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Net soil–atmosphere fluxes mask patterns in gross production and consumption of nitrous oxide and methane in a managed ecosystem

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Abstract. Nitrous oxide (N_2O) and methane (CH_4) are potent greenhouse gases that are both produced and consumed in soil. Production and consumption of these gases are driven by different processes, making it difficult to infer their controls when measuring only net fluxes. We used the trace gas pool dilution technique to simultaneously measure gross fluxes of N_2O and CH_4 throughout the growing season in a cornfield in northern California, USA. Net N_2O fluxes ranged 0–4.5 mg N m^{-2} d^{-1} with the N_2O yield averaging 0.68 ± 0.02. Gross N_2O production was best predicted by net nitrogen (N) mineralization, soil moisture, and soil temperature ($R^2 = 0.60$, $n = 39$, $p < 0.001$). Gross N_2O reduction was correlated with the combination of gross N_2O production rates, net N mineralization rates, and CO_2 emissions ($R^2 = 0.74$, $n = 39$, $p < 0.001$). Overall, net CH_4 fluxes averaged -0.03 ± 0.02 mg C m^{-2} d^{-1}. The methanogenic fraction of carbon mineralization ranged from 0 to 0.27 % and explained 40 % of the variability in gross CH_4 production rates ($n = 37$, $p < 0.001$). Gross CH_4 oxidation exhibited a strong positive relationship with gross CH_4 production rates ($R^2 = 0.67$, $n = 37$, $p < 0.001$), which reached as high as 5.4 mg C m^{-2} d^{-1}. Our study is the first to demonstrate the simultaneous in situ measurement of gross N_2O and CH_4 fluxes, and results highlight that net soil–atmosphere fluxes can mask significant gross production and consumption of these trace gases.

1 Introduction

Greenhouse gas emissions from soils are major contributors to climate change (Ciais et al., 2013). While carbon dioxide (CO_2) is the most abundant greenhouse gas in the atmosphere, both nitrous oxide (N_2O) and methane (CH_4) are more potent with 298 and 34 times the global warming potential of CO_2 on a 100-year timescale, respectively (Myhre et al., 2013). Both N_2O and CH_4 are produced and consumed in soils by microbially mediated redox-sensitive processes. However, most studies only measure net soil–atmosphere exchange of N_2O and CH_4. This approach cannot differentiate between production and consumption of these trace gases and thus limits our ability to infer controls on these processes and to diagnose model inaccuracies in predicting net N_2O and CH_4 fluxes. This hinders predictions of how soil–atmosphere N_2O and CH_4 fluxes will respond to future changes in land use practices or climate change.

Agricultural soils account for nearly two-thirds of global soil emissions of N_2O, which is produced from nitrification and denitrification of fertilizer nitrogen (N) that supports agroecosystem productivity (Ciais et al., 2013). Managing soil N_2O emissions from agroecosystems can go beyond direct reductions in N_2O production from decreased fertilizer inputs because denitrifying bacteria can consume N_2O to dinitrogen gas (N_2), completing the N cycling. Nitrous oxide consumption is not generally considered to be an important process in upland soils because it is an anaerobic process. Rates of N_2O reduction to N_2 decrease as O_2 and NO_3^- availability increases (Weier et al., 1993; Firestone et

al., 1980). Theoretically, this results in a high N_2O yield ($N_2O / (N_2O + N_2)$) in unsaturated soil where diffusive re-supply of O_2 and the production of NO_3^- from nitrification would inhibit N_2O reduction. Thermodynamics also predict that high soil NO_3^- from fertilizer N inputs in agricultural soils would lead to high N_2O yields. However, N_2O yields average 0.375 ± 0.035 in agricultural soil and span the entire range from 0 to 1 in oxic, upland soils (Schlesinger, 2009; Stevens and Laughlin, 1998). This high variability, in part, reflects the difficulty in measuring rates of N_2O reduction to N_2, particularly under field conditions (Groffman et al., 2006). It also reflects other important factors that influence the N_2O yield, such as soil type (Woli et al., 2010), labile C (Weier et al., 1993), and pH (Stevens et al., 1998). The lower-than-expected average N_2O yield in agricultural soils and large range in N_2O yields in upland soil in general also suggests that N_2O reduction to N_2 could play an important role in mitigating soil N_2O emissions to the atmosphere in agroecosystems.

Upland soils globally consume atmospheric CH_4 at a rate similar to the accumulation of CH_4 in the atmosphere (Ciais et al., 2013), and thus changes in the CH_4 sink strength of soils could influence atmospheric CH_4 concentrations. The inhibition of CH_4 oxidation associated with fertilizer application of NO_3^- (Aronson and Helliker, 2010), urea (Mosier et al., 1991), and NH_4^+ (Bedard and Knowles, 1989) is thought to cause lower net rates of CH_4 uptake in agricultural systems compared to natural ecosystems (Nesbit and Breitenbeck, 1992; Bender and Conrad, 1994; Koschorreck and Conrad, 1993; Dutaur and Verchot, 2007; Mosier et al., 1991). Inhibition by NH_4^+ has been attributed to enzymatic substrate competition due to the similarities between the CH_4 monooxygenase and NH_4^+ monooxygenase enzymes (Gulledge and Schimel, 1998) as well as toxicity effects from nitrite produced during NH_4^+ oxidation (King and Schnell, 1994). However, the effect of N on CH_4 oxidation varies by soil (Gulledge et al., 1997), and at least some of this effect is due to inhibition by salts included in the fertilizer applications (Adamsen and King, 1993; Dunfield et al., 1993; Gulledge and Schimel, 1998; Nesbit and Breitenbeck, 1992). In addition, the response of CH_4 oxidation to NH_4^+ and NO_3^- may depend on the methanotrophic community; for example the high affinity type II methane-oxidizing bacteria that dominate under low (< 1000 ppm) CH_4 conditions (Bender and Conrad, 1992) may be less sensitive to mineral N availability (Jang et al., 2011; Reay and Nedwell, 2004; Wang and Ineson, 2003). Thus, there remains uncertainty surrounding N inhibition of CH_4 oxidation as the mechanism leading to low net rates of CH_4 uptake in agricultural soils.

A major confounding factor in studies assessing controls on CH_4 oxidation is the simultaneous occurrence of methanogenesis and CH_4 oxidation. Net changes in CH_4 concentrations under oxic soil conditions are assumed to reflect only CH_4 oxidation (e.g., Nesbit and Breitenbeck,

1992) because methanogenesis occurs only under highly reducing conditions (Conrad, 1996). However, von Fischer and Hedin (2002) demonstrated that CH_4 production occurred in a wide range of dry, oxic soils with water-filled pore space as low as 20 %. Similarly, Teh et al. (2005) documented the occurrence of methanogenesis under well-aerated conditions in an upland tropical forest soil. Macroaggregates can support net CH_4 efflux in unsaturated soil (Jackel et al., 2001; Sey et al., 2008), likely because O_2 consumption in the centers of the aggregates exceeds diffusive re-supply of O_2 to create reducing conditions (Sexstone et al., 1985). Microsites of methanogenesis could also occur in the rhizosphere where high rates of O_2 consumption from rhizosphere priming could create reducing conditions (Cheng et al., 2003). Because the controls on methanogenesis and CH_4 oxidation are likely very different, the co-occurrence of these processes means that we must measure gross rates of both processes simultaneously to elucidate the mechanisms driving patterns in net soil–atmosphere CH_4 fluxes.

We used the stable isotope trace gas pool dilution technique to measure gross N_2O and CH_4 fluxes in cornfield soils throughout the growing season in order to improve our understanding of trace gas dynamics in upland soils of agroecosystems. Fertilized agroecosystems are typically large net N_2O sources and small net CH_4 sinks (Haile-Mariam et al., 2008; Kessavalou et al., 1998; Gelfand et al., 2013; Nangia et al., 2013; Robertson et al., 2000). However, little is known about the rates of gross production and consumption of these gases in upland soils, or their controlling factors. Different controls on production and consumption processes may result in complex responses of net soil–atmosphere gas fluxes to climate or land management. Thus, the objectives of this study were to quantify field rates of gross N_2O and CH_4 production and consumption, and explore environmental and plant-mediated controls on these rates.

2   Materials and methods

2.1   Study site

The study site was a cornfield planted on a drained peatland located on Twitchell Island (38.11° N, 121.65° W) in the Sacramento–San Joaquin River delta region of northern California. The region is very productive agriculturally, producing USD 500 million in crops in 1993 (Ingebritsen and Ikehara, 1999). The climate is Mediterranean with a winter wet season and summer dry season. The mean annual temperature is 15.1 °C, and mean annual precipitation is 335 mm (Hatala et al., 2012). The soils consist of mucky clay over buried peat and are classified as fine, mixed, superactive, thermic Cumulic Endoaquolls (Drexler et al., 2009). The field was fertilized once, at seeding, at a rate of 118 kg N ha^{-1} with UAN 32, which consists of 45 % ammonium nitrate, 35 % urea, and 20 % water. The water table was

maintained around 50 cm soil depth throughout the growing season via subsurface irrigation.

2.2 Study design

We measured gross and net fluxes of CO_2, CH_4, and N_2O at five time points during the growing season from May to November 2012 on the following days after seeding (DAS): 11 (germination stage), 24 (seedling stage), 59 (peak growth stage), 94 (flowering stage), and 171 (senesced stage). The corn began senescing around DAS 104 and was harvested on DAS 178. We performed measurements in row and inter-row locations with the assumption that plant effects, if any, would be greater in the rows where the corn was growing (Cai et al., 2012; Haile-Mariam et al., 2008; Kessavalou et al., 1998). We established three parallel transects spaced 50 m apart. We measured gross production and consumption of CH_4 and N_2O as well as net fluxes of CO_2, CH_4, and N_2O along the northernmost transect and measured only net fluxes in the other two transects. In each transect, we used paired measurements in the bed (in between corn rows) and furrow (in row) with replicate pairs spaced 10 m apart ($n = 4$ pairs per transect). After each gas flux measurement was completed, we measured air, chamber headspace, and soil temperature at the surface flux chamber location. We also used an auger to sample the soil from the chamber footprint in 10 cm increments to 50 cm depth for the gross flux transect and only 0–10 cm depth in the net flux transects. The soils were processed the next day for determination of gravimetric soil moisture and net rates of nitrogen (N) mineralization and nitrification as described below.

2.3 Laboratory assays

We determined net rates of N mineralization and nitrification from 6-day laboratory incubations. We mixed each soil core by hand and subsampled 15 g for extraction in 75 mL of 2 M KCl, 10 g for determination of gravimetric soil moisture, and 50 g for incubation in Mason jars kept in the dark at ambient temperature. The jars were covered in perforated plastic wrap to minimize evaporation during the incubation. After 6 days, the soils in the jars were mixed and 15 g of soil was subsampled for KCl extractions. The KCl extracts were analyzed colorimetrically for NH_4^+ and NO_3^- concentrations on a Lachat QuickChem flow injection auto-analyzer (Lachat Instruments, Milwaukee, WI, USA). We calculated net N mineralization rates from the change in NH_4^+ plus NO_3^- concentrations over the incubation period and net nitrification rates from the change in NO_3^- concentrations over the incubation period.

The remaining soil (not utilized in the net rates incubation) was air dried for archival. Air-dried samples from the May sampling date were ground in a Spex Mill (Metuchen, NJ, USA) for total C and N analyses on a vario MICRO cube elemental analyzer (Elementar, Hanau, Germany).

2.4 Gas flux measurements

We used the stable isotope trace gas pool dilution technique to measure field rates of gross N_2O and CH_4 production and consumption (von Fischer and Hedin, 2002; Yang et al., 2011). We injected 10 mL of isotopically enriched spiking gas into the headspace of a 28 L surface flux chamber inserted 6 cm into the soil surface. The spiking gas consisted of 70 ppm N_2O at 98 atom % [15]N enrichment, 280 ppm CH_4 at 99 atom % [13]C enrichment, and 28 ppm SF_6 to achieve a ^{15}N-N_2O enrichment of 5.42 atom % and ^{13}C-CH_4 enrichment of 5.61 atom %. This spiking gas injection increased the chamber headspace gas composition by 25 N_2O, 100 CH_4, and 10 ppb SF_6. We sampled the chamber headspace at 5, 15, 30, 45, and 60 min after spiking gas injection. We analyzed samples on a Shimadzu GC-14A gas chromatograph (Columbia, MD, USA) equipped with a thermal conductivity detector, flame ionization detector, and electron capture detector for determination of CO_2, CH_4, N_2O, and SF_6 concentrations. We analyzed separate samples for ^{15}N-N_2O and ^{13}C-CH_4 on an IsoPrime 100 continuous flow isotope ratio mass spectrometer interfaced with a trace gas preconcentration unit (Isoprime Ltd, Cheadle Hulme, UK) and Gilson GX271 autosampler (Middleton, WI). The trace gas analyzer was equipped with a combustion furnace using palladium to catalyze the conversion of CH_4 to CO_2 for isotopic analysis after CO and CO_2 were scrubbed from the sample (Fisher et al., 2006). One out of the 40 gross N_2O flux measurements and three out of the 40 gross CH_4 flux measurements were lost due to autosampler needle clogs that occurred during isotopic analysis.

Gross N_2O and CH_4 production and consumption rates were estimated using the pool dilution model as described by Yang et al. (2011) and von Fischer and Hedin (2002). The iterative model solves for gross production rates based on the isotopic dilution of the isotopically enriched chamber headspace pool of N_2O or CH_4 by natural abundance N_2O or CH_4 emitted by the soil. Gross consumption rates were estimated from the empirical loss of the [15]N_2O or [13]CH_4 tracer, using the loss of the SF_6 tracer to account for physical losses such as diffusion. We note that gross N_2O consumption rates are not equivalent to N_2 production via denitrification because heterogeneous [15]N_2O distribution in the soil and complete denitrification intracellularly could lead to underestimates of N_2 production (Well and Butterbach-Bahl, 2013; Yang et al., 2013). We assumed that the isotopic composition of produced N_2O was 0.3431 atom % [15]N and the fractionation factor associated with N_2O reduction to N_2 was 0.9924. The justification for these assumptions is discussed by Yang et al. (2011). We assumed that the isotopic composition of produced CH_4 was 1.0473 atom %, based on measurements of the ^{13}C isotopic composition of soil CH_4 in a nearby study site (Y. Teh, personal communication, 2011). We assumed that the fractionation factor associated with CH_4 oxidation was 0.98 as justified by von Fischer and Hedin (2002). Sen-

sitivity analyses performed by both Yang et al. (2011) and von Fischer and Hedin (2002) showed that the pool dilution model output is not sensitive to these assumed values at the high isotopic enrichments used. Net fluxes of CO_2, N_2O, and CH_4 were determined from the change in concentration over time using an iterative model that fits an exponential curve to the data (Matthias et al., 1978). Fluxes were considered to be zero when the relationship between trace gas concentration and time was not significant at $p = 0.05$. The methanogenic fraction of C mineralization was calculated as the gross CH_4 production rate divided by the sum of the gross CH_4 production rate and CO_2 production rates.

2.5 Statistical analyses

We used SYSTAT version 13 (SPSS Inc., Evanston, IL, USA) to perform statistical analyses and Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA, USA) to run the iterative pool dilution model. We log transformed the data to meet the normality assumptions of ANOVAs; soil moisture, soil temperature, soil C and N concentrations, and soil C : N ratios did not require transformation. We analyzed net and gross fluxes of CO_2, N_2O, and CH_4 using sampling date as the within-subjects factor and location (i.e., bed versus furrow) as the between-subject factor in repeated measures ANOVAs. We also analyzed net N mineralization and nitrification rates using sampling date as the within-subjects factor, and soil depth and location as the between-subjects factors in repeated measures ANOVAs. We explored relationships between trace gas fluxes and potential drivers (soil moisture, air and soil temperatures, soil NH_4^+ and NO_3^- concentrations, net N mineralization and nitrification rates, soil C and N concentrations, etc.) using linear regressions. We determined the model that best fit observed trace gas flux data using backwards stepwise multiple linear regressions starting with all potential explanatory variables; the best model fit was determined by minimizing the Akaike information criterion. Statistical significance was determined at p values < 0.05.

3 Results

3.1 Soil characteristics and N cycling

Air and soil temperature differed significantly among sampling dates ($p < 0.05$, Table 1). Mean air temperature spanned a small range from a low of $24.5 \pm 0.7\,°C$ on DAS 171 to a high of $28.2 \pm 0.7\,°C$ on DAS 94. Soil temperature was more variable, with the lowest mean soil temperature on DAS 171 at $14.8 \pm 0.1\,°C$ and the highest mean soil temperature on DAS 59 at $24.2 \pm 0.3\,°C$.

In surface soils (0–10 cm depth), gravimetric soil moisture ranged from $0.24 \pm 0.01\,g\,H_2O\,g^{-1}$ soil on DAS 94 to $0.38 \pm 0.02\,g\,H_2O\,g^{-1}$ soil on DAS 11 (Table 1). Soil moisture decreased as the growing season progressed until DAS 171, when soil moisture increased to a value intermediate of

that on DAS 59 and 94 (Table 1). Soil moisture was significantly higher in the row than in the inter-row on DAS 11 and 24 only (Table 3). Mean soil moisture increased significantly with depth (Table 2), although differences were not statistically significant for all dates (Table 3).

Soil NH_4^+ concentrations differed significantly among sampling dates and were lowest at the beginning (DAS 11) and end (DAS 171) of the study (Table 3). The inclusion of an outlier plot on DAS 94 increased the mean NH_4^+ concentration to $62.5 \pm 46.4\,\mu g\,N\,g^{-1}$. Soil NH_4^+ concentrations decreased significantly from 0–10 to 20–30 cm depth (Tables 2–3) and were higher in rows than inter-rows (Table 3). Across all sampling dates, concentrations at 0–10 cm depth averaged 34.8 ± 20.1 in rows and $12.9 \pm 2.0\,\mu g\,N\,g^{-1}$ in inter-rows. Soil NO_3^- concentrations were lower on DAS 11 than all other sampling dates (Table 3), averaging 53.5 ± 7.2 on DAS 11 and $215 \pm 33\,\mu g\,N\,g^{-1}$ across all other sampling dates at 0–10 cm depth. Soil NO_3^- concentrations decreased with depth (Tables 2–3). On DAS 59 and 94 only, soil NO_3 concentrations were higher in rows ($387 \pm 117\,\mu g\,N\,g^{-1}$) than in inter-rows ($156 \pm 23\,\mu g\,N\,g^{-1}$) (Table 3).

Across the entire data set ($n = 216$), net N mineralization rates averaged 3.3 ± 0.5 and net nitrification rates averaged $2.7 \pm 0.6\,\mu g\,N\,g^{-1}\,d^{-1}$. Net N mineralization and nitrification rates did not differ significantly among soil depths, sampling locations, or sampling dates (Table 3), although rates trended higher at 0–10 cm depth across all sampling dates and locations (Table 2). Across all sampling dates and soil depths, 96 % of the variability in net nitrification rates was explained by net N mineralization rates ($p < 0.001$, $n = 215$, Table 4).

Total C and N concentrations for soils sampled on DAS 11 differed between row and inter-row sampling locations (soil C, $F_{1,30} = 5.295$, $p = 0.03$; soil N, $F_{1,30} = 4.546$, $p = 0.04$) but not among soil depths (Table 2). Both soil C and N concentrations were higher in rows than in inter-rows, averaging $16.1 \pm 0.8\,\%$ C and $0.99 \pm 0.03\,\%$ N in rows and $13.7 \pm 0.5\,\%$ C and $0.89 \pm 0.02\,\%$ N in inter-rows. Soil C : N ratios averaged 15.8 ± 0.2 overall ($n = 40$), and did not differ significantly between sampling locations or among soil depths.

3.2 Gross and net N_2O fluxes

Across the entire data set, net N_2O fluxes ranged 0–4.5 and averaged $1.6 \pm 0.2\,mg\,N\,m^{-2}\,d^{-1}$ ($n = 112$). Net N_2O fluxes differed significantly among sampling dates ($F_{4,56} = 3.0$, $p = 0.03$) but not between sampling locations (Fig. 1a). Net N_2O fluxes were best predicted by net N mineralization, soil moisture, and soil CO_2 emissions together ($R^2 = 0.49$, Table 4).

Gross N_2O production ranged 0.09–6.6 mg N m^{-2} d^{-1} and gross N_2O reduction rates ranged 0.00–0.95 mg N m^{-2} d^{-1}. The N_2O yield averaged 0.68 ± 0.02 ($n = 40$). Both gross N_2O production and consumption rates differed sig-

Table 1. Environmental and soil (0–10 cm depth) variables by sampling date (mean ± SE).

Variable	F statistic	Sampling date				
		DAS 11 ($n = 8$)	DAS 24 ($n = 24$)	DAS 59 ($n = 24$)	DAS 94 ($n = 16$)	DAS 171 ($n = 24$)
Air temperature (°C)	$F_{4,56} = \mathbf{3.4}$	27.6 ± 0.9 a	26.8 ± 1.2 a	25.8 ± 0.5 ab	28.2 ± 0.7 a	24.5 ± 0.7 b
Soil temperature (°C)	$F_{4,56} = \mathbf{245}$	18.4 ± 0.2 a	22.1 ± 0.3 b	24.2 ± 0.3 c	22.8 ± 0.2 b	14.8 ± 0.1 d
Soil moisture (g H_2O g^{-1} soil)	$F_{4,24} = \mathbf{34}$*	0.38 ± 0.02	0.34 ± 0.02	0.35 ± 0.01	0.24 ± 0.01	0.32 ± 0.01

Degrees of freedom are shown in subscripts, and statistically significant F statistics at $P < 0.05$ are indicated by bold text. Letters indicate statistically significant differences among sampling dates. * One transect was excluded from the repeated measures ANOVA because data are missing for one sampling date.

Table 2. Soil characteristics and N cycling rates across all sampling dates by soil depth in the gross flux transect (mean ± SE).

Variable	N	P value	0–10 cm	10–20 cm	20–30 cm	30–40 cm	40–50 cm
Soil moisture (g H_2O g^{-1})	40	< 0.001	0.34 ± 0.01 a	0.35 ± 0.01 a	0.37 ± 0.01 ab	0.40 ± 0.01 b	0.46 ± 0.02 c
NH_4^+ concentration (µg N g^{-1})	40	< 0.001	23.3 ± 9.6 a	15.2 ± 6.3 b	7.0 ± 1.8 b	5.0 ± 0.7 b	5.7 ± 0.8 b
NO_3^- concentration (µg N g^{-1})	40	< 0.001	183 ± 28 a	110 ± 22 b	58.9 ± 8.4 c	41.9 ± 6.1 c	29.5 ± 3.2 c
Net mineralization (µg N g^{-1} d^{-1})	40		5.9 ± 2.6	1.0 ± 0.9	1.5 ± 0.5	1.8 ± 0.7	3.3 ± 0.5
Net nitrification (µg N g^{-1} d^{-1})	40		6.7 ± 2.4	1.7 ± 0.8	2.1 ± 0.5	2.3 ± 0.7	3.8 ± 0.5
Soil C concentration (%)	8*		14.1 ± 0.5	15.4 ± 1.6	14.8 ± 0.9	15.2 ± 1.6	15.0 ± 0.9
Soil N concentration (%)	8*		0.93 ± 0.02	0.96 ± 0.07	0.98 ± 0.05	0.91 ± 0.06	0.93 ± 0.05

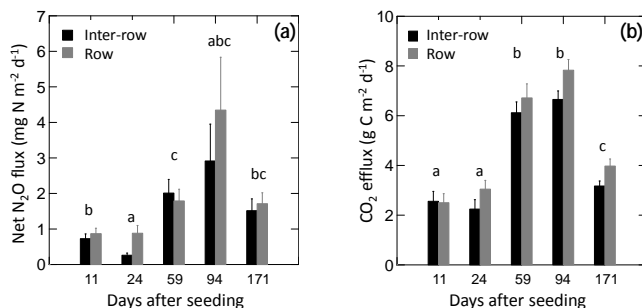Letters indicate statistically significant differences among soil depths. * Data from DAS 11 only.

Figure 1. Mean **(a)** net N_2O flux and **(b)** CO_2 efflux for all three transects ($n = 24$ per sampling date except $n = 16$ on DAS 94) in inter-rows (black bars) and rows (grey bars). Error bars represent standard errors, and different letters indicate statistically significant differences among sampling dates.
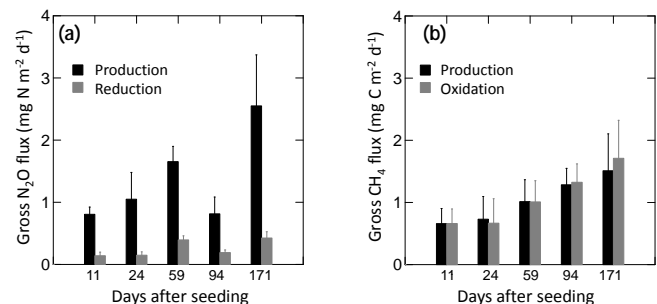

Figure 2. Mean **(a)** gross N_2O production rates (black bars) and reduction rates (grey bars) and **(b)** gross CH_4 production rates (black bars) and oxidation rates (grey bars). Error bars represent standard errors ($n = 8$ per sampling date).

nificantly among sampling dates ($F_{4,20} = 4.5$, $p = 0.009$ and $F_{4,20} = 4.4$, $p = 0.01$, respectively) but not between sampling locations (Fig. 2a). The highest gross production and consumption rates occurred on DAS 59 and 171. Overall, gross N_2O production rates were best predicted by net N mineralization, soil moisture, soil temperature, and soil CO_2 emissions ($R^2 = 0.60$, Table 4). At peak growth (DAS 59 and 94), these variables explained 89 % of the variability in gross N_2O production rates ($n = 15$, $p < 0.001$). When the corn was not actively growing, gross N_2O production was most strongly correlated with CO_2 emissions alone ($R^2 = 0.68$, $n = 24$, $p < 0.001$).

Gross N_2O reduction rates increased with gross N_2O production rates ($R^2 = 0.60$, $n = 39$, $p < 0.001$, Fig. 3a). Rates were also positively correlated with soil CO_2 emissions ($R^2 = 0.36$, $n = 39$, $p < 0.001$); this relationship was stronger when the corn was not actively growing (DAS 11, 24, and 171), with 80 % of the variability in gross N_2O reduction rates explained by CO_2 emissions on these dates ($n = 24$, $p < 0.001$, Fig. 3b). Gross N_2O reduction was most strongly correlated with the combination of gross N_2O production rates, net N mineralization rates, and CO_2 emissions ($R^2 = 0.74$, $n = 39$, $p < 0.001$, Table 4).

Table 3. Results from repeated measures ANOVAs with sampling date, the interaction of sampling date and soil depth, and the interaction of sampling date and sampling location as the within-subjects, and soil depth and sampling location as the between-subjects factors.

	Sampling date	Soil depth	Sampling location	Sampling date* Soil depth	Sampling date* Sampling location
Soil moisture (g H_2O g^{-1})	$F_{4,120} = \mathbf{135}$	$F_{4,30} = \mathbf{31}$	$F_{1,30} = \mathbf{5.1}$	$F_{16,120} = \mathbf{1.9}$	$F_{4,120} = \mathbf{4.6}$
NH_4^+ concentration (µg N g^{-1} d^{-1})	$F_{4,120} = \mathbf{7.9}$	$F_{4,30} = \mathbf{7.7}$	$F_{1,30} = \mathbf{4.0}$	$F_{16,120} = 0.90$	$F_{4,120} = 1.9$
NO_3^- concentration (µg N g^{-1} d^{-1})	$F_{4,120} = \mathbf{17}$	$F_{4,30} = \mathbf{36}$	$F_{1,30} = \mathbf{18}$	$F_{16,120} = 1.0$	$F_{4,120} = \mathbf{7.1}$
Net mineralization (µg N g^{-1} d^{-1})	$F_{4,120} = 1.5$	$F_{4,30} = 1.5$	$F_{1,30} = 1.5$	$F_{16,120} = 1.1$	$F_{4,120} = 1.7$
Net nitrification (µg N g^{-1} d^{-1})	$F_{4,120} = 1.4$	$F_{4,30} = 0.22$	$F_{1,30} = 1.9$	$F_{16,120} = 0.31$	$F_{4,120} = 1.8$

Degrees of freedom are shown in subscripts, and statistically significant F statistics at $P < 0.05$ are indicated by bold text.

Table 4. Coefficients for multiple linear regressions predicting trace gas fluxes using soil variables.

Dependent variable	N	R^2	Effect	Coefficient	SE	P value
Log(Net nitrification, µg N g^{-1} d^{-1})	215	0.96	Constant	0.162	0.020	<0.001
			Log(Net N mineralization, µg N g^{-1} d^{-1})	0.906	0.012	<0.001
Log(CO_2 emissions, g C m^{-2} d^{-1})	96	0.15	Constant	0.466	0.195	0.02
			Soil moisture (g H_2O g^{-1})	−1.019	0.416	0.02
			Soil temperature (°C)	0.022	0.007	0.002
Log(Net N_2O flux, mg N m^{-2} d^{-1})	56	0.49	Constant	−1.671	0.743	0.03
			Log(Net N mineralization)	1.342	0.274	<0.001
			Soil moisture	4.356	1.539	0.007
			Log(CO_2 emissions)	1.404	0.288	<0.001
Log(Gross N_2O production, mg N m^{-2} d^{-1})	39	0.60	Constant	1.743	0.453	0.001
			Log(Net N mineralization)	0.516	0.139	0.001
			Soil moisture	2.226	0.839	0.01
			Soil temperature	−0.043	0.013	0.002
			Log(CO_2 emissions)	1.056	0.180	<0.001
Log(Gross N_2O reduction)	39	0.74	Constant	−2.525	0.556	<0.001
			Log(Net N mineralization)	0.680	0.258	0.01
			Log(Gross N_2O production)	0.983	0.226	<0.001
			Log(CO_2 emissions)	1.199	0.292	<0.001
Log(Gross CH_4 production, mg C m^{-2} d^{-1})	37	0.17	Constant	2.264	0.199	<0.001
			Log(CO_2 emissions)	0.921	0.348	0.01
Log(Gross CH_4 oxidation)	37	0.79	Constant	0.794	0.621	0.21
			Log(Gross CH_4 production)	1.090	0.142	0.002
			Soil temperature	−0.086	0.024	0.001
			Log(CO_2 emissions)	1.096	0.335	<0.001

3.3 Gross and net CH_4 fluxes

Net CH_4 fluxes ranged from −1.3 to 0.44 mg C m^{-2} d^{-1} but net fluxes were not detectable for 94 out of 112 measurements. Overall net CH_4 fluxes averaged −0.03 ± 0.02 mg C m^{-2} d^{-1}. Using the trace gas pool dilution technique, we detected gross CH_4 production in 36 out of 37 measurements. Gross CH_4 production reached as high as 5.4 mg C m^{-2} d^{-1} with rates trending higher throughout the growing season (Fig. 2b). However, rates were only significantly different between DAS 11 and 94

($F_{4,12} = 4.1$, $p = 0.03$). Gross CH_4 production rates were marginally significantly higher in rows than in inter-rows ($F_{1,3} = 5.8$, $p = 0.10$). Overall, gross CH_4 production rates were weakly correlated to soil CO_2 emissions ($R^2 = 0.17$, Table 4) but exhibited a stronger positive correlation with the methanogenic fraction of C mineralization ($R^2 = 0.40$, $n = 37$, $p < 0.001$, Fig. 4a), which ranged from 0 to 0.27 % and averaged 0.06 ± 0.01 %. The strength of the relationship increased to $R^2 = 0.60$ ($n = 23$, $p < 0.001$) when considering only dates when the corn was not actively growing (Fig. 4a). When only peak growth sampling dates were con-
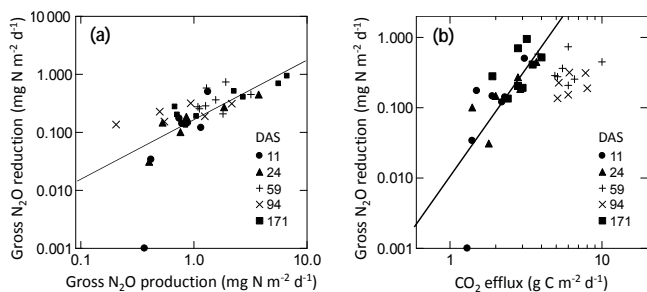
Figure 3. Gross N_2O reduction rates versus **(a)** gross N_2O production and **(b)** CO_2 efflux. Symbols represent sampling on different days after seeding (DAS): circles are DAS 11, triangles are DAS 24, pluses are DAS 59, crosses are DAS 94, and squares are DAS 171. **(a)** The line represents the regression line for all sampling dates together, $\mathrm{Log}_{10}(y) = [1.567 \times \log_{10}(x)] - 2.573$ ($R^2 = 0.60$, $n = 39$, $p < 0.001$), and **(b)** the line represents the regression line for sampling dates when the corn was not at peak growth (DAS 11, 24, and 171), $\mathrm{Log}_{10}(y) = [3.663 \times \log_{10}(x)] + 0.822$ ($R^2 = 0.80$, $n = 24$, $p < 0.001$).

Figure 4. **(a)** Gross CH_4 production rates versus methanogenic fraction of C mineralization, and **(b)** gross CH_4 oxidation rates versus gross CH_4 production rates. Symbols represent sampling on different days after seeding (DAS): circles are DAS 11, triangles are DAS 24, pluses are DAS 59, crosses are DAS 94, and squares are DAS 171. The solid lines represent the regression line for all sampling dates together, **(a)** $\mathrm{Log}_{10}(y) = [18.953 \times \log_{10}(x)] + 2.245$ ($R^2 = 0.40$, $n = 37$, $p < 0.001$) and **(b)** $\mathrm{Log}_{10}(y) = [1.308 \times \log_{10}(x)] - 1.028$ ($R^2 = 0.67$, $n = 37$, $p < 0.001$). The dashed line represents the regression line for DAS 11, 24, and 171 only, $\mathrm{Log}_{10}(y) = [22.681 \times \log_{10}(x)] + 1.904$ ($R^2 = 0.60$, $n = 23$, $p < 0.001$).

sidered (DAS 59 and 94), 57 % of the variability in gross CH_4 production rates was predicted by the combination of CO_2 emissions, net N mineralization, and net nitrification ($n = 14$, $p = 0.03$).

Gross CH_4 oxidation did not differ significantly among sampling dates (Fig. 2b), averaging 1.1 ± 0.2 mg $C\,m^{-2}\,d^{-1}$ across all measurements ($n = 37$). Rates were marginally significantly higher in rows than in inter-rows ($F_{1,3} = 6.1$, $p = 0.09$). Gross CH_4 oxidation showed a strong positive relationship with gross CH_4 production ($R^2 = 0.67$, $n = 37$, $p < 0.001$). When gross CH_4 production rates exceeded 0.22 mg $C\,m^{-2}\,d^{-1}$, gross CH_4 oxidation rates exhibited a tight $1:1$ relationship with gross CH_4 production rates (slope $= 1.06 \pm 0.05$; $R^2 = 0.95$, $n = 27$, $p < 0.001$, Fig. 4b). Below this threshold of gross CH_4 production, gross CH_4 oxidation was not correlated to gross CH_4 production rates alone, but was strongly correlated to the combination of gross CH_4 production and soil temperature ($R^2 = 0.67$, $n = 10$, $p = 0.02$); oxidation rates exhibited a negative relationship with soil temperature ($R^2 = 0.40$, $n = 10$, $p = 0.05$). Overall, gross oxidation rates were best predicted by the combination of gross CH_4 production rates, soil temperature, and CO_2 emissions ($R^2 = 0.79$, Table 4).

3.4 CO_2 emissions

Carbon dioxide emissions ranged 0.6–10.5 g $C\,m^{-2}\,d^{-1}$ across the entire data set. Emissions trended higher in the rows than in the inter-rows after the corn germinated, but repeated measures ANOVA showed that CO_2 emissions differed significantly among sampling dates ($F_{4,56} = 80.1$, $p < 0.001$) but not between row and inter-row locations (Fig. 1b). The highest CO_2 emissions occurred on DAS 59 and 94, at the height of the growing season, averag-
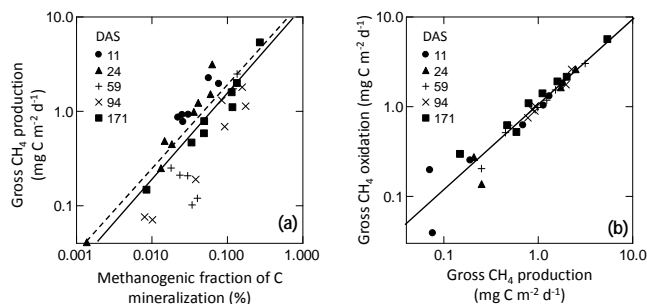
ing 6.7 ± 0.2 g $C\,m^{-2}\,d^{-1}$; the lowest emissions occurred on DAS 11 and 24 at the beginning of the growing season, averaging 2.6 ± 0.2 g $C\,m^{-2}\,d^{-1}$. The variability in CO_2 emissions was poorly explained by environmental and soil variables with soil moisture and soil temperature together as the best, yet weak, predictors ($R^2 = 0.15$, Table 4).

4 Discussion

4.1 N_2O dynamics

Net N_2O fluxes at our study site were comparable to those reported for other fertilized crop fields (Gelfand et al., 2013; Smith et al., 2011; Stevens and Laughlin, 1998; Nangia et al., 2013; Robertson et al., 2000), averaging 1.5 ± 0.2 mg $N\,m^{-2}\,d^{-1}$ across the growing season. Prior field estimates of N_2O yield using $^{15}NH_4$ or $^{15}NO_3$ addition at application rates of 200–300 kg N ha^{-1} span a wide range from 0.06 to 0.7 (Mosier et al., 1986; Rolston et al., 1976, 1978, 1982). In contrast, the N_2O yield varied little throughout the growing season at our site, averaging 0.68 ± 0.02, despite significant differences in both net and gross N_2O fluxes among sampling dates. This is similar to a field estimate of the N_2O yield for a nearby pasture on the same soil type (0.70 ± 0.04; Yang et al., 2011). Soil NO_3^- concentrations in surface soils (0–10 cm depth) were 1–2 orders of magnitude greater in the cornfield than in the pasture, so it is surprising that the N_2O yields were similar. Soil NO_3^- concentration was the strongest predictor of N_2O yield in a US Midwest cornfield soil incubated in the laboratory (Woli et al., 2010).

Other factors such as soil pH, labile C availability, or soil aggregation may have played a more important role in controlling the N_2O yield in our cornfield (Sey et al., 2008).

The best predictors of gross N_2O production and consumption changed over the growing season, likely reflecting the influence of plant–microbial competition for N on N_2O dynamics. This is a novel finding because, to our knowledge, this is the first study that has made repeated measurements of gross N_2O dynamics over the growing season in the presence of active plant-microbial competition for N. When the corn was actively growing, 89 % of the variability in gross N_2O production was explained by soil moisture, soil temperature, net N mineralization, and CO_2 emissions together. In contrast, when the corn was not actively growing, both gross N_2O production and reduction were best predicted by soil CO_2 emissions alone. This may reflect the role of CO_2 emissions as proxy for the availability of labile C as an electron donor for denitrification; during the growing season, the contribution of autotrophic respiration to soil CO_2 emissions obscured this role. Net N mineralization was an explanatory variable for gross N_2O production only during the growing season when plant uptake of N could have limited N_2O production.

Overall, gross N_2O reduction rates were strongly correlated to gross N_2O production rates. This relationship was also observed in a managed grassland with high soil mineral N concentrations and net soil N_2O emissions (Yang et al., 2011), but not in a salt marsh with low mineral N availability where net N_2O uptake by soil occurred (Yang and Silver, 2016). The strong relationship between N_2O production and reduction may have driven the well-constrained N_2O yields in both this study and the managed grassland study because N_2O reduction increased proportionally to N_2O production rates. Additional studies using the trace gas pool dilution technique in the field could elucidate whether or not this relationship holds only in soils with high mineral N concentrations to drive high rates of N_2O production.

4.2   CH$_4$ dynamics

The small and zero net CH_4 fluxes we observed, which are typical of cornfields (Mosier et al., 2006), masked gross CH_4 fluxes which were 2 orders of magnitude greater. Net CH_4 fluxes were generally undetectable because CH_4 oxidation was tightly coupled to methanogenesis, especially at high gross CH_4 production rates. The ability of methanotrophs to adjust activity to match, but not exceed, rates of methanogenesis could reflect oxidation of soil-derived CH_4 at high concentrations near methanogenic microsites but not atmospheric CH_4 at low concentrations in the bulk soil. There are a few mechanisms that could drive a stimulatory effect of high CH_4 concentrations on CH_4 oxidation without increasing oxidation rates at atmospheric concentrations (Benstead and King, 1997). First, high microsite CH_4 concentrations can increase the number of methanotrophs as well as shift

the methanotrophic community composition from high affinity type II methanotrophs, who consume CH_4 at low concentrations, to low affinity type I methanotrophs, who consume CH_4 only at high concentrations, in or near the methanogenic microsites (Bender and Conrad, 1992, 1995). Second, the enzyme affinity of type II methanotrophs can change from high affinity in the presence of atmospheric CH_4 concentrations to low affinity at high CH_4 concentrations, thereby reducing their capability to oxidize CH_4 at low concentrations (Dunfield et al., 1999). Third, high CH_4 availability may be needed to stimulate enzyme synthesis (Bender and Conrad, 1992, 1995; Nesbit and Breitenbeck), and thus methanotrophic activity may be induced only near methanogenic microsites and not in the bulk soil. Additional studies investigating gross CH_4 dynamics in soil aggregates or through the soil profile could provide insight into the mechanisms coupling CH_4 production and consumption. Regardless of the mechanisms, our observations suggest that using in situ methods that preserve spatial variability in soil CH_4 concentrations and allow for the occurrence of both CH_4 production and oxidation, such as the trace gas pool dilution technique, is important for accurately characterizing CH_4 dynamics in soil.

Gross CH_4 production rates were strongly positively correlated with the methanogenic fraction of C mineralization, an index of anaerobic soil microsites where electron acceptors are depleted relative to C supply (von Fischer and Hedin, 2007). Von Fischer et al. (2007) found that the methanogenic fraction was constrained below 0.04 % and gross CH_4 production rates below $1\,mg\,C\,m^{-2}\,d^{-1}$ in tropical and temperate forest soils with less than 60 % water-filled pore space. Though the slope of the relationship between gross CH_4 production rates and the methanogenic fraction observed here was similar to that reported by von Fischer et al. (2007), the maximum methanogenic fraction observed here was nearly 7 times greater. The maximum gross CH_4 production rate was also an order of magnitude greater than the maximum rate of $0.5\,mg\,C\,m^{-2}\,d^{-1}$ reported by von Fischer and Hedin (2002) for a range of unsaturated upland soils in which net CH_4 fluxes were near zero (-0.2 to $0.2\,mg\,C\,m^{-2}\,d^{-1}$). This suggests a higher potential for the development of methanogenic microsites in these drained peatland soils, which are rich in C.

The near-zero net CH_4 fluxes measured in our cornfield are consistent with other studies in agricultural systems, but the relatively high gross CH_4 oxidation rates we documented challenge the paradigm that agricultural soils have low potential for CH_4 oxidation compared to unsaturated soils in natural ecosystems (Bender and Conrad, 1994; Koschorreck and Conrad, 1993; Mosier et al., 1991; Nesbit and Breitenbeck, 1992; Zhuang et al., 2013). Our soils had high NH_4^+ and NO_3^- concentrations, which did not limit the ability of methanotrophs to completely consume soil-derived CH_4. Undisturbed soils in which CH_4 production and consumption occur simultaneously could behave differently than manipu-

lated soils incubated in the laboratory under conditions to isolate CH_4 oxidation from CH_4 production, and vice versa. Application of the trace gas pool dilution technique to other agricultural fields could reveal whether or not the tight coupling of CH_4 production and consumption rather than low rates of CH_4 production and oxidation could be responsible for the general observation of small and near-zero net CH_4 fluxes in agricultural ecosystems. A greater understanding of limitations on gross CH_4 oxidation under field conditions is needed to accurately predict how land use change will alter soil–atmosphere CH_4 exchange and to better manage agricultural soils to be atmospheric CH_4 sinks.

Our data provide circumstantial evidence that plants could mediate gross CH_4 dynamics in upland soil both directly and indirectly. An increase in plant C inputs to the soil over the growing season may have directly driven a steady, though not statistically significant, increase in rates of methanogenesis by providing more C substrate to support methanogenesis. Both gross CH_4 production and oxidation rates were approximately 2.5 times greater at DAS 171 compared to DAS 11. This trend in gross CH_4 fluxes cannot be explained by changes in environmental variables such as soil temperature, which peaked in the middle of the growing season, and soil moisture, which decreased over the growing season. However, von Fischer and Hedin (2007) showed that methanogenesis was not limited by C supply in a wide range of upland soils, but rather, it was limited by the number of anaerobic microsites that could support methanogenesis in the soils. Our data also support the latter mechanism controlling methanogenesis: we observed a strong relationship between gross CH_4 production and the methanogenic fraction of C mineralization (an index of the abundance of anaerobic soil microsites) on DAS 11, 24, and 171, when root respiration likely did not contribute significantly to CO_2 effluxes. We also observed higher gross CH_4 production and oxidation rates in rows than in inter-rows, suggesting that plants could indirectly control methanogenesis through rhizosphere priming, fueling biological O_2 demand for C mineralization (Zhu et al., 2014) that creates a greater number of anaerobic soil microsites supporting methanogenesis.

5 Conclusions

Our study demonstrates that the anaerobic processes of N_2O reduction to N_2 and methanogenesis can play important roles in mediating soil–atmosphere greenhouse gas fluxes in upland crop field soils where these processes have previously been discounted. Moreover, despite high soil NO_3^- and NH_4^+ concentrations that theoretically inhibit N_2O reduction to N_2 as well as CH_4 oxidation, gross N_2O reduction rates were approximately one-third of gross N_2O production rates and CH_4 oxidation kept pace with methanogenesis that reached relatively high rates for unsaturated soil. Our field measurements of gross N_2O and CH_4 fluxes thus challenge our current understanding of the controls on the production and consumption of N_2O and CH_4 in upland soils. The strong correlations that gross N_2O and CH_4 fluxes exhibited with soil characteristics and soil N cycling process rates can help guide controlled studies to investigate the controls on the processes that lead to the production and consumption of N_2O and CH_4. A better understanding of the controls on these processes can help refine modeling efforts to characterize the effects of anoxic microsites in unsaturated soil on greenhouse gas emissions (Riley et al., 2011) and also inform land management decisions to mitigate soil greenhouse gas emissions from crop fields.

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