a short term study conducted at the end of the snow free season and we do not yet know if net consumption of N_2O within these types of soils occurs during other seasons.

Methane varied between small production and consumption in the wetland (Fig. 3b). CH_4 fluxes were higher after precipitation events in the wetland and for chambers that

BGD
10, 18277–18308, 2013

were consuming CH_4, fluxes approached zero after rainfall, indicating that the balance between production and consumption was shifting. This small, transient shift in the balance between production and consumption in soils may be missed under less frequent sampling strategies.

Small episodic responses to precipitation events were evident among all three gases, with N_2O, CH_4 and CO_2 fluxes increasing, but no clear trend was evident from this short time period late in the snow-free season. Volumetric soil moisture in the wetland site varied little (Fig. 3) over the sampling period as the water table was near the surface, hence neither large nor small precipitation events influenced moisture greatly. In early September of 2011, one set of manual samples was taken from chambers located with 1 m of the automated chambers. Fluxes calculated from these measurements agreed well with fluxes measured by the automated system (Fig. 3a–c red triangles). The automated fluxes of all three trace gases are in agreement with those measured in a deciduous forest in eastern Canada for a similar time period to this study (Ullah and Moore, 2011).

3.4 Agricultural field in North Dakota

Unlike the forested wetland site, the alfalfa field was consistently a source of N_2O (Fig. 4a). Peaks in N_2O emissions followed precipitation events most notably in late spring (Fig. 4a). Highest N_2O flux values were measured near the end of April and in May, when microbial activity was likely stimulated by optimum soil temperature and moisture (Phillips et al., 2009). A few larger pulses were observed with the manual system, originating from two specific chambers, but were not present at the same time period for the automated chambers. The coefficient of variation (%CV) among the chambers sampled can be used as an indicator of spatial variability. The manual system had greater mean spatial variation in N_2O flux among chambers (mean = 26 µg N m^{-2} hr^{-1}, CV = 90 %) compared to measurements from the automated chambers sampled concurrently with the manual chambers (mean = 9 µg N m^{-2} hr^{-1}, CV = 60 %). Much of the high spatial variation in N_2O flux among the manual chambers came from a few cham-

BGD
10, 18277–18308, 2013

bers in April (Fig. 4a). These chambers may have captured what has been termed a "hot spot"; localized high microbial activity within the soil structure.

Methane fluxes had no clear regular temporal variation over the growing season. The manual method showed much greater variability of CH_4 fluxes (Fig. 4b), with both consumption and some episodic net emissions of CH_4, whereas the automated system showed consistent soil CH_4 uptake. Mean spatial variation among the chambers sampled manually was greater (mean = −36 µg C $m^{-2} hr^{-1}$, CV = 115 %) compared to the concurrent automated chamber measurements (mean = −23 µg C $m^{-2} hr^{-1}$, CV = 57 %). However, it should be noted that the high spatial variation for the manually measured CH_4 fluxes was evident throughout the growing season (Fig. 4b) as opposed to being attributed to specific dates as was seen for N_2O fluxes. Episodic emissions of CH_4 were not restricted to the same chambers.

Flux of CO_2 showed the greatest agreement between methods, with the manual technique showing lower variation compared to the automated system (Fig. 4c). This may be a signal-to-noise phenomenon, whereby there is better agreement between methods when the fluxes are consistently above detection limits for CO_2 and less often so for N_2O and CH_4. Spatial variation of CO_2 fluxes observed among chambers was slightly lower (mean = 92 mg C $m^{-2} hr^{-1}$, CV = 30 %) for manually compared to automated (mean = 104 mg C $m^{-2} hr^{-1}$, CV = 39 %). As has been previously observed (Savage et al., 2009), patterns of CO_2 flux followed soil temperature trends and rapid transient pulses of CO_2 were observed following precipitation events.

3.5 Capturing transient responses to changes in soil moisture in North Dakota

Automated and manual measurements of GHGs showed rapid, transient responses to precipitation events (Fig. 5). Increases in N_2O and CO_2 fluxes followed precipitation, with the greatest responses during the mid-growing season. Transient pulse responses of N_2O and CO_2 decreased over time from precipitation and subsequently as soil moisture decreased (Fig. 5a and c). The manually sampled chambers showed a greater ini-

BGD
10, 18277–18308, 2013

tial response to precipitation but as soils dried out there was good agreement between automated and manual measurements. Methane was generally consumed at this site, however during precipitation events CH_4 fluxes approached zero (Fig. 5), and as soils dried out greater rates of consumption were observed, particularly measured from the manual chambers.

Carbon dioxide flux increases in response to precipitation is a result of increased microbial decomposition and is generally a function of the length of the antecedent dry period as well as the magnitude and duration of precipitation (Borken et al., 2006; Savage et al., 2009). This response was similarly characterized by both the manual sampling and automated systems.

The high temporal frequency of automated system flux measurements of each GHG clearly characterized transient responses to precipitation events. The manual sampling strategy of three times per week at this ND site was also able to characterize much of the transient GHG responses to precipitation events, although less frequent manual sampling may miss many of these responses.

3.6 Manual and automated flux comparison

Automated and manual measurements were conducted concurrently in ND between 23 March and 4 June 2012 (74 days). Manual and automated measurements, taken at similar sample times (n = 136, only data for which there was both automated and manual measurements available were used) and all the automated measurements ($n \approx 7400$) for the crop cycle season are plotted in Fig. 6a–c. The range of variation in measured N_2O and CH_4 flux across the entire crop cycle season is much greater for the manual measurements compared to the concurrent automated measurements. However, the range of variation is similar between the manual fluxes and the entire season of automated measurement. It may be that, by random chance, the placement of some of the manual chambers captured "hot spots" missed by the placement of the automated chambers. However the high frequency sampling of the automated sys-

BGD
10, 18277–18308, 2013

tem also captured a few "hot moments" missed by the less frequent manual sampling strategy (Fig. 5).

Seasonal crop cycle fluxes (over a 74 day measurement period) were determined for CO_2, CH_4 and N_2O for each automated and manual chamber. Manual and concurrent automated fluxes were multiplied by 24 to obtain a daily flux, while all automated hourly fluxes were summed over the entire 74 day sampling period. Missing data were linearly interpolated between sample points for both manual and automated fluxes. A crop cycle sum was determined for each manual (n = 6) and each automated chamber (n = 5) and plotted in Fig. 6d–f. Up-scaling of the manual measurements to seasonal estimates lead to a greater range of seasonal crop estimates compared to the automated data. When calculating the manual seasonal estimates, fluxes were linearly interpolated between sample points. Because each manual chamber measurement affected the interpolated estimate for a 2–3 day period when calculating seasonal sums (see dotted lines in Fig. 5), the seasonal estimates from the manual method were clearly more strongly affected by the few "hot spots" and "hot moments" among manually sampled chambers. Although the range of variation in measured fluxes using the automated and manual system was similar across the entire season, any individual "hot spot" and "hot moment" flux had less influence on the overall seasonal estimate in the automated measurement dataset because it was used to represent only one hour of emissions.

Comparison of manual and automated measurements indicates that there is considerable heterogeneity in GHG fluxes both spatially ("hot spots") and temporally ("hot moments"). Ideally, a measurement system would include a few automated chambers with high temporal resolution of measurements and many more, less frequently sampled manual chambers to assess spatial variation.

3.7 Diel trends in GHG fluxes

Diel model fits were observed for N_2O and CO_2 fluxes (Fig. 7) with peak fluxes ranged between 2 p.m. and 5 p.m., a similar range in time observed for peak air and soil temperature (Fig. 7d). This indicates that N_2O and CO_2 fluxes closely followed diel temper-

BGD
10, 18277–18308, 2013

ature patterns. In both cases, covariation of soil microbial activity with soil temperature is the most parsimonious explanation, although diel patterns of root activity cannot be ruled out for CO_2 (Savage et al., 2013). There was a small diel pattern in CH_4 uptake rates (Fig. 7), with an average of 1 µg C $m^{-2} hr^{-1}$ (amplitude) between morning and evening time periods, and the highest rate of CH_4 uptake occurring when soils were warmest. The small diel amplitude for CH_4 fluxes indicates methanotrophic activity may not be as sensitive to changes in temperature at this time scale as is the microbial activity that produces N_2O and CO_2.

The mean daily flux, calculated from the model fits, occurred between 9 and 10 a.m., which coincides with the timeframe (9 a.m. to noon) that manual samples are collected in ND. This indicates that the manual sampling technique and sampling timeframe utilized in ND is representative of the daily mean flux.

4 Conclusions

The new QCLAS system was integrated in-line with an existing automated system for measuring soil CO_2 flux. The response time and sensitive measurements of N_2O and CH_4 provides confidence in the measurement of small changes in chamber headspace concentrations of both gases over a short period of time, thus reducing the time needed per flux measurement, increasing the frequency which sampling can occur, and reducing artifacts or modified soil concentration gradients. In the case of N_2O, the higher sensitivity and improved precision of measurements conferred confidence that the measurement of N_2O consumption in a forested wetland was significantly different from zero flux. Diel patterns, linked to diel temperature patterns were demonstrated with the automated system for all GHG fluxes. Manually sampling at a time of day typical of the daily mean flux and at a sampling frequency of three times per week during the growing season captured transient responses of GHG's to precipitation events. However, the influence of "hot spots" and "hot moments", particularly on N_2O fluxes, has a substantial influence when up-scaling. A combination of high frequency automated measurements

BGD
10, 18277–18308, 2013

and spatially distributed sampling strategy would need to be employed to capture both "hot moments" and "hot spots" respectively. This combination would provide the opportunity to capture and characterize transient responses to rapidly changing environmental conditions and spatial heterogeneity for all three gases, which will be valuable to improve modeling efforts and estimates of annual fluxes of these three important greenhouse gases.

Acknowledgements. The authors are grateful to Mark Zahniser, Dave Nelson and Barry McManus of Aerodyne Research. We would like to thank our colleagues, Holly Hughes, Nicanor Saliendra and Justin Feld.

This work was supported by USDA ARS Integrated Resource Management Project (Project 5445-xx10-001-00D) and by NASA (Grant #NNX11AF20G).

References

Borken, W., Savage, K., Davidson, E. A., and Trumbore, S. E.: Effects of experimental drought on soil respiration and radiocarbon flux from a temperate forest soil, Glob. Change Biol., 12, 177–193, 2006.

Chapuis-Lardy, L., Wrage, N., Metay, A., Chotte, J.-L. and Bernoux, M.: Soils, a sink for N_2O?, A review, Glob. Change Biol., 13, 1–17, 2007.

Davidson, E. A.: Pulses of nitric oxide and nitrous oxide flux following wetting of dry soil: an assessment of probable sources and importance relative to annual fluxes, Ecol. Bull., 42, 149–155, 1992.

Davidson, E. A. and Schimel, J. P.: Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane, in: Biogenic Trace Gases: Measuring Emissions from Soil and Water, edited by: Matson, P. A. and Harriss, R. C., Blackwell Science, Oxford, 327–357, 1995.

Davidson, E. A. and Trumbore, S. E.: Gas diffusivity and production of CO_2 in deep soils of the eastern Amazon, Tellus B, 47, 550–565, 1995.

Davidson, E. A., Savage, K., Verchot, L. V., and Navarro, R. I.: Minimizing artifacts and biases in chamber-based measurements of soil respiration, Agr. Forest Meteorol., 113, 21–37, 2002.

BGD
10, 18277–18308, 2013

Davidson, E. A., Richardson, A. D., Savage, K. E., and Hollinger, D. Y.: A distinct seasonal pattern of the ratio of soil respiration to total ecosystem respiration in a spruce-dominated forest, Glob. Change Biol., 12, 230–239, 2006.

Davidson, E. A., Nepstad, D. C., Ishida, F. Y., and Bando, P. M.: Effects of an experimental drought and recovery on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest, Glob. Change Biol., 14, 2582–2590, 2008.

Fernandez, I. J., Rustad, L. E., and Lawrence, G. B.: Estimating total soil mass, nutrient content and trace metals in soils under a low elevation spruce-fir forest, Can. J. Soil Sci., 73, 317–328, 1993.

Firestone, M. K. and Davidson, E. A.: Microbiological basis of NO and N_2O production and consumption in soil, in: Exchange of trace gases between terrestrial ecosystems and the atmosphere, edited by: Andreae, M. O. and Schimel, D. S., John Wiley & Sons, New York, 7–21, 1989.

Frasier, R., Ullah, S., and Moore, T. R.: Nitrous oxide consumption potential of well-drained forest soils in southern Quebec, Geomicrobiol. J., 27, 53–60, 2010.

Levine, E. R., Knox, R. G., and Lawrence, W. T.: Relationships between soil properties and vegetation at the Northern Experimental Forest, Howland, Maine, Remote Sens. Environ., 47, 231–241, 1994.

Nelson, D. D., McManus, B., Urbanski, S., Herndon, S., and Zahniser, M. S.: High precision measurements of atmospheric nitrous oxide and methane using thermoelectrically cooled mid-infrared quantum cascade lasers and detectors, Spectrochim. Acta A, 60, 3325–3335, 2004.

Parkin, T. B., Venterea, R. T., and Hargreaves, S. K.: Calculating the detection limits of chamber-based soil greenhouse gas flux measurements, J. Environ. Qual., 41, 705–715, doi:10.2134/jeq2011.0394, 2012.

Phillips, R. L., Tanaka, D., Archer, D., and Hanson, J.: Fertilizer application timing influences greenhouse gas fluxes over a growing season, J. Environ. Qual., 38, 1569–1579, 2009.

Savage, K. E. and Davidson, E. A.: A comparison of manual and automated systems for soil CO_2 flux measurements: trade-offs between spatial and temporal resolution, J. Exp. Bot., 54, 891–899, 2003.

Savage, K., Davidson, E., and Richardson, A. D.: A conceptual and practical approach to data quality and analysis procedures for high-frequency soil respiration measurements, Funct. Ecol., 22, 1000–1007, 2008.

BGD
10, 18277–18308, 2013

Savage, K., Davidson, E. A., Richardson, A. D., and Hollinger, D. Y.: Three scales of temporal resolution from automated soil respiration measurements, Ag. For. Met., 149, 2012–2021, 2009.
Savage, K., Davidson, E. A., and Tang, J.: Diel patterns of autotrophic and heterotrophic respiration among phenological stages, Glob. Change Biol., 19, 1151–1159, 2013.
Schlesinger, W.: An estimate of the global sink for nitrous oxide in soils, Glob. Change Biol., 19, 2929–2931, doi:10.1111/gcb.12239, 2013.
Soil Survey Staff: Official soil series description, USDA Washington, DC, available at: http://soils.usda.gov/technical/classification/osd/index.html (last access: 24 April 2009), 2008.
Ullah, S. and Moore, T. R.: Biogeochemical controls on methane, nitrous oxide, and carbon dioxide fluxes from deciduous forest soils in eastern Canada, JGR, 116, G03010, doi:10.1029/2010JG001525, 2011.
Verchot, L. V., Davidson, E. A., Cattânio, J. H., Ackerman, I. L., Erickson, H. E., and Keller, M.: Land use change and biogeochemical controls of nitrogen oxide emissions from soils in eastern Amazonia, Global Biogeochem. Cy., 13, 31–46, 1999.
Verchot, L. V., Davidson, E. A., Cattânio, J. H., and Ackerman, I. L.: Land-use change and biogeochemical controls of methane fluxes in soils of eastern Amazonia, Ecosystems, 3,41–56, 2000.

BGD
10, 18277–18308, 2013

Table 1. Comparison of QCLAS gas concentrations with NOAA high precision calibration standards.

	QCLAS (ppb)	NOAA calibration standards (ppb)	% Difference
N_2O-calibration gas	353.24 (*0.04*)	353.63 *(0.15)*	−0.11 %
N_2O-calibration gas	305.41 (*0.04*)	307.29 *(0.11)*	−0.61 %
CH_4-calibration gas	2116.27 (*0.31*)	1975.02 *(0.30)*	7.1 %
CH_4-calibration gas	1764.63 (*0.26*)	1644.15 *(0.30)*	7.3 %

QCLAS data – mean (*stdev)* (n = 60).
Calibration gas are high precision calibration gas standards. Values represent the average measurement and *(stdev)* represents the repeatability of a single calibration.

BGD
10, 18277–18308, 2013

Table 2. Nomenclature.

QCLAS	Quantum Cascade Laser Absorption Spectrometer
GC	Gas Chromatography

BGD
10, 18277–18308, 2013

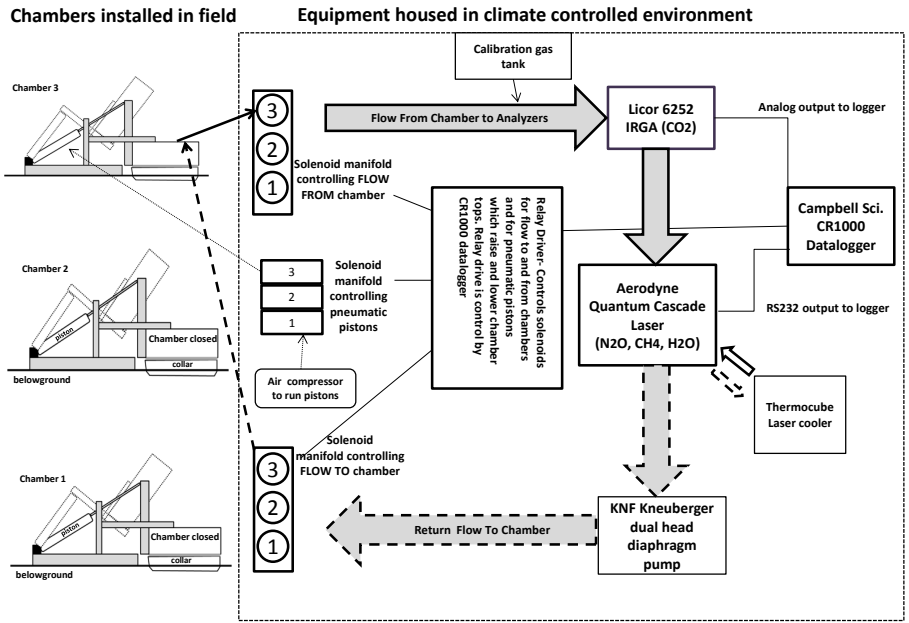

Fig. 1. Schematic of 3 chambers and automated sampling system (diagram is not to scale). Solid grey arrows show flow coming FROM closed chamber #3 to IRGA, then QCLAS. The dashed grey arrows are return flow via the diaphragm pump and BACK TO closed chamber #3. Thermocube dashed lines indicate flow of 25 % ethanol to the QCLAS and back to the cool laser. The three chambers on the left show the chamber tops in the closed position, with a shadow effect showing what the chambers would look like in an open position. Only one chamber is in the closed position at any one time. All the equipment within the dashed square is housed in an environmentally protected, temperature controlled enclosure.

BGD
10, 18277–18308, 2013

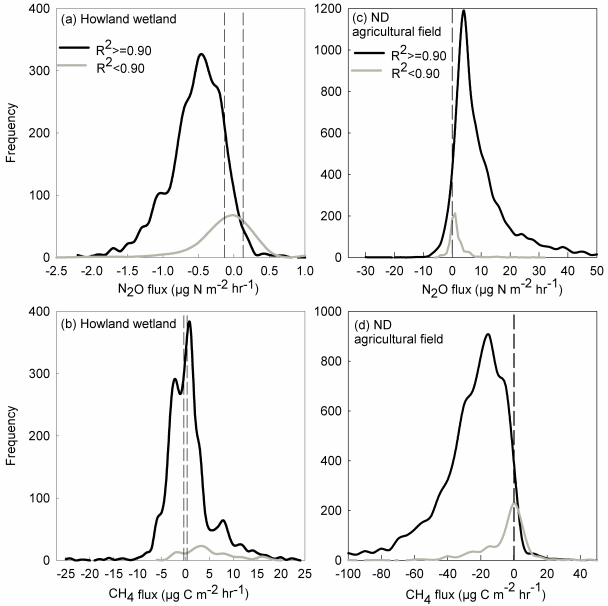

Fig. 2. Frequency distribution of automated N_2O and CH_4 fluxes for Howland wetland and North Dakota agricultural field, stratified by criteria of whether simultaneous CO_2 flux measurements were of high quality. When the R^2 values of the linear regression of the simultaneous CO_2 flux measurements were < 0.9, then it is assumed that the chambers did not function properly and that measurements of all three gas fluxes were unreliable. When the R^2 values of the linear regression of the simultaneous CO_2 flux measurements were > 0.9, it is assumed that the N_2O and CH_4 flux measurements are also reliable, including those that are below the detection limit (i.e., not significantly different from a flux of zero). Dashed lines indicate minimum detectable flux range calculated by the Parkin method (Sect. 3.1) for each gas. A total of ≈ 7400 fluxes for each GHG were measured in North Dakota and ≈ 3000 fluxes for each GHG in Howland Forest.

BGD
10, 18277–18308, 2013

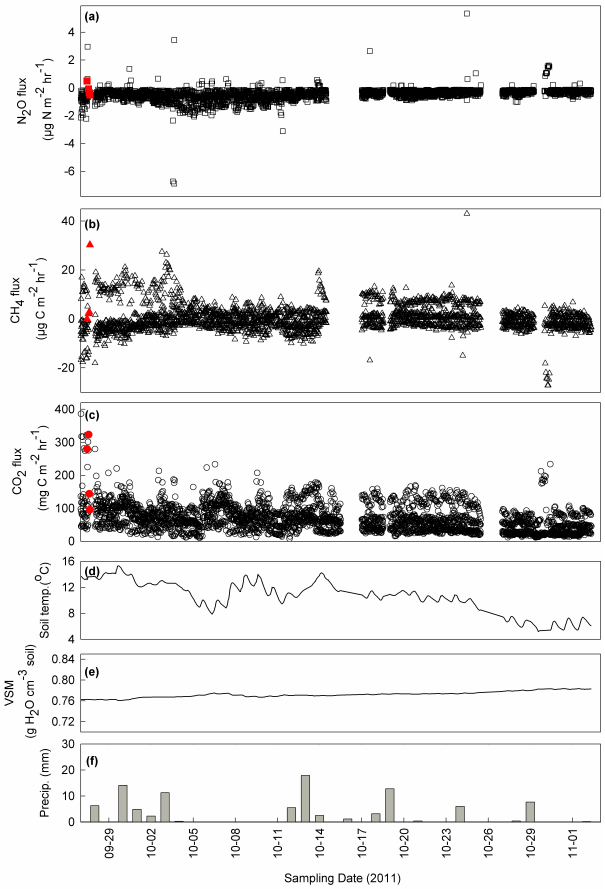

Fig. 3. Howland Forest wetland data: **(a)** N_2O flux, **(b)** CH_4 flux, **(c)** CO_2 flux, **(d)** soil temperature at 10 cm depth, **(d)** VSM = volumetric soil moisture at 10 cm, **(e)** daily precipitation. Open black symbols are automated fluxes (five chambers); solid red symbols are manual fluxes (four chambers).

BGD
10, 18277–18308, 2013

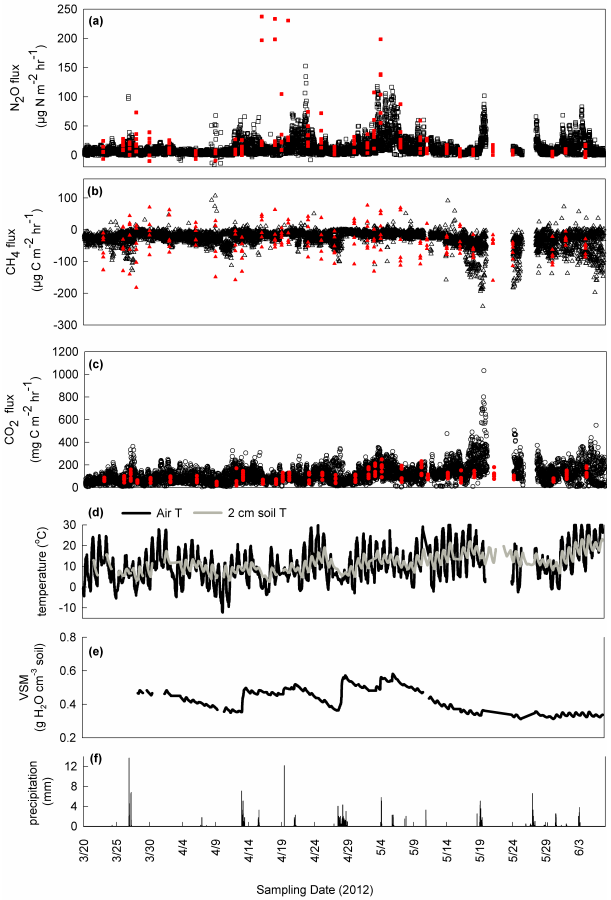

Fig. 4. ND alfalfa field: **(a)** N_2O flux, **(b)** CH_4 flux, **(c)** CO_2 flux, **(d)** temperature, **(e)** VSM = volumetric soil moisture, **(f)** precipitation. Open black symbols are automated fluxes (five chambers); solid red symbols are manual fluxes (six chambers).

BGD
10, 18277–18308, 2013

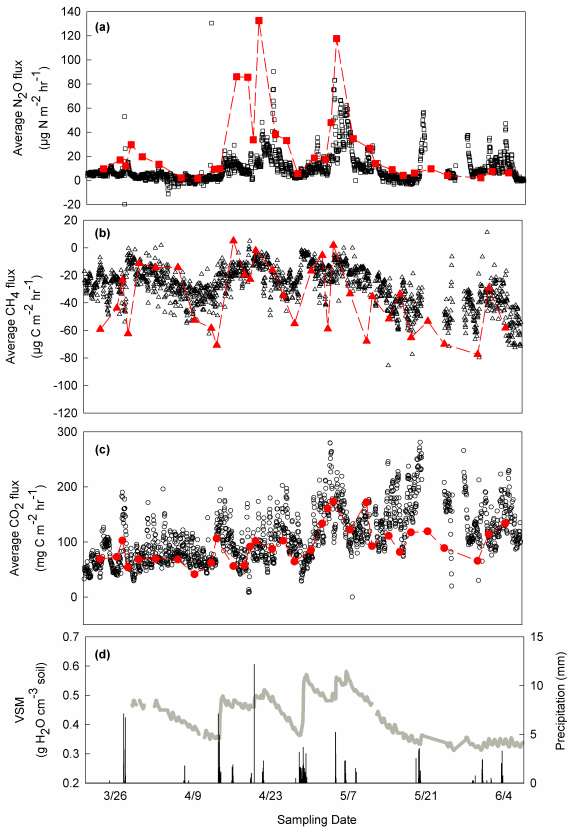

Fig. 5. Hourly averaged fluxes for automated (black symbols, $n = 5\,h^{-1}$) and manual (red symbols, $n = 6\,h^{-1}$) measurements. **(a)** N_2O, **(b)** CH_4, **(c)** CO_2 flux. **(d)** Solid gray line is volumetric soil moisture and bars are hourly precipitation. Dotted lines connect the manual chamber flux measurement symbols in order to illustrate how interpolation between measurement dates affects the ND seasonal sum estimate (see text).

BGD
10, 18277–18308, 2013

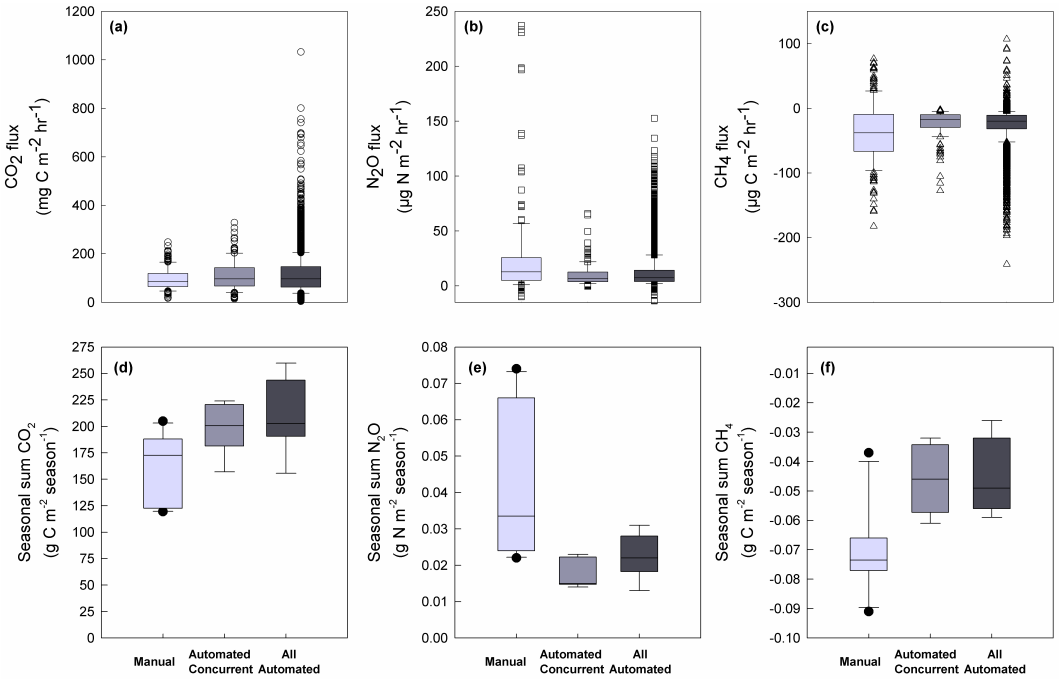

Fig. 6. Caption on next page.

BGD
10, 18277–18308, 2013

Fig. 6. Box plots of individual fluxes measured in ND using the manual and automated methods. Data show manual samples (light gray), automated measurements concurrent to manual samples (dark grey) and all automated data (black). **(a)** CO_2 flux, **(b)** N_2O flux and **(c)** CH_4 flux, $n = 136$ for manual and concurrent automated fluxes and $n \approx 7400$ for all automated fluxes. Seasonal crop cycle sum (74 days) of **(d)** CO_2, **(e)** N_2O and **(f)** CH_4. Manual and concurrent sums are interpolated and summed over the 74 days for each chamber, and all automated seasonal estimates are summed at an hourly timescale for the 74 day period for each chamber. The means and variance for seasonal sum estimates are based on $n = 6$ manual chambers and $n = 5$ automated chambers.

BGD
10, 18277–18308, 2013

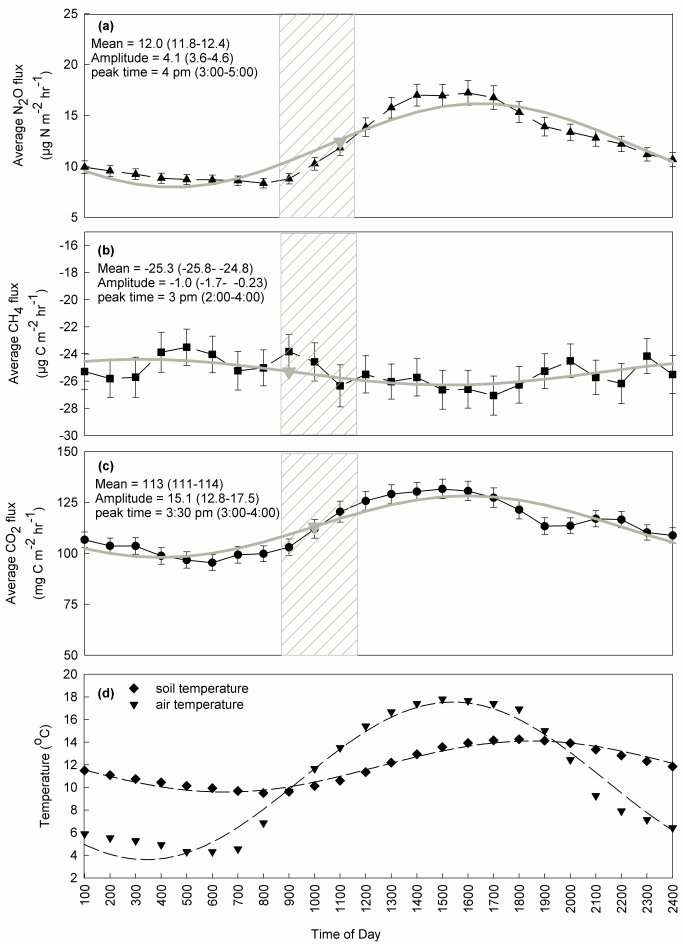

Fig. 7. Caption on next page.

BGD
10, 18277–18308, 2013

Fig. 7. Diel trends from automated measurements of, **(a)** N_2O, **(b)** CH_4, **(c)** CO_2, **(d)** soil temperature at 2 cm and air temperature, for one alfalfa crop cycle. Symbols are the average and standard errors of hourly fluxes rates per GHG. Grey line is the diel sinewave fit to all data. Grey symbols are the average flux rate for fitted trend and the grey cross hatch area denotes the time of day manual samples are measured. Diel trends in soil and air temperature are averages per hour.

BGD
10, 18277–18308, 2013