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Short-term drought response of N₂O and CO₂ emissions from mesic agricultural soils in the US Midwest



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ABSTRACT

Climate change is causing the intensification of both rainfall and droughts in temperate climatic zones, which will affect soil drying and rewetting cycles and associated processes such as soil greenhouse gas (GHG) fluxes. We investigated the effect of soil rewetting following a prolonged natural drought on soil emissions of nitrous oxide (N₂O) and carbon dioxide (CO₂) in an agricultural field recently converted from 22 years in the USDA Conservation Reserve Program (CRP). We compared responses to those in a similarly managed field with no CRP history and to a CRP reference field. We additionally compared soil GHG emissions measured by static flux chambers with off-site laboratory analysis versus in situ analysis using a portable quantum cascade laser and infrared gas analyzer. Under growing season drought conditions, average soil N₂O fluxes ranged between 0.2 and 0.8 μ g N m⁻² min⁻¹ and were higher in former CRP soils and unaffected by nitrogen (N) fertilization. After 18 days of drought, a 50 mm rewetting event increased N₂O fluxes by 34 and 24 fold respectively in the former CRP and non-CRP soils. Average soil CO₂ emissions during drought ranged from 1.1 to 3.1 mg C m⁻² min⁻¹ for the three systems. CO₂ emissions increased ~ 2 fold after the rewetting and were higher from soils with higher C contents. Observations are consistent with the hypothesis that during drought soil N₂O emissions are controlled by available C and following rewetting additionally influenced by N availability, whereas soil CO₂ emissions are independent of short-term N availability. Finally, soil GHG emissions estimated by off-site and in situ methods were statistically identical.

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1. Introduction

Future climate change is predicted to have large effects on water cycling and availability, with overall intensification of both rainfall and droughts (Betts et al., 2007; Durack et al., 2012). Rewetting of soils after droughts and especially the first rain event after a drought can have a large effect on soil GHG emissions (e.g., Bergsma et al., 2002; Xu et al., 2004; Kim et al., 2012). Rewetting dry soils typically induces large fluxes of both N₂O and CO₂ during laboratory incubations of soils from seasonally-dry, semi-arid, and some temperate climates (Birch, 1958; Prieme and Christensen,

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2001; Mikha et al., 2005; Beare et al., 2009; Borken and Matzner, 2009).

Field studies of GHG drought responses are less common, and most have been performed in semi-arid or seasonally dry soils (i.e., Hao et al., 1988; Davidson, 1992; Garcia-Monteil et al., 2003; Barton et al., 2008) and show a strong overall increase in soil GHG emissions on rewetting (reviewed by Austin et al., 2004; Kim et al., 2012). The few studies of soils in mesic climates show mixed results, with an increase of GHG fluxes in Wales gully mire soils (e.g., Dowrick et al., 1999), an increase in intensively managed pastures (Kim et al., 2010), an increase in sandy-loam arable soils (Jørgensen et al., 1998), and no effect or a decrease in GHG fluxes in Danish heathland (e.g., Larsen et al., 2011).

Studies of the effect of rewetting on soil GHG emissions from mesic agricultural sites are even more scarce. Hernandez-Ramirez et al. (2009) showed in laboratory incubations that agricultural soils receiving repeated manure application may be prone to higher N₂O emissions on rewetting than soils receiving chemical

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fertilizers. Ruser et al. (2006) showed in a laboratory incubation the importance of carbon availability for soil N₂O flux during rewetting of nitrate-fertilized agricultural soils. Denmead et al. (2010) found that frequent wetting and high carbon contents were main factors affecting soil N₂O fluxes from rewetted Australian sugarcane soils.

Here we use a naturally occurring drought in the US Midwest to investigate the effect of rewetting on in situ soil N₂O and CO₂ emissions in two fertilized no-till agricultural sites with different land-use histories. One site was recently converted from 22 years in the USDA CRP, with correspondingly high soil C contents. A second site had been farmed continuously over this period. And a third site was still in a CRP grassland. Our objective is to examine the hypothesis that during drought soil N₂O emissions are modulated by soil C and after rewetting additionally influenced by N availability, whereas CO₂ emissions are independent of shortterm N availability. We additionally used the static chamber method to compare a newly developed quantum cascade laser technique for measuring in situ N₂O fluxes vs. the standard off-site gas-chromatography method.

2. Methods

2.1. Study site and soil properties

The experiment was conducted at the Great Lakes Bioenergy Research Center (GLBRC; http://glbrc.org/) Michigan field site, part of the Kellogg Biological Station Long-term Ecological Research (LTER) site (KBS; lter.kbs.msu.edu) in southwest Michigan USA (42°24'N, 85°24'W, 288 m asl). The mean annual air temperature at KBS is 10.1 °C, ranging from a monthly mean of -9.4 °C in January to 28.9 °C in July. Annual rainfall averages 1027 mm yr⁻¹, evenly distributed seasonally; potential evapotranspiration exceeds precipitation for about four months of the year. The soils are well-drained Typic Hapludalfs that developed on glacial outwash (Robertson and Hamilton, 2015) of the co-mingled soil series Boyer loamy sand, Kalamazoo loam, and Osthemo sandy loam (Bhardwaj et al., 2011).

The experiments were conducted on three fields, two under continuous no-till corn (*Zea mays*) management (AGR; 11 ha and CRP; 19.5 ha) and a third reference site (REF; 9 ha) under perennial smooth brome grass (*Bromus inermis* L.) managed as CRP land (www.fsa.usda.gov/FSA) for the last 25 years. The two agricultural sites differed in land-use history. The AGR site was under a corn—soybean (*Glycine max* (L.) Merr) rotation for at least a few decades before conversion to continuous no-till corn in 2010. The former CRP site was converted from CRP grassland in 2009 and managed as continuous no-till corn since 2010 (Gelfand et al., 2011; Zenone et al., 2013). The fields also differed in soil C and total N contents, extractable nitrate (NO₃⁻) pools, pH, and productivity (Table 1).

Soil temperature (T_{soil}) at three depths (-2, -5, and -10 cm) and volumetric water content (VWC, 0-30 cm) were measured continuously at each site by CS 107 and CS 616 sensors, respectively (Campbell Scientific, Inc., UT, USA).

2.2. Soil GHG emission measurements, flux calculations, and techniques comparison

To measure soil GHG fluxes we used the static chamber method (Holland et al., 1999) modified for our site (http://lter.kbs.msu.edu/ protocols/113). In May 2012, eight pairs of stainless steel cylindrical chambers (28.5 cm I.D. and 25 cm high) equipped with a vent for pressure equilibration were installed in each field along 50 m transects, at least 5 m apart, and inserted to a ~5 cm soil depth. At the agricultural sites pairs of chambers were installed between the adjacent corn rows avoiding areas with tractor tracks; in the REF site paired chambers were installed 20–30 cm apart. There was no vegetation inside chambers at the agricultural sites; in the REF site the brome grass was low when chambers were installed and was clipped towards the end of the experiment as needed for lid placement.

Soil GHG fluxes were measured from each pair of chambers using two measurement techniques. The first technique, hereafter denoted as "GC off site," is based on taking headspace gas samples (10 ml) every 10-15 mins over a 40-60 mins closure period while the chamber is covered with a gas-tight lid, for a total of 4 samples per closure. The samples were stored over-pressurized in glass vials and analyzed for N₂O and CO₂ concentrations in the laboratory using a gas chromatograph (7890A Agilent Technologies Inc., DE, USA) equipped with an ECD for N₂O and an infrared gas absorption analyzer (LI-820, LI-COR, NE, USA) for CO₂ analyses (http://lter.kbs.msu.edu/protocols/113). The second technique, hereafter denoted as "QCL in situ," is based on field analysis using a closed-path quantum cascade laser (QCL) analyzer ($N_2O/CO-23d$; Los Gatos Research Inc., CA, USA) for measurements of N₂O concentrations and a closed-path infrared gas analyzer (LI-7000, LI-COR, NE, USA) for measurements of CO₂ concentrations. During the measurement period, the headspace air inside each chamber was circulated through the QCL analyzer for $\sim 5 \text{ mins}$ and gas concentrations were analyzed at 2 s intervals with results stored in a data logger.

Soil fluxes of N₂O and CO₂ were calculated as the changing rate in gas concentration in the chamber headspace over the incubation period corrected for ambient air temperature. For direct comparison of the GC off site and QCL in situ techniques, a total of 54 individual field measurements were conducted across a variety of soil temperature and moisture conditions. We performed two types of measurements using the same chamber. For the first comparison we covered individual chambers with gas-tight lids with 3 sampling ports, one port for syringe sampling for the GC off-

Table 1

Soil properties and aboveground productivity in two agricultural systems with different land-use histories: former CRP grassland (CRP) and former agricultural (AGR) sites, and a reference (REF) grassland.

System	Bulk density ^a (Mg m ⁻³)	рН ^а	C (g kg ⁻¹)	N	$\begin{array}{l} \text{ANPP}^{\text{b}} \\ (\text{g}\text{m}^{-2}\text{yr}^{-1}) \end{array}$	NO3 ⁻ pool ^c (μgNg ⁻¹)	Fertilization ^d (kg ha ⁻¹)
CRP	1.5 (0.1)	5.7 (0.1)	30.9 (7.7)	2.8 (0.7)	681 (61)	2.7 (0.3)/14.3 (2.7)	218
AGR	1.6 (0.1)	5.9 (0.1)	14.3 (3.0)	1.3 (0.2)	628 (84)	2.9 (0.7)/8.3 (2.0)	218
REF	1.5 (0.1)	6.1 (0.0)	30.6 (8.3)	2.7 (0.6)	341 (42)	0.9 (0.1)/1.4 (0.2)	0

^a Soil bulk density and total C and N were measured in 2009 in 0–10 cm soil layer of the studied sites (±S.E. *n* = 10). Soil pH (water pH) measured in November 2012 from 0 to 25 cm soil layer.

^b ANPP: Aboveground Net Photosynthetic Productivity (dry matter) measured in October 2012; CRP and AGR were under corn crops.

^c May and November soil pools. Extractable NO₃⁻ were measured using soil samples taken by 2 cm diameter push probe to the depth of 25 cm from ten stations across each field. The extractable NO₃⁻ was measured after KCl extraction using colorimetric method (Robertson et al., 1999)

 $^{
m d}$ Applied as 28% UAN (Urea–Ammonium–Nitrate solution) with ${\sim}40\%$ ammonium nitrate and ${\sim}30\%$ urea.

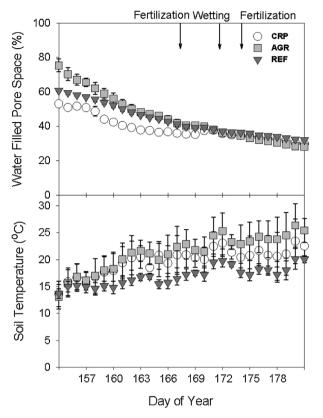


Fig. 1. Daily averages of soil WFPS (0–30 cm layer) and soil temperature (0–20 cm layer). Arrows indicate the timing of management and the artificial rainfall event.

site method and another two ports for continuous sampling by QCL for the QCL in situ method. During methods comparison, we measured head-space concentrations of N_2O and CO_2 continuously by the QCL in situ method and took vial samples from the same chamber for the laboratory GC off site method. For the second comparison, we measured individual chambers with QCL in situ and then, immediately after, by GC off site methods.

Soil GHG emissions were measured at the CRP site between June 4 and June 28, 2012 (Day of Year 156 and 180), at the AGR site between DOY 156 and 174, and at the REF site between DOY 156 and 173. The measurements took place between \sim 7 AM and \sim 8 PM, with randomized sampling across the experimental fields. Each field was sampled in a random order between 1 and 3 times per sampling day. In total we sampled fields during 16 individual days.

During the study period, chambers were removed from the agricultural fields and reinstalled two times: on June 13–16 (DOY 165–168) for fertilization and herbicide application and on June 21–22 (DOY 173–174) for side-dress N fertilization. In both cases at least 12 h elapsed between chamber re-installation and measurements. Chambers at the REF site were left undisturbed throughout the study period.

2.3. QCL instrument details

The QCL analyzer used off-axis integrated cavity output spectroscopy to provide high precision, in situ measurements of N_2O concentrations without a need to cool down the laser beam with liquid nitrogen or other coolants. The QCL analyzer has a precision of 0.1 ppb in 1 s with a measurement frequency of up to 10 Hz. The measurement range for N_2O is 1–4000 ppb, which is suitable for soil flux measurement with a short chamber closure time. The analyzer is stable within a temperature range of 10–

 $35 \,^{\circ}$ C. For field measurements we connected the analyzer to chambers by Teflon tubing.

2.4. Agricultural management, productivity, and water addition experiment

The agricultural fields were managed according to farming practices in the area. Nitrogen fertilizer was applied to both agricultural sites as 28% UAN (Urea–Ammonium–Nitrate solution) with ~40% ammonium nitrate and ~30% urea at rates of 35 kg N ha⁻¹ at planting (~DOY 121), 135 kg N ha⁻¹ on DOY 166, and 48 kg N ha⁻¹ on DOY 174 for a total of 218 kg N ha⁻¹ applied by injecting liquid fertilizer into soil between the corn rows to a depth of ~15 cm. The REF site was not fertilized.

To examine the effect of a rain event on soil GHG emissions, we added 50 mm (50 Lm^{-2}) of water at all three sites at night between DOY 171 and 172. Water was added by sprinkling an area of 0.5 m^2 per chamber over several minutes for a total of 8 pairs of chambers per site. Rain events of 50 mm are not uncommon in the region: during the past 25 years, rain events of similar magnitude occurred at least once in more than 50% of the years, and more than once in 30% of the years (http://lter.kbs.msu.edu/datatables/7). Likewise, the probability of rain events with rain intensity between 66 and 112 mm h⁻¹ is one per 25 years within a 90% confidence interval (http://hdsc.nws.noaa.gov/hdsc/pfds/pfds_map_cont.html?

bkmrk=mi). The intensity of the rain would affect effective rewetting and runoff from fields. In the present study no runoff during water addition was observed and all applied water penetrated the soils. Therefore, while our artificial rain event was relatively intensive no observable runoff occurred during the water addition.

Measurements of soil GHG emissions were taken during the two days following wetting at all sites. Soil volumetric water content (VWC) before and after the wetting events was measured by a CS HS2 portable sensor in the 0–12 cm soil layer (Campbell Scientific, Inc., UT USA). Then we used field bulk densities to calculate water filled pore space (WFPS):

$$\mathsf{WFPS}(\%) = \left(P_{\mathsf{W}} \times \frac{D_{\mathsf{b}}}{S_{\mathsf{t}}}\right) \times 100$$

where: P_w is water content (ml water g^{-1} soil). D_b is bulk density (g cm⁻³), and S_t is total porosity (%) (Dane and Topp, 2002).

Aboveground net primary productivity (ANPP) was measured by hand harvesting plants from 1 m^2 quadrats at 10 locations per field across all fields in October 2012.

2.5. Statistical analysis

The data analysis was conducted in PROC MIXED (SAS Institute Inc, 2009). The flux data for each date was analyzed separately. The statistical model for the analysis included the fixed effect of systems (CRP, AGR, and REF), and the random effect of individual chamber nested within the systems on those dates when more than one flux measurements were obtained from each chamber. The assumption of normality of the residuals was tested by examining normal probability plots and stem-and-leaf plots of the residuals. The homogeneity of variances assumption was assessed visually by examining the side-by-side box plots and checked using Levene's test for equal variances. When necessary, the analysis with unequal variances was performed using "repeated/group=" statement of PROC MIXED. Multiple comparisons among the treatment means were conducted using *t*-tests when the effect of the treatments was found to be statistically significant at 0.05 level.

Due to high inter-chamber variability we are presenting results from individual chambers rather then averages. However, for calculation of relative response to wetting we calculated an

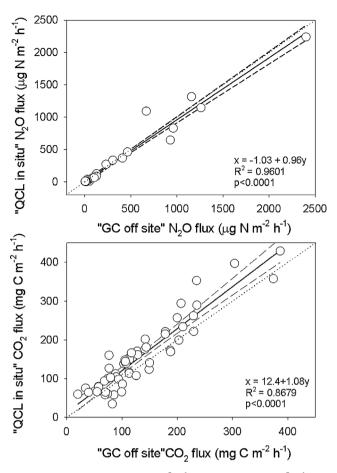


Fig. 2. Comparison of (a) N₂O–N (μ g m⁻²h⁻¹) and (b) CO₂–C (mg m⁻²h⁻¹) fluxes measured from the same chambers by "QCL in situ" and "GC off site" techniques (solid line; 54 individual chamber/incubations) during field incubations. The dotted line represents a 1:1 relationship; the dashed line represents the 95% confidence interval.

average and cumulative soil GHG emissions using a linear interpolation between individual measurement times. For the linear interpolation we used an hourly time step, consistent with the measurements.

For the comparison between "GC off site" and "QCL in situ" we performed regression analysis using SigmaPlot 11 software (Systat Software, Inc.).

3. Results

3.1. Weather

During the study period the weather was hot (air temperatures up to 35 °C) and dry, with only three rain events, each less than 1 mm (<1 L m⁻²), on DOY 168, 169, and 170. During these events the rain did not penetrate the soil surface more than 1 mm and had no effect on WFPS (Fig. 1). Soil temperature continuously increased over the study period, reaching more than 25 °C at 0–20 cm depth (Fig. 1) between DOY 170 and 180. Soil temperatures were lower and less variable at the REF site than at the agricultural sites, where they exhibited high diurnal variability with a range of >10 °C (Fig. 1).

3.2. Comparison of "QCL in situ" and "GC off site" techniques

The two techniques were well correlated, with an R^2 of 0.96 and 0.87 for N₂O and CO₂ fluxes, respectively (Fig. 2a,b). Cumulative

fluxes of N_2O and CO_2 , calculated by linear interpolation between individual measurement points for each method independently, were very similar as well, ranging from 4.8 ± 0.3 to 117.0 ± 30.6 mg N_2O-N m $^{-2}~$ and $~29.5\pm3.0~$ to $~82.8\pm4.1$ g $~CO_2-C$ m $^{-2}~$ across systems (Table 2).

3.2. Soil GHG emissions

Soil emissions of N₂O during the rainless dry period (DOY 154– DOY 170; Fig. 3) at REF and AGR sites were almost four times lower than soil N₂O emissions from the former CRP site: 0.2 ± 0.0 , 0.2 ± 0.0 and $0.8 \pm 0.1 \,\mu g \, N_2 O - N \, m^{-2} \, min^{-1}$, for REF, AGR, and CRP sites, respectively (Table 3). Fertilization of the agricultural sites at a rate of ~135 kg N ha⁻¹ with 28% UAN solution had no effect on soil N₂O emissions during this time (Fig. 3).

Soil emissions of CO₂ during the same period were lowest at the AGR site, intermediate at the former CRP site, and highest at the REF site, and ranged from 1.1 ± 0.1 to 1.9 ± 0.1 to 3.1 ± 0.1 mg CO₂-C m⁻² min⁻¹, respectively (Table 3).

After the artificial rain event all sites exhibited a sharp increase in soil WFPS and GHG fluxes (Table 3). The overall effect of a single wetting event was a 3 to 34 fold increase in N₂O emissions across the study sites (Table 4). Average soil N₂O fluxes after wetting ranged from $0.6 \pm 0.1 \ \mu g \ N_2 O - N \ m^{-2} \ min^{-1}$ at the REF site to $27.6 \pm 6.3 \ \mu g \ N_2 O - N \ m^{-2} \ min^{-1}$ at the former CRP site, with the AGR site having intermediate fluxes of $4.8 \pm 1.7 \ \mu g \ N_2 O - N \ m^{-2} \ min^{-1}$ (Table 3).

Soil CO₂ fluxes also increased with wetting, although with a smaller magnitude than N₂O fluxes, undergoing 1.4, 1.6, and 2.2 fold increases at the CRP, REF, and AGR sites, respectively (Table 3). After wetting, CO₂ fluxes ranged from 2.4 ± 0.2 to 2.8 ± 0.2 to 5.0 ± 0.3 mg CO₂-C m⁻² min⁻¹ for AGR, CRP, and REF sites, respectively (Table 3).

After the rewetted soils dried to pre-wetting WFPS (DOY 175), soil GHG emissions at the former CRP site returned to pre-wetting levels of $0.8 \pm 0.2 \ \mu g N m^{-2} min^{-1}$ and $2.3 \pm 0.1 mg C m^{-2} min^{-1}$ for N₂O and CO₂, respectively, despite additional fertilization with 48 kg N ha⁻¹ on DOY 173 and higher soil temperatures than earlier (Table 2, Figs. 1 and 3). Overall, soil N₂O emissions were highest at the former CRP site, intermediate at the AGR site, and lowest at the REF site, while soil CO₂ emissions were highest at the REF site, intermediate at the former CRP site, and lowest at the AGR site (Table S1).

Cumulative fluxes of N₂O were 4.8 ± 0.3 , 13.0 ± 3.6 , and 117.0 ± 30.6 mg N₂O–N m⁻² for the REF, AGR, and CRP sites, respectively during the study period. The CO₂ fluxes followed the opposite order with the highest fluxes of 73.9 ± 2.2 g CO₂–C m⁻² at the REF site and the lowest fluxes of 29.7 ± 2.1 g CO₂–C m⁻² at the AGR site (Table 2; "GC off site" column).

4. Discussion

Our results demonstrate that rewetting fertilized agricultural soils after a short-term drought in a temperate mesic climate can

Table 2

Cumulative fluxes of CO₂–C (gm⁻²) and N₂O–N (mgm⁻²) between DOY 156 and DOY 173 from the study sites, calculated by linear interpolation from measurements by static chambers method by "GC off site" and "QCL in situ" techniques. Linear interpolation was performed on an hourly basis (±S.E. n=8 chambers).

System	N ₂ O-N		CO ₂ -C		
	"GC off site"	"QCL in situ"	"GC off site"	"QCL in situ"	
	(៣៛	g m ⁻²)	$(g m^{-2})$		
CRP	117.0 (30.6)	122.9 (41.1)	59.1 (2.5)	55.4 (3.3)	
AGR	13.0 (3.6)	9.6 (3.4)	29.7 (2.1)	29.5 (3.0)	
REF	4.8 (0.3)	4.8 (1.0)	73.9 (2.2)	82.8 (4.1)	

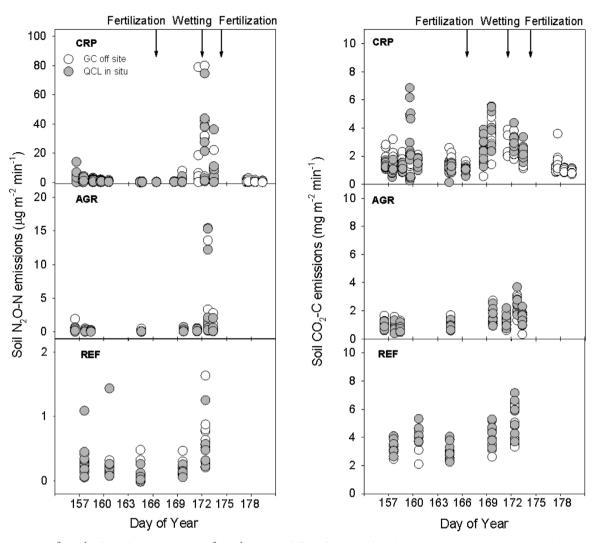


Fig. 3. Soil N₂O-N (µg m⁻²min⁻¹; left panel) and CO₂-C (mg m⁻²min⁻¹; right panel) fluxes from individual chambers measured over the study period. Note that the *y*-axis scale changes between different panels. Arrows indicate the timing of management and the artificial rainfall event.

have a large effect on soil GHG emissions, comparable to those in semi-arid climates where soils experience longer droughts. Our observations are consistent with the hypothesis that the magnitude of soil N_2O emissions are controlled by available C and

following rewetting additionally influenced by N availability, whereas soil CO_2 emissions are independent of short-term N availability.

Table 3

Average soil fluxes of CO_2-C (mg m⁻²min⁻¹) and N₂O-N (μ g m⁻²min⁻¹) before the wetting event (Dry, DOY 154–DOY 170), immediately after the wetting event (Wet, DOY 171–DOY 174), and after complete drying of the soils (Post-Wet, DOY 177–DOY 179) (mean \pm S.E., n = 14–16 chambers).

Period	System	N_2O-N^a (µg m ⁻² min ⁻¹)	CO_2-C^a (mg m ⁻² min ⁻¹)	WFPS ^b (%)
Dry	CRP	0.8 (0.1)	1.9 (0.2)	26.9 (2.3)
•	AGR	0.2 (0.0)	1.1 (0.1)	24.4 (2.0)
	REF	0.2 (0.0)	3.1 (0.1)	8.6 (0.5)
Wet	CRP	27.6 (6.3)	2.8 (0.2)	44.0 (4.0)
	AGR	4.8 (1.7)	2.4 (0.2)	51.9 (1.9)
	REF	0.6 (0.1)	5.0 (0.3)	31.6 (2.0)
Post-Wet	CRP	0.8 (0.2)	2.3 (0.1)	11.1 (1.0)
	AGR	n.d. ^c	n.d.	n.d.
	REF	n.d.	n.d.	n.d.

^a Differences between individual daily fluxes are provided in Table S1.

^b WFPS was measured by a manual CS HS2 sensor near chambers (see Section 2). "Dry" values represent WFPS of the experimental fields at the day of measurements before the rewetting. "Wet" values represent WFPS within wetted area of 0.5 m^2 on the day of measurements after the rewetting. WFPS of wetted areas at the second day after artificial rain application (DOY 173) were $32.8 \pm 2.3\%$ and $38.8 \pm 1.7\%$ for CRP and AGR sites, respectively. For continuous WFPS measured by the CS 616 sensor see Fig. 1.

^c Not determined.

Table 4 Relative increase in soil GHG emissions from the study sites after an artificial rain event, calculated as ratio of the average soil flux before and after artificial rainfall event.

	CRP	AGR (After/before)	REF
N ₂ O	34.5	24.0	3.0
CO ₂	1.5	2.2	1.6

4.1. Nitrous oxide fluxes

Soil C appears to play a modulating role in soil N₂O emissions from agricultural fields: we measured four times higher soil N₂O emissions from the former CRP field with its higher soil C content than from the AGR field (C contents of $30.9 \pm 7.7 \, g \, kg^{-1}$ vs. $14.3 \pm 3.0 \, g \, kg^{-1}$; Table 1) during drought despite ~20% lower WFPS for the CRP field (Fig. 1, Table 3) and identical fertilization. Soil C content seems to modulate the N₂O emissions also during the rewetting. We measured higher N₂O emissions after the rewetting event from the former CRP field as compared to the AGR field despite an identical fertilization regime and WFPS (Fig. 1, Table 3).

Post-rewetting fluxes of N₂O from the former CRP field also were 6 times higher than those from the AGR field. After rewetting, soil fluxes at the former CRP field increased up to 34 times for a short time, reaching $27.6 \pm 6.3 \,\mu$ g N₂O–N m⁻² min⁻¹. Soil fluxes at the AGR field, in contrast, increased to 24 times following rewetting, reaching 4.8 μ g N₂O–N m⁻² min⁻¹. Similar control of soil N₂O emissions by soil carbon and moisture has also been shown for acidic sugarcane soils in Australia (Denmead et al., 2010). Jørgensen et al. (1998) also showed a similar ~40 fold increase of soil N₂O emissions after rewetting of a temperate region hay field after harvest. The strong response of soil N₂O fluxes to fertilization usually observed in agricultural systems (Bouwman et al., 2002) was restricted in AGR and CRP fields by drought.

Our results also support earlier reports on the control of soil N_2O emissions by N availability (e.g., Groffman et al., 2000). Emissions from the unfertilized REF site with low extractable NO_3^- pools (Table 1) were lower than those from the agricultural sites despite high soil C content and available water after rewetting.

Single events of very high fluxes following rewetting may have an increasingly important effect on overall N₂O budgets in future mesic region agricultural ecosystems given the predicted intensification of the water cycle with climate change (Betts et al., 2007). In the present study, the duration of high fluxes in response to the rewetting event was \sim 5 days, with a peak rate the day after the rewetting event. Within 24h after rewetting we measured >50% reduction of soil N₂O emissions at the AGR and CRP sites, and close to pre-wetting levels within \sim 100 h at the CRP site (DOY 176, Fig. 3) The post-rewetting increase in soil N₂O emissions observed here brought the cumulative N₂O flux during the measurement period of 24 days to ${\sim}120\,mg\,N\,m^{-2}$ in the former CRP site. These shortterm emissions are comparable to earlier estimates of an annual cumulative N₂O emission of \sim 127 mg N m⁻² estimated for a no-till corn-soybean-wheat (Triticum aestivum L) rotation nearby (Robertson et al., 2000) and an annual cumulative N₂O emission of 80- $150 \text{ mg} \text{ N} \text{ m}^{-2}$ estimated from a moderately drained soil under NT corn in South Dakota (Lehman and Osborne, 2013), but were lower than the $787 \text{ mg} \text{ N} \text{ m}^{-2}$ estimated for fine-loamy soil under an NT corn-soybean rotation in Iowa (Parkin and Kaspar, 2006).

Based on our results we can identify three major factors controlling soil N_2O emissions at our study sites: (1) water availability—soil N_2O fluxes were low at times of low water availability, even after fertilization; (2) carbon availability—soil N_2O emissions were lower in sites with lower soil C content, even after a wetting event increased water availability; and (3) nitrogen availability—once water was available, soil N_2O emissions were higher at the fertilized sites and were low at the reference site, despite high soil C concentrations.

4.2. Carbon dioxide fluxes

Observed soil CO_2 emissions, consistent with our hypothesis, were independent of short-term soil N availability. We did not detect any increase in soil CO_2 emissions after fertilization, but sites with higher soil C content exhibited higher CO_2 emissions than sites with lower soil C content (Table S1). In comparison to soil N₂O fluxes, soil CO_2 emissions exhibited a weak response to rewetting.

Differences in available soil C, originating both from the soil organic C and plant/litter at these sites (Table 1; Zenone et al., 2013) can explain the site differences in soil CO₂ emissions we observed. Highest CO₂ emissions were measured at the REF site, with decreasing emissions at the former CRP site and significantly lower emissions at the AGR site (Table 3). The brome grass in the REF site had well developed, perennial root systems, while the former CRP and AGR sites were under recently planted corn. Therefore, higher CO₂ emissions during the drought from the REF as compared to agricultural sites was most likely connected to both phenological differences between perennial brome grass and corn as well soil C content.

The response of soil CO₂ emissions to wetting were much lower than the response of N₂O emissions and ranged from 1.5 to 1.6 to 2.2 fold increases for former CRP, REF, and AGR soils, respectively (Table 4). Higher and more variable soil CO₂ emissions from CRP and REF sites (Fig. 3) potentially masked response to the rewetting. Overall, similar soil CO₂ responses to wetting have been reported for other croplands (Kim et al., 2012).

Based on our results we can identify two major factors controlling soil CO_2 emissions at our study sites: (1) water availability—soil CO_2 fluxes were low at times of low water availability, even in soils with high total C content; and (2) carbon availability—soil CO_2 emissions were lower in sites with lower soil C content, even after a wetting event increased water availability.

4.3. Methods comparison

Both techniques for measuring soil GHG emissions—laboratory GC analysis of GHG concentrations and the newly developed quantum cascade laser coupled with infra-red gas absorption analysis for simultaneous in situ measurements—provided equivalent results and can be used interchangeably using the static chamber method (Fig. 2).

5. Conclusions

Results support our initial hypothesis that soil N₂O emissions on rewetting are controlled by N availability within the constraints of soil carbon as affected by land use history, while soil CO₂ emissions on rewetting are controlled solely by carbon availability. Our results demonstrate the tight coupling among water, carbon, and nitrogen cycles for soil N₂O emissions from crop and grassland ecosystems in a temperate climate. Increasing N availability by fertilization caused an increase in soil N₂O emissions only when coupled with an increase in water availability. The magnitude of this increase, however, was determined by soil C availability. In contrast, soil CO₂ emissions were controlled by both soil C and water availability but exhibited no response to fertilization with N. We conclude further that both techniques for measuring soil GHG emissions—laboratory GC analysis of GHG concentrations and the newly developed quantum cascade laser coupled with infra-red gas absorption analyzer for simultaneous in situ measurements provided equivalent results and can be used interchangeably using the static chamber method.

[Kroon et al., 2010]

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.agee.2015.07.005.

References

- Austin, A.T., Yahdjian, L., Stark, J.M., Belnap, J., Porporato, A., Norton, U., Ravetta, D.N. A., Schaeffer, S.M., 2004. Water pulses and biogeochemical cycles in arid and semiarid ecosystems. Oecologia 141, 221–235.
- Barton, L., Kiese, R., Gatter, D., Butterbach-Bahl, K., Buck, R., Hinz, C., Murphy, D.V., 2008. Nitrous oxide emissions from a cropped soil in a semi-arid climate. Global Change Biol. 14, 177–192. doi:http://dx.doi.org/10.1111/j 1365-2486.2007.01474. x.
- Beare, M.H., Gregorich, E.G., St-Georges, P., 2009. Compaction effects on CO₂ and N₂O production during drying and rewetting of soil. Soil Biol. Biochem. 41, 611– 621.
- Bergsma, T.T., Robertson, G.P., Ostrom, N.E., 2002. Influence of soil moisture and land use history on denitrification end-products. J. Environ. Qual. 31, 711–717.
- Betts, R.A., Boucher, O., Collins, M., Cox, P.M., Falloon, P.D., Gedney, N., Hemming, C., Jones, C.D., Sexton, D.M.H., Webb, M.J., 2007. Projected increase in continental runoff due to plant responses to increasing carbon dioxide. Nature 448, 1037– 1041
- Bhardwaj, A.K., Zenone, T., Jasrotia, P., Robertson, G.P., Chen, J., Hamilton, S.K., 2011. Water and energy footprints of bioenergy crop production on marginal lands. GCB Bioenergy 3, 208–222.
- Birch, H.F., 1958. The effect of soil drying on humus decomposition and nitrogen availability. Plant Soil 10, 9–31.
- Borken, W., Matzner, E., 2009. Reappraisal of drying and wetting effects on C and N mineralization and fluxes in soils. Global Change Biol. 15, 808–824.
- Bouwman, A.F., Boumans, L.J.M., Batjes, N.H., 2002. Emissions of N₂O and NO from fertilized fields: summary of available measurement data. Global Biogeochem. Cycles 16, 1058.
- Dane, J.H., Topp, C.G., 2002. Water content. Methods of Soil Analysis: Part 4 Physical Methods. Soil Science Society of America press, Madison, WI, pp. 417–545.
- Davidson, E.A., 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Sci. Soc. Am. J. 56, 95–102.
- Denmead, O.T., Macdonald, B.C.T., Bryant, G., Naylor, T., Wilson, S., Griffith, D.W.T., Wang, W.J., Salter, B., White, I., Moody, P.W., 2010. Emissions of methane and

nitrous oxide from Australian sugarcane soils. Agric. For. Meteorol. 150, 748-756.

- Dowrick, D., Hughes, S., Freeman, C., Lock, M., Reynolds, B., Hudson, J., 1999. Nitrous oxide emissions from a gully mire in mid-Wales, UK, under simulated summer drought. Biogeochemistry 44, 151–162.
- Durack, P.J., Wijffels, S.E., Matear, R.J., 2012. Ocean salinities reveal strong global water cycle intensification during 1950 to 2000. Science 336, 455–458.
- Garcia-Monteil, D.C., Streudler, P.A., Piccolo, M., Neill, C., Melillo, J., Cerri, C.C., 2003. Nitrogen oxide emissions following wetting of dry soils in forest and pastures in Rondonia, Brazil. Biogeochemistry 64, 319–336.
- Gelfand, I., Zenone, T., Jasrotia, P., Chen, J., Hamilton, S.K., Robertson, G.P., 2011. Carbon debt of Conservation Reserve Program (CRP) grasslands converted to bioenergy production. PNAS 108, 13864–13869.
- Groffman, P.M., Brumme, R., Butterbach-Bahl, K., Dobbie, K.E., Mosier, A.R., Ojima, D., Papen, H., Parton, W.J., 2000. Evaluating annual nitrous oxide fluxes at the ecosystem scale. Global Biogeochem. Cycles 14, 1061–1070.
- Hao, W.M., Scharffe, D., Crutzen, P.J., Sanhueza, E., 1988. Production of N₂O, CH₄, and CO₂ from soils in the tropical savanna during the dry season. J. Atmos. Chem. 7, 93–105.
- Hernandez-Ramirez, G., Brouder, S.M., Smith, D.R., Van Scoyoc, G.E., Michalski, G., 2009. Nitrous oxide production in an Eastern Corn Belt soil: sources and redox range. Soil Sci. Soc. Am. J. 73, 1182–1191.
- Holland, E.A., Robertson, G.P., Greenberg, J., Groffman, P.M., Boone, R.D., Gosz, J.R., 1999. Soil CO₂, N₂O, and CH₄ exchange. Pages 185–201. In: Robertson, G.P., Bledsoe, C.S., Coleman, D.C., Sollins, P. (Eds.), Standard Soil Methods for Longterm Ecological Research. Oxford University Press, Oxford, UK.
- Jørgensen, R.N., Jørgensen, B.J., Nielsen, N.E., 1998. N₂O emission immediately after rainfall in a dry stubble field. Soil Biol. Biochem. 30, 545–546.
- Kim, D.-G., Vargas, R., Bond-Lamberty, B., Turetsky, M.R., 2012. Effects of soil rewetting and thawing on soil gas fluxes: a review of current literature and suggestions for future research. Biogeosciences 9, 2459–2483.
- Kim, D.-G., Mishurov, M., Kiely, G., 2010. Effect of increased N use and dry periods on N₂O emission from a fertilized grassland. Nutr. Cycl. Agroecosyst. 88, 397–410.
- Larsen, K.S., Andresen, L.C., Beier, C., Jonasson, S., Albert, K.R., Ambus, P.E.R., Arndal, M.F., Carter, M.S., Christensen, S., Holmstrup, M., Ibrom, A., Kongstad, J., Van Der Linden, L., Maraldo, K., Michelsen, A., Mikkelsen, T.N., Pilegaard, K.I.M., PriemÉ, A., Ro-Poulsen, H., Schmidt, I.K., Selsted, M.B., Stevnbak, K., 2011. Reduced N cycling in response to elevated CO₂, warming, and drought in a Danish heathland: synthesizing results of the CLIMAITE project after two years of treatments. Global Change Biol. 17, 1884–1899.
- Lehman, R.M., Osborne, S.L., 2013. Greenhouse gas fluxes from no-till rotated corn in the upper Midwest. Agric. Ecosyst. Environ. 170, 1–9.
- Mikha, M.M., Rice, C.W., Milliken, G.A., 2005. Carbon and nitrogen mineralization as affected by drying and wetting cycles. Soil Biol. Biochem. 37, 339–347.
- Parkin, T.B., Kaspar, T.C., 2006. Nitrous oxide emissions from corn-soybean systems in the Midwest. J. Environ. Qual. 35, 1496–1506.
- Prieme, A., Christensen, S., 2001. Natural perturbations, drying-wetting and freezing-thawing cycles, and the emission of nitrous oxide, carbon dioxide and methane from farmed organic soils. Soil Biol. Biochem. 33, 2083–2091.
- Standard Soil Methods for Long-term Ecological Research. In: Robertson, G.P., Goleman, D.C., Bledsoe, C.S., Sollins, P. (Eds.), Oxford University Press, Inc., New York.
- Robertson, G.P., Paul, E.A., Harwood, R.R., 2000. Greenhouse gases in intensive agriculture: contributions of individual gases to the radiative forcing of the atmosphere. Science 289, 1922–1925.
- Robertson, G.P., Hamilton, S.K., 2015. Conceptual and experimental approaches to understanding agricultural ecosystems. In: Hamilton, S.K., Doll, J.E., Robertson, G.P. (Eds.), The Ecology of Agricultural Ecosystems: Long-term Research on the Path to Sustainability. Oxford University Press, New York, New York, USA in press.
- Ruser, R., Flessa, H., Russow, R., Schmidt, G., Buegger, F., Munch, J.C., 2006. Emission of N₂O, N₂ and CO₂ from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. Soil Biol. Biochem. 38, 263–274.
- Xu, L.K., Baldocchi, D.D., Tang, J.W., 2004. How soil moisture, rain pulses, and growth alter the response of ecosystem respiration to temperature. Global Biogeochem. Cycles 18, GB4002 4010.1029/2004GB002281.
- Zenone, T., Gelfand, I., Chen, J., Hamilton, S.K., Robertson, G.P., 2013. From set-aside grassland to annual and perennial cellulosic biofuel crops: effects of land use change on carbon balance. Agric. For. Meteorol. 182–183, 1–12.

Date	CRP		AGR		REF	
	N ₂ O	CO ₂	N ₂ O	CO_2	N_2O	CO_2
	$(\mu g m^{-2} h^{-1})$	$(mg m^{-2} h^{-1})$	$(\mu g m^{-2} h^{-1})$	$(mg m^{-2} h^{-1})$	$(\mu g m^{-2} h^{-1})$	$(mg m^{-2} h^{-1})$
4-Jun	115 (26) ^b *	102 (8) ^b	12 (4) ^a	61 (5) ^a	n.d.	n.d.
5-Jun	51 (7) ^b	83 (5) ^b	7 (1) ^a	55 (8) ^a	9 (2) ^a	202 (8) ^c
6-Jun	29 (5) ^b	73 (6) ^b	$4(1)^{a}$	51 (7) ^a	n.d.	n.d.
8-Jun	25 (3) ^a	96 (4) ^a	n.d.	n.d.	8 (2) ^b	235 (11) ^b
12-Jun	11 (1) ^b	83 (7) ^b	$4(1)^{a}$	64 (7) ^a	3 (1) ^a	180 (7) ^c
17-Jun	45 (16) ^c	223 (18) ^b	9 (1) ^b	97 (8) ^a	6 (1) ^a	232 (11) ^b
19-Jun	442 (159) ^b	151 (16) ^b	9 (112) ^a	75 (7) ^a	n.d.	n.d.
20-Jun	829 (190) ^c	167 (11) ^a	144 (50) ^b	143 (11) ^a	19 (3) ^a	298 (19) ^b
21-Jun	208 (74) ^b	116 (8) ^b	22 (6) ^a	83 (9) ^a	n.d.	n.d.
25-Jun	34 (6)	86 (10)	n.d. [#]	n.d.	n.d.	n.d.
26-Jun	19 (5)	61 (3)	n.d.	n.d.	n.d.	n.d.
27-Jun	14 (4)	56 (4)	n.d.	n.d.	n.d.	n.d.

Table S1. Comparison between average soil N2O and CO2 emissions from studied sites at individual sampling dates (mean \pm S.E., n = 14-16 chambers).

* Dates with different lowercase letters within rows are significantly different (p < 0.05) for N_2O and CO_2 fluxes, respectively. [#] n.d. = not determined