Soil O_2 controls denitrification rates and N_2O yield in a riparian wetland

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[1] Wetland soil oxygen (O_2) is rarely measured, which limits our understanding of a key regulator of nitrogen loss through denitrification. We asked: (1) How does soil [O_2] vary in riparian wetlands? (2) How does this [O_2] variation affect denitrification rates and end products? and (3) How does [O_2] variation and previous exposure to O_2 affect trace gas fluxes? We collected a continuous seven-month record of [O_2] dynamics in a "wet" and "dry" riparian zone. In April 2009, soil [O_2] ranged from 0 to 13% and consistently increased with increasing distance from the stream. [O_2] gradually declined in all sensors until all sensors went anoxic in early September 2009. In mid-fall, a dropping water table increased soil [O_2] to 15–20% within a 2–3 day period. We measured denitrification using the Nitrogen-Free Air Recirculation Method (N-FARM), a direct measurement of N_2 production against a helium background. Denitrification rates were significantly higher in the wetter areas, which correlated to lower O_2 conditions. Denitrification rates in the drier areas correlated with [O_2] in the early spring and summer, but significantly decreased in late summer despite decreasing O_2 concentrations. Increasing [O_2] significantly increased core N_2O production, and therefore may be an important control on nitrous oxide yield. Field N_2O fluxes, however, were highly variable, ranging from 0 to 800 ug N m^{-2} hr^{-1} with no differences between the wet and dry sites. Future research should focus on understanding the biotic and abiotic controls on O_2 dynamics, and O_2 dynamics should be included in models of soil N cycling and trace gas fluxes.

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1. Introduction

[2] Denitrification is the microbial metabolism that oxidizes organic carbon while reducing nitrate (NO_3^-) under hypoxic or anaerobic conditions. Since the end product of the reaction is the dominant atmospheric gas, N_2, the process is notoriously difficult to measure despite decades of methodological development [*Groffman et al.*, 2006]. Therefore, denitrification remains one of the greatest uncertainties in nitrogen mass balance studies at ecosystem [*Steinheimer et al.*, 1998], regional [*van Breeman et al.*, 2002] and global [*Galloway et al.*, 2008; *Gruber and Galloway*, 2008] scales.

[3] Point-scale measurements of denitrification that have been made in aquatic and terrestrial ecosystems indicate that a variety of ecosystems denitrify at highly variable rates. However, constrained mass balance studies suggest that approximately 50% of the 270 Tg N added annually to terrestrial ecosystems crosses the threshold into aquatic ecosystems [*Seitzinger et al.*, 2006]. This points to the importance of aquatic-terrestrial interfaces for removing N; however, the controls and function of these dynamic transitional zones remains poorly characterized. Riparian zone wetlands are one class of these transitional areas, and are often considered to be "hotspots" for biogeochemical processes, including denitrification [*Vidon*, 2010; *Mayer et al.*, 2007]. As such, they are important zones for intercepting NO_3^- before it moves into aquatic ecosystems where it can cause downstream eutrophication and harmful algal blooms [*Howarth et al.*, 2011; *Paerl et al.*, 2002]. Riparian zones are defined in part by their high degree of spatial and temporal variation in denitrification [*Harms and Grimm*, 2008] and greenhouse gas (GHG) fluxes [*DeSimone et al.*, 2010]. Understanding how this temporal and spatial heterogeneity in biogeochemical functions translates into patterns of nutrient removal remains a key challenge to modeling and predicting biogeochemical dynamics linked aquatic and terrestrial ecosystems [*Grimm et al.*, 2003; *McClain et al.*, 2003].

[4] During denitrification, a fraction of the NO_3^- is not fully reduced and escapes as nitrous oxide, N_2O. N_2O is the most potent of the three biogenic greenhouse gases (including methane, CH_4, and carbon dioxide, CO_2) with a radiative forcing ~300× that of CO_2. Atmospheric N_2O has been increasing due to increased reactive N (e.g., NO_3^-) from agricultural activities [*Galloway et al.*, 2004; *Davidson*, 2009]. Higher NO_3^- concentrations, low pH and the presence of O_2 tend to promote increased N_2O fluxes [*Firestone et al.*, 1980; *Bollmann and Conrad*, 1998; *Robertson and Groffman*,

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2007]. The ability to reduce N_2O is encoded by the *nosZ* gene, which is more sensitive to O_2 than other denitrification genes [*Richardson et al.*, 2009]. The N_2O mole fraction (N_2O / [N_2O + N_2]), also called the N_2O yield, is use to express the proportion of gaseous loss to N_2O via denitrification. N_2O yields are generally low in wetlands (<0.1), but can be considerably higher in upland soils (≥0.4) [*Beaulieu et al.*, 2011; *Schlesinger*, 2009]. There is great interest in and uncertainty about N_2O yields in transitional zones such as riparian buffers [*Groffman et al.*, 1992; *Reay et al.*, 2009]. N_2O is also produced by nitrification, a microbial metabolism that converts ammonium (NH_4^+) to NO_3^-. The complex interactions between producing and consuming processes make field-level N_2O fluxes notoriously difficult to interpret. Field-level N_2O fluxes are tied to water-filled pore space (WFPS) [*Pathak and Nedwell*, 2001], which is also linked to O_2 dynamics.

[5] In addition to N_2O, microbes are responsible for the production and consumption of methane (CH_4) and carbon dioxide (CO_2). CH_4 is produced through methanogenesis, another form of anaerobic microbial metabolism. Methanogenesis tends to occur once all other electron donors (e.g., O_2, nitrate) are exhausted. Methanogenesis rates can be enhanced by labile substrates [*Glatzel et al.*, 2004; *Yavitt and Lang*, 1990] and warmer seasons [*Gleason et al.*, 2009; *Yavitt et al.*, 2000]. Ecosystem-level controls on fluxes include water table fluctuations [*Altor and Mitsch*, 2006; *Gleason et al.*, 2009] and plant productivity and vascular transport [*Whiting and Chanton*, 1993]. Stable water levels promote larger CH_4 fluxes over variable or "pulsing" hydrology [*Altor and Mitsch*, 2006], suggesting a potential connection to O_2 and more oxidizing conditions under pulsing hydrology. However, work in tropical rain forest soils has suggested that CH_4 fluxes can remain high even at 9–19% soil O_2 [*Teh et al.*, 2005].

[6] While O_2 is generally considered the dominant proximal control of the microbial metabolisms that perform denitrification and produce and consume the three biogenic GHGs, O_2 is seldom measured in terrestrial ecosystems [*Silver et al.*, 1999]. Consequently, our understanding of how soil [O_2] varies is limited. This restricts our understanding of how soil O_2 variation affects ecosystem processes including GHG production [*Whalen*, 2005], nutrient dynamics [*Crawford*, 1992], and redox [*Pett-Ridge and Firestone*, 2005]. The direct effects of O_2 on denitrification have been tested in laboratory settings, often on cultures isolated from soils or from soil "slurries" [*Firestone et al.*, 1980; *Fazzolari et al.*, 1998; *Parkin and Tiedje*, 1984; *Sexstone et al.*, 1985]; however, there have been few studies that have evaluated O_2 controls on intact core denitrification (but see *Parkin and Tiedje* [1984]) or in situ GHG fluxes.

[7] In this study we asked: 1) How does soil [O_2] vary in riparian wetlands? 2) How does this [O_2] variation affect denitrification rates and end products? and 3) How does seasonal variation in [O_2] affect greenhouse gas fluxes? We hypothesized that soil [O_2] would be spatially and temporally dynamic, with concentrations depending on proximity to the stream, which influences water table and also depend on season, which controls plant and microbial consumption of O_2 and soil moisture content. We further hypothesized that areas and periods of decreased soil [O_2] would have increased denitrification rates and CH_4 production, but expected that that N_2O fluxes would be highest in areas with the most variable O_2 levels. To answer these questions, we tested five hypotheses: 1) Soil O_2 was dynamic, with [O_2] dependent on proximity to the stream and water table; 2) Soil [O_2] would vary seasonally; 3) Areas of decreased soil [O_2] would have increased denitrification rates; 4) Decreasing soil [O_2] would increase N_2O fluxes; and 5) Biogenic greenhouse gases, including CH_4 and N_2O, would increase under decreased [O_2] conditions. Though we already understand how O_2 affects denitrification from microcosm studies, this study expands our understanding to how field-level fluctuations in soil [O_2] and subsequent differential exposure of the in situ microbial community to soil O_2 can control denitrification rates and end products. More practically, previous studies have shown that O_2 effects on denitrification are strong and immediate, suggesting that continuous measurements of in situ [O_2] levels may be a useful tool temporal scaling of point measurements.

2. Materials and Methods

2.1. Study Sites

[8] Our study site was located on the property of the Cary Institute of Ecosystem Studies in Millbrook, NY, (USA) adjacent to Gifford Stream, a first order, groundwater-fed tributary of the East Branch of Wappingers Creek. Vegetation in the area is predominantly mature sugar maples (*Acer saccharum*) mixed with younger ash (*Fraxinus sp.*) and birch (*Betula lenta*). The nearby fields were in agricultural production through the middle of the 20th century, but have been managed as mowed fields in more recent decades. The areas draining into our research site are gravelly loam soils (Hoosic series) derived from schist [*Soil Survey Staff*, 2006].

[9] Our sampling site was a 2 m × 4 m plot of riparian wetland immediately adjacent to the stream (Figure 1a). The site was characterized by wetland plants including skunk cabbage (*Symplocarpus foetidus*) and jewelweed (*Impatiens capensis*). Soils were characterized by a 10-cm organic horizon, underlain by outwash from the adjacent stream (Fluvaquentic Humaquept, *Soil Survey Staff* [2006]). These soils were water-saturated from early winter through spring, but dried up considerably during the growing season. The site was divided into the "wet" zone, closer to the stream, which was more fully inundated though it did not have standing water, and the "dry" zone, which had lower soil moisture, but was only 1-m from the "wet" area.

[10] Five intact soil cores (2.4 cm diameter × 8 cm length) were collected from both areas monthly and immediately taken to the lab for analysis. Samples were taken by driving a piece of sharpened PVC pipe, split down the side and then taped together, into the soil. After removing the pipe from the soil, the tape was removed and intact cores could be accessed.

2.2. Soil O_2 and Moisture Measurements

[11] Four Apogee diffusion-head soil O_2 sensors (SO-100 series, Apogee Instruments, Logan UT; accuracy <0.02%/day, repeatability ±0.001% O_2) per plot were buried with the diffusion heads at 6-cm. Sensors were spaced approximately 0.5 m apart from the upper portion of the dry zone (sensor #1)

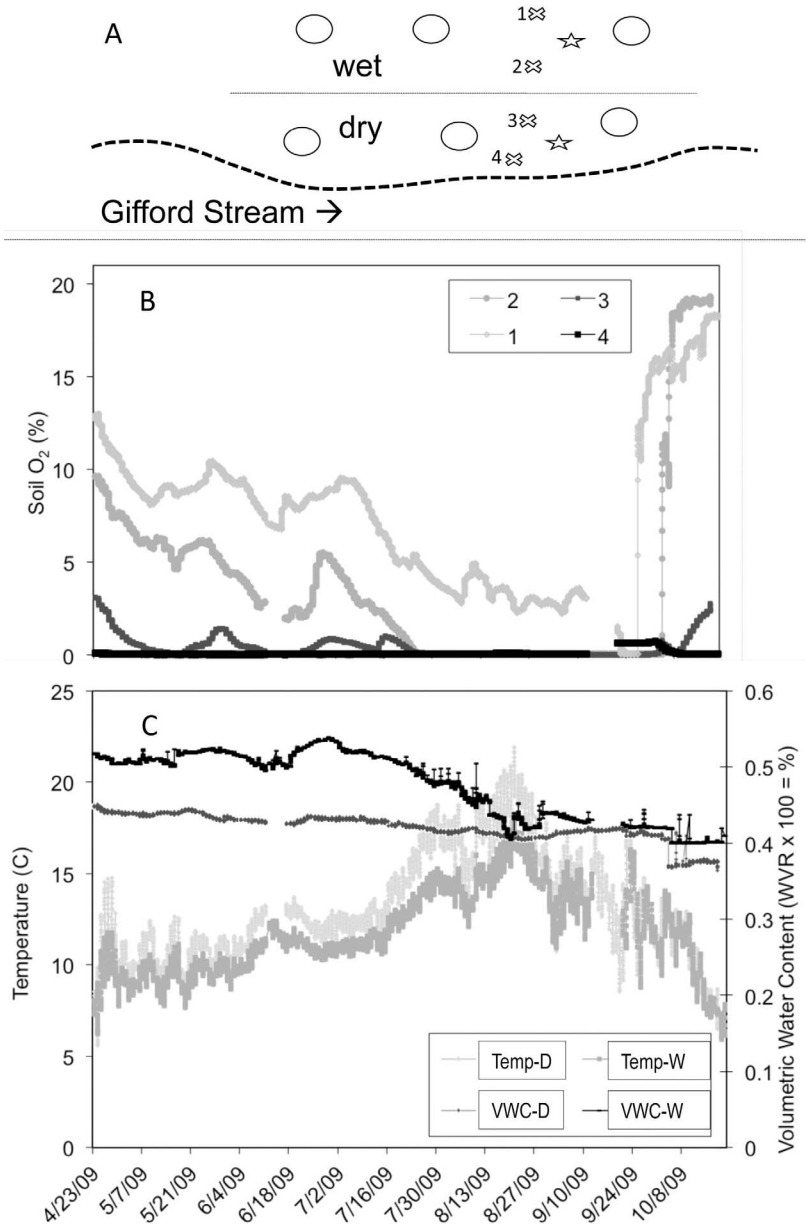

Figure 1. (a) Plot layout for the Gifford Riparian Wetland, which contained sensors for (b) soil oxygen, soil moisture and (c) temperature. Grey circles represent the location of static gas flux chambers. Numbered "x" symbols represent the location of O_2 sensors, with seasonal O_2 concentrations for the sensors in Figure 1b. Stars represent the soil moisture and temperature sensors with corresponding data in Figure 1c. "Temp-D" and "VWC-D" refer to the temperature and volumetric water content sensors from the dry zone; the same abbreviations followed by "−W" applies to the wet zone sensors.

to the lower portion of the wet zone (sensor #4) (Figure 1a). O_2 sensors #1 and 4 also recorded soil temperature. The sensors were controlled by a Campbell Scientific Data logger (CR-800; Campbell Scientific, Logan UT), which also controlled two Campbell CS616 water content reflectometers to measure soil moisture in the wet and dry areas (Figure 1c). Sensors were calibrated prior to deployment, and were set to collect soil [O_2] and volumetric water content (VWC) every hour.

2.3. Measuring Denitrification With the Nitrogen-Free Air Recirculation Method (N-FARM)

[12] Our N-FARM flow-through core measurement system is described by *Burgin et al.* [2010] and is based on those built and described by others [*Butterbach-Bahl et al.*, 2002; *Swerts et al.*, 1995]. Cores were encased in glass bottles with gas-tight lids connected to a gas-tight flow injection system built from Swagelok connections (Swagelok, Crawford Fitting Co., Solon, OH) inline with a Shimadzu GC8A gas

Table 1. Average N_2 and N_2O Fluxes Measured From Cores in Different Months at Different O_2 Concentrations

		N_2 Flux μg N m^{-2} hr^{-1}		N_2O Flux μg N m^{-2} hr^{-1}	
Month in 2009	Percent O_2	Dry	Wet	Dry	Wet
May	0	1657 ± 201	**2053 ± 216**[a]	6.3 ± 5.6	**6.0 ± 0.6**
	5	**907 ± 131**	1076 ± 132	**28.5 ± 14.1**	11.6 ± 2.9
June	0	2331 ± 168	**2644 ± 146**	56.8 ± 17.8	**−30.6 ± 23.6**
	5	**1972 ± 455**	1486 ± 205	**31.0 ± 6.8**	35.5 ± 6.9
	10	1454 ± 437	1233 ± 272	31.3 ± 13.1	48.5 ± 16.1
July	0	2725 ± 195	**2813 ± 289**	5.5 ± 3.2	**3.5 ± 2.1**
	5	**1410 ± 245**	1662 ± 160	**45.0 ± 15.1**	20.5 ± 1.7
August	0	1305 ± 204	**2489 ± 344**	0.0 ± 0.0	**32.5 ± 29.5**
	5	**926 ± 134**	1577 ± 177	**51.3 ± 38.3**	67.3 ± 31.0
September	0	926 ± 207	**2377 ± 149**	0.0 ± 0.0	**0.0 ± 0.0**
	5	**1002 ± 194**	1268 ± 102	**137.5 ± 24.4**	13.8 ± 11.8
	10	470 ± 88	857 ± 145	58.0 ± 10.1	10.0 ± 2.0
October	0	525 ± 131	**2560 ± 300**	0.0 ± 0.0	**0.0 ± 0.0**
	20	**353 ± 97**	997 ± 259	**82.5 ± 15.1**	49.6 ± 32.6

[a]The O_2 concentration based on in situ sensor information at the time of sample collection is denoted by boldface text.

chromatograph (GC; Kyoto, Japan) with a thermal conductivity detector (TCD) to measure N_2, CO_2, and O_2 and an electron capture detector (ECD) to measure N_2O. The glass jars were housed in a Plexiglas box, which was filled with water over the top of the lids to aid in preventing air leaks into the jars. The system has a total of 10 jars; for each experiment, four cores from each the wet and dry areas were analyzed, and two jars remained empty as blanks. The advantages and disadvantages of the N-FARM have been addressed previously [*Burgin et al.*, 2010], but briefly, the major advantage of our system is the ability to precisely measure very small changes in [N_2] and [N_2O] (detection limits described below) on relatively large soil samples (whole, intact cores). The major limitation of this method is the very low throughput of the analysis; it generally takes 7–10 days to analyze eight cores (including "killed" cores, see below for detail), depending on the number of [O_2] treatments and rates of denitrification.

[13] Once cores were loaded into jars, a gas mixture of helium and oxygen (HelOx), with O_2 concentrations at 0% (ultra high purity He), 5, 10 and 20% was used to replace the existing N_2 containing atmosphere. As in other systems, the incubation gas was repeatedly injected into the cores and then removed by very low vacuum (500 torr; K. Butterbach-Bahl, personal communication, 2009), which switched with a slight over-pressurization (860 torr) at 90-s intervals. Methods development tests showed that a 14-h vacuum/flush cycle on 90-s intervals resulted in 560 switches, creating a long and effective serial dilution and evacuation of the headspace, which removed all traces of atmospheric N_2 thereby negating the large background interference that would dilute the signal of denitrification we were trying to measure. After the 14-h flush/vacuum cycle, the HelOx gas was flushed through the cores (with no vacuum) for an additional 2 h to ensure the cores were at equilibrium.

[14] Once cores were done flushing, the system was set to "incubate" mode wherein gases that were produced by the cores accumulated in the jars. Gases were sampled at time intervals that were dependent on the rates of production, but were generally 5–6 h for low [O_2] incubation conditions and 12–24 h for high [O_2] incubations. For each month, both the wet and dry site cores were run at the lowest recorded [O_2] from the site data (Figure 1, generally 0% O_2; Table 1) and highest recorded [O_2] (Figure 1, O_2 varied by season; Table 1). In June and September, the same cores were run at multiple O_2 concentrations to examine the effects of different O_2 concentrations on denitrification activity.

[15] To sample the headspace of the cores, 50-mL (approximately 1/10th the volume of one core) was released from a pressurized chamber into the core, slightly over-pressurizing the headspace. After mixing, this over-pressurization was released and allowed to flush the system lines and loops, which contained a total volume of approximately 10 mL. The sample from the loop was then transferred onto the GC columns. Flux rates were calculated by regression of N_2-N versus time of incubation corrected for the blanks and any dilution that occurred via sampling. These were expressed in areal terms by dividing by the area of the core cylinder.

[16] To ensure that measured N_2 production was coming from denitrification and not from leakage or degassing from small soil pores, we used the rate of N_2 production in "killed" cores to correct for any background N_2 that may not have been flushed from the soil pore space. After being run as "live" for ambient denitrification rates, the same cores were killed by autoclaving three times over two days at 134°C for 60 min. Killed cores were only incubated at 0% O_2 (anoxic conditions) which would maximize any potential denitrification. The rates of N_2 flux from killed cores were very low (50.8 ± 8.1) in comparison to the live cores (∼500–3000 μg N m^{-2} h^{-1}), ensuring we were measuring a strong signal of denitrification activity.

2.4. Soil-Atmosphere Trace Gas Flux Methods

[17] Our field trace gas flux method was similar to that described previously [*Bowden et al.*, 1991]. We used 287 mm-dia, 5 cm-tall PVC cylinders for chambers with gas sampling ports in the center of the chamber lid. These lids were placed on PVC base rings of the same size, which were permanently installed at the site. Ten mL gas samples were collected using a syringe at 0, 10, 20, and 30 min after the placement of the chamber lids onto the bases. Samples were transferred to evacuated glass vials which were stored at room temperature before analysis by gas chromatography with ECD (N_2O), TCD (CO_2) and flame ionization detection (FID, CH_4). Fluxes were calculated from the linear rate of

Table 2. Monthly Soil NO_3^- and NH_4^+ Concentrations at Dry and Wet Sampling Sites

	Dry Zone		Wet Zone	
	NO_3^-	NH_4^+	NO_3^-	NH_4^+
	mg N kg Dry Soil^{-1}			
May	0.3 ± 0.1	3.2 ± 0.1	BDL[a]	3.2 ± 0.6
June	0.4 ± 0.1	2.2 ± 0.6	N/A[b]	N/A
July	BDL	6.0 ± 0.3	BDL	4.0 ± 0.3
August	BDL	3.1 ± 0.2	BDL	1.8 ± 0.3
September	0.3 ± 0.1	3.1 ± 0.1	BDL	1.1 ± 0.1
October	N/A	N/A	2.6 ± 0.4	0.8 ± 0.1

[a]Below detection limit.
[b]Not available.

change in gas concentration, corrected for the chamber volume, outside temperature during the collection and surface area of the underlying soil. We collected samples monthly from three chambers in each the wet and dry zones of the Gifford Riparian Wetland.

2.5. Soil Characteristics

[18] Composite soil samples were taken every month from the wet and dry zones (Table 2). Soil organic matter content was determined in August 2009 by loss on ignition at 450°C for 4 h. The wet zone soils were 7.2 ± 0.7% carbon, whereas the dry zone soil was 7.6 ± 0.2% carbon. Concentrations of inorganic N (NO_3^- and NH_4^+; Table 2) were determined by extraction with 2M KCl and colorimetric analysis with a Lachat Flow Injection Analyzer.

2.6. Statistical Analysis

[19] Mean values of the response variables (gas fluxes) were calculated from four replicate cores or three replicate field gas flux chambers. When appropriate, fluxes were log transformed to normalize data. A one-way Analysis of Variance (ANOVA) was conducted to test for differences in N_2 or N_2O flux between the wet versus dry zones. The effects of site (e.g., wet versus dry zones) and month of measurement on greenhouse gas dynamics were assessed with a two-way repeated measures ANOVA (with interactions) of plot means from three replicate gas flux chambers from each sampling date. Effects with a $p < 0.05$ were determined to be significant. ANOVA was performed using JMP 9.0.

3. Results

[20] Soil [O_2] ranged from 0 to 20% depending on the proximity to the stream and the season (Figure 1). Soil O_2 was consistently low in the area closest to the stream (sensor 4) and increased further from the stream (sensor 1, Figure 1b). Soil [O_2] was also higher in the spring, and decreased over the course of the late spring and summer. All four sensors were briefly anoxic for a week in late September, after which occurred a very fast (<3 days) switch to completely oxic conditions in the two sensors furthest from the stream (sensors 1 and 2, Figure 1b), with a more muted increase in [O_2] in sensor 3. The volumetric water content (VWC) of the wet area was consistently ~5% higher that that of the dry area throughout much of the spring and summer (Figure 1c). The VWC of the two areas converged in late summer (September) and remained similar until early

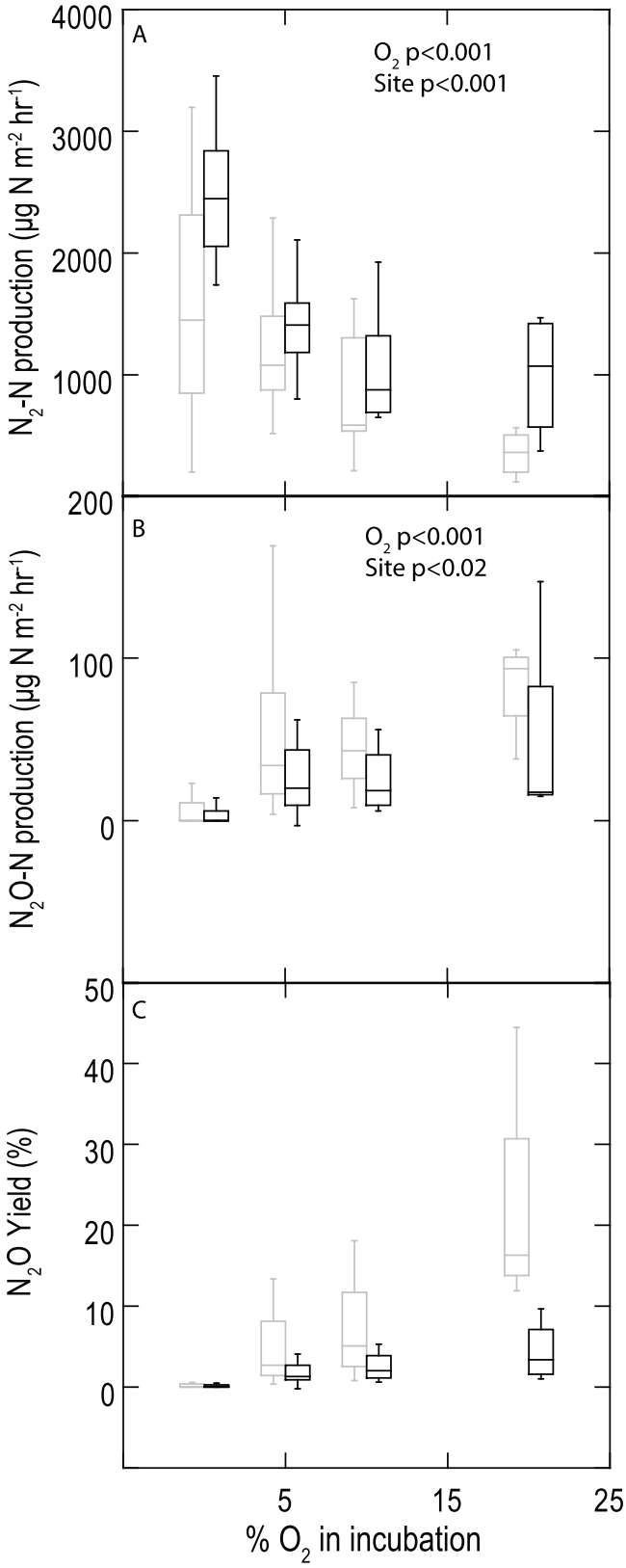

Figure 2. (a) N_2 production, (b) N_2O production, and (c) N_2O yield (expressed as a percentage) from wet (black) and dry (gray) zone cores at different O_2 concentrations. Whiskers denote the minimum and maximum measured values and the box's middle line denotes the median value.

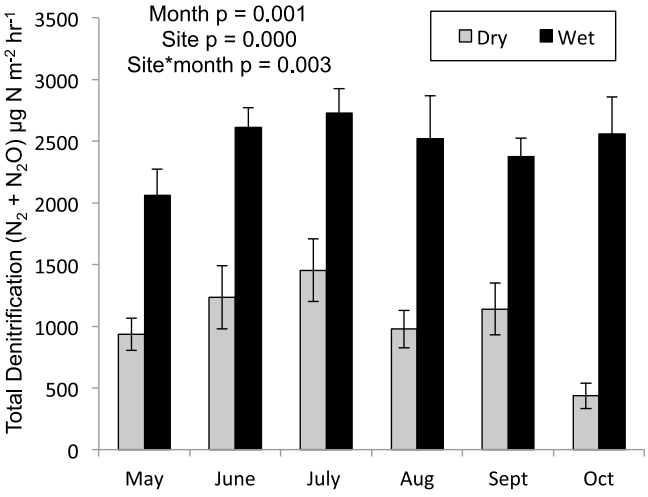

Figure 3. Total denitrification over a six-month period in wet and dry zone soils. Bars represent the mean denitrification rate (N_2 + N_2O) measured in four cores (±1 standard error of the mean) per zone at field appropriate O_2 concentrations in each month. Rates for N_2 and N_2O production are in Table 2.

October when the VWC of the dry area quickly dropped, coincident with the rapid increase in soil [O_2] (Figures 1b and 1c). The wet area was also consistently 1–2°C cooler than the dry area for most of the spring and summer before converging in early fall (Figure 1c). In the period before the rapid [O_2] switch in late September, soil [O_2] was significantly correlated with VWC in the dry site (dry sensor 1 r = 0.92, sensor 2 = 0.93), and had a much weaker correlation in the wet site (sensor 3 r = 0.51, sensor 4 r = −0.51). Soil [O_2] was also significantly correlated with soil temperature in the dry site (dry sensor 1 r = −0.83, sensor 2 = −0.82), and again had a much weaker correlation in the wet site (sensor 3 r = −0.54, sensor 4 r = 0.57). In both sites, however, soil temperature and VWC were significantly correlated (dry r = −0.88; wet r = −0.80), indicating that the effects of VWC (soil moisture) and temperature on [O_2] dynamics cannot be separated.

[21] N_2 production was generally 5–10× greater than N_2O production from cores collected in the "wet" and "dry" zones (Figures 2b and 2c). Increasing [O_2] significantly decreased N_2 production ($F_{3,104}$ = 21.5; p < 0.001) and significantly increased N_2O production ($F_{3,108}$ = 20.8; p < 0.001) in both the wet and dry sites (Figure 2). The wet site produced significantly more N_2 than the dry site (Figure 2a; $F_{1,104}$ = 9.4; p = 0.003). In general, the dry site cores produced more N_2O than the wet site cores, though the difference was not statistically significant (Figure 2b; $F_{1,108}$ = 2.1; p < 0.15). N_2O yield, which is a composite of both N_2 and N_2O production, ranged from ∼0–36% in the dry site and 0–6.5% in the wet site. N_2O yield was consistently higher in the dry zone compared to the wet zone and increased with increasing O_2 (Figure 2c).

[22] Denitrification rates, calculated as the sum of N_2 and N_2O fluxes and corrected for field-appropriate O_2 concentrations (Table 1), were generally 2× higher in the wet zone compared to the dry zone (Figure 3; $F_{3,111}$ = 11.4; site p = 0.000; month p = 0.001). The presence of a significant interaction term between month and site (p = 0.003) indicates that the difference in denitrification rates between the wet and dry areas is not consistent across time; this is apparent by comparing the difference in the sites in July and October. The major factor driving this difference in denitrification rates is the soil [O_2] (Figure 1b). Dry zone N_2 fluxes ranged form a low of 353 μg N m^{2-} hr^{-1} in October to a high of 1972 μg N m^{2-} hr^{-1} in June (Table 2). Wet zone N_2 fluxes were relatively uniform, ranging from a low of 2053 μg N m^{2-} hr^{-1} in May to a high of 2813 μg N m^{2-} hr^{-1} in July (Table 2). The maximum denitrification for the wet zone was 2813 μg N m^{2-} hr^{-1} (July) and 2725 μg N m^{2-} hr^{-1} (July) for the dry zone, indicating that both zones could reach similar denitrification potentials under the optimal conditions (Table 2).

[23] CO_2 fluxes were significantly higher in the wet site compared to the dry site (p = 0.02 for effect of site; p = 0.49 for sample month; p = 0.76 for month*site) and showed a clear seasonal pattern in the wet zone with maximal fluxes of 37 mg C m^{2-} hr^{-1} in July and much lower fluxes in the spring and fall (Figure 4a). This pattern was absent, however, in the dry zone where CO_2 fluxes were much more consistent between months, often around 10 mg C m^{2-} hr^{-1} (Figure 4a). N_2O fluxes ranged from 0–0.8 ng N m^{2-} hr^{-1} and did not correlate with season or site, and were often near zero in both the dry and wet zones (Figure 4b). CH_4 fluxes ranged from 0–258 μg C m^{2-} hr^{-1} and were similarly variable with no consistent seasonal pattern (Figure 4c). In general, the wet and dry zone had similar CH_4 fluxes with the exception of June and July in which the dry zone had a significantly higher flux than the wet zone (Figure 4c).

4. Discussion

4.1. Improved Estimates of Denitrification in Forests

[24] Our results demonstrate that the combination of our N-FARM technique [*Burgin et al.*, 2010; M. V. Kulkarni et al., A comparison of denitrification rates as measured using direct flux and 15N tracer methods in northeastern forest soils, submitted to *Biogeochemistry*, 2011] and an understanding of field-level variation in soil O_2 dynamics (Figure 1b) yields better constrained estimates of in situ denitrification rates (Figure 3). Direct measurement of N_2 production without any inhibitors or supplemental NO_3^- stimulation is rare, especially in soils [*Groffman et al.*, 2006]. The high atmospheric background of N_2 necessitates that these measurements be made in enclosure-type systems, which introduce some of their own limitations, including sampling disturbance effects and lag time between sampling and measurement. In spite of these limitations, we found significant differences in the denitrification rates between the wet and dry zone soils across O_2 levels (Figure 2).

[25] The range of denitrification rates (353–2813 μg N m^{-2} hr^{-1}) that we measured under [O_2] matched to field conditions (Figure 1b) corresponds to 22.4–67.5 mg N m^{-2} day^{-1}. This is comparable to the range of rates we measured at these same sites in 2008 [*Burgin et al.*, 2010], as well as those documented for other riparian ecosystems, including 19 mg N m^{-2} day^{-1} in a Georgia hardwood riparian zone [*Lowrance et al.*, 1995] and 3–82 mg N m^{-2} day^{-1} in a Pennsylvania hardwood riparian zone [*Watts and Seitzinger*, 2000]. Extrapolating monthly rates (Figure 3) yields a range of 45–109 kg N ha^{-1} $season^{-1}$ (assuming a 184 d season),

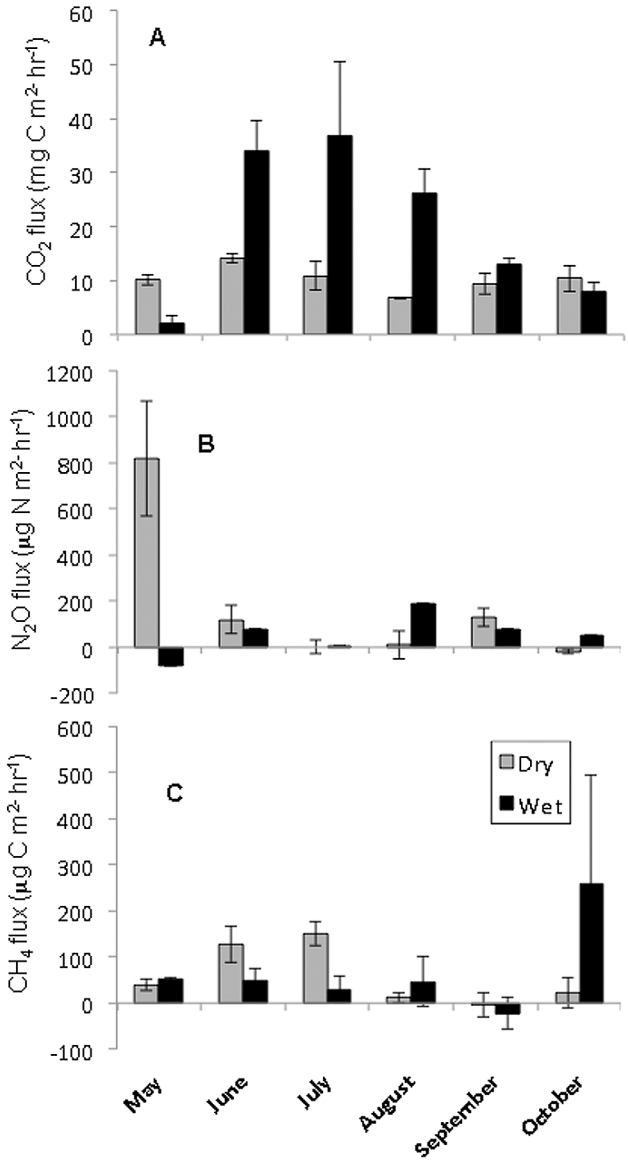

Figure 4. Field fluxes of (a) carbon dioxide, (b) nitrous oxide, and (c) methane for dry (gray bars) and wet (black bars) zone soils collected once per month. Bars are an average of three replicate static chambers ±1 standard error of the mean.

which is comparable to the range measured in Tuttlingen (Germany) forests (14–94 kg N ha^{-1} $year^{-1}$) using a similar system to directly measure N_2 and N_2O [*Dannenmann et al.*, 2008].

[26] While comparable to estimated denitrification ranges from other studies, our scaled range of 45–109 kg N ha^{-1} $season^{-1}$ is high compared to the amount of denitrification thought to occur in Northeastern deciduous forests. Although mass balance studies frequently show large amounts of missing N, denitrification is thought to be unimportant to northeastern forests because early studies suggested that N gas fluxes were low in the region [*Bowden and Bormann*, 1986; *Davidson and Swank*, 1990]. These studies, however, only measured N_2O production across a limited number of sites. More recent studies using improved methodology for measuring N_2 fluxes, including the data we present herein, indicate that N_2 is the dominant end product of denitrification [*Dannenmann et al.*, 2008]. Our results agree with this finding and strengthen the idea that N_2O fluxes may not be a good predictor of overall denitrification activity.

4.2. Understanding O_2 Dynamics in Riparian Wetlands

[27] The basic question asked herein is: How does soil O_2 vary in riparian wetlands? Though O_2 has long been recognized as an important driver for determining microbial metabolism, relatively little is known about field-level O_2 dynamics in soils [*Burgin et al.*, 2010; *Liptzin et al.*, 2011; *Silver et al.*, 1999]. We found support for our hypotheses that: 1) soil O_2 was dynamic, with O_2 concentrations dependent on proximity to the stream and water table, and 2) soil O_2 would vary seasonally (Figure 1). While few studies have measured soil O_2, those that have find [O_2] is dynamic under varying hydrologic conditions resulting from connection to a water table [*Burgin et al.*, 2010], seasonal water table dynamics [*Faulkner and Patrick*, 1992; *Megonigal et al.*, 1993] or precipitation [*Liptzin et al.*, 2011; *Silver et al.*, 1999]. Despite small differences in water content between the dry and wet zones (Figure 1b), water dynamics are also clearly linked to soil [O_2] variation in the Gifford Riparian Wetland (Figure 1a).

[28] The most striking observations from the soil O_2 record were the low values at high temperature and relatively low water content in mid summer, and the rapid shift from complete anoxia to oxic conditions, which occurred in late September over a period of less than three days (Figure 1). The mid-summer pattern of decreasing [O_2] was likely driven by plants, from both direct oxygen consumption by root respiration and stimulation of microbial respiration by root exudation and turnover [*Woldendorp*, 1962]. A similar rapid shift in fall was also documented in the Gifford Riparian Wetland in 2008 [*Burgin et al.*, 2010], though the shift occurred much earlier in the season, likely because 2008 was drier than 2009. This shift did not correspond to any changes in precipitation, but was correlated with a slight decrease in soil VWC (Figure 1). We therefore hypothesize that the rapid switch occurs because the soil has dried to the point that the macropores no longer have water blocking the diffusion of atmospheric air into the soils. Plant senescence may also play a role. Rapid transitions such as these are known to occur in soils and are thought to be important in controlling microbial processes and gas fluxes [*Metivier et al.*, 2009]. These rapid increases in [O_2] have also been documented in the generally low-O_2 rain forest soils under extended dry periods [*Liptzin et al.*, 2011] and floodplain wetlands of the Savannah River [*Megonigal et al.*, 1993]. This rapid switch is a stark contrast to the gradual decline in [O_2] for most of the season, which took months to gradually become anoxic (Figure 1a). A similar pattern to that documented in Gifford Wetland was also seen in forested wetlands, wherein a late spring rise in the water table corresponded to decreasing soil [O_2] and mid-summer drying led to increased soil [O_2] [*Megonigal et al.*, 1993]. Clearly both physical (e.g., water dynamics) and biological (e.g., plant and microbial community) factors control soil [O_2]; however, the relative contribution of these to the overall pattern of soil O_2 concentration remains unknown. More research in both the areas of soil O_2 dynamics across various ecosystems, coupled with

bench-scale manipulations of biotic and abiotic factors would enhance our nascent understanding of soil O_2 dynamics and drivers.

4.3. Controls on Denitrification Rates and End Products

[29] The second question we sought to address was: How does O_2 variation affect denitrification rates and end products? O_2 controls denitrification through inhibition of denitrification enzymes; however, not all denitrifying bacteria respond similarly to the presence of oxygen [*Abou Seada and Ottow*, 1985; *Morley et al.*, 2008]. Our results indicate that increasing soil O_2 concentration clearly decreases denitrification rates and increases the fraction of N_2O in the final end products (Figure 2), lending support to our 3rd and 4th hypotheses. The connection between O_2 concentration, denitrification rates and N_2O flux has been known for over thirty years [*Firestone et al.*, 1980]; however, our findings extend this understanding by providing the additional context of an increased understanding of field-level variation in O_2 and how this can feedback to affect denitrification and N_2O yield.

[30] The relationship between soil O_2 and denitrification differed between the wet and dry sites, with higher denitrification rates in the wet site at any given level of O_2 (Figure 2). One likely explanation is that soil macropore [O_2] (measured by the soil O_2 probes (Figure 1)), and microsite [O_2] (where denitrification occurs) differs between the sites due to differences in moisture content and soil properties (texture, organic matter content). These results suggest that establishing relationships between denitrification and [O_2] in different soil types may be a useful approach for scaling results from field to landscape and regional scales [*Groffman and Tiedje*, 1989].

[31] The different O_2:denitrification relationships that we observed in the wet versus dry zones are likely due to differences in microbial community acclimation to the particular environmental conditions. That is, the wet zone had significantly more denitrification than the dry zone soils at each soil [O_2] because a microbial community more acclimated to anoxic conditions was present. It has recently been suggested that knowledge of denitrifier abundance may not lend additional predictive power to understanding the controls on denitrification [*Attard et al.*, 2011]. However, our new method appears sensitive enough to discern differences in denitrification under nearly identical conditions (O_2, Figure 2; available N, Table 1; organic carbon, section 2.5). This suggests that other methods to measure denitrification (e.g., the commonly used acetylene block technique) are not sensitive enough to distinguish differences in the denitrification activity of microbial communities acclimated to even slight variation in environmental conditions.

[32] While our new method appears sensitive enough to distinguish differences in the denitrification capacity of the wet and dry zones, it cannot discern whether the N_2O generated is from nitrification or denitrification. O_2 is known to affect both processes by increasing the proportion of transformation going to N_2O [*Bollmann and Conrad*, 1998]. *Bollmann and Conrad* [1998] found that nitrification was the main source of N_2O at lower soil moistures, whereas denitrification predominated N_2O fluxes at higher soil moistures. Thus, in more aerated soils, the majority of N_2O fluxes are thought to stem from nitrification [*Bremner and Blackmer*, 1981]. Given that we cannot distinguish the two processes using our N-FARM method, we warn that the estimates of N_2O yield may be an overestimation of N_2O flux due to denitrification (Figure 2c). However, given the high soil moisture contents of these soils (Figure 1c), it is likely that much of the N cycling activity is due to denitrification.

[33] The controls on N_2O production are of particular interest because N_2O currently accounts for 6% of radiative forcing and destroys stratospheric ozone [*Intergovernmental Panel on Climate Change*, 2008]. N_2O yield increased with increasing exposure to O_2 and ranged from 0 to 36%, similar to the range reported in two literature reviews of N_2O yield [*Beaulieu et al.*, 2011; *Schlesinger*, 2009]. The balance between electron donors (organic C) and acceptors (NO_3^-) is often invoked to predict N_2O yield [*Firestone and Davidson*, 1989]. Other studies have cited a connection between N_2O yield and soil moisture or water filled pore space [*Bergsma et al.*, 2002; *Ciarlo et al.*, 2007; *Rudaz et al.*, 1999; *Ruser et al.*, 2006; *Scheer et al.*, 2008]. However, our data suggests that soil O_2 is perhaps the dominant control on N_2O yield. [O_2] is highly correlated with water filled pore space, consistent with the often-observed connection between soil moisture and N_2O yield as well. The distinctive connection between soil [O_2] and N_2O yield in different soils suggest that measuring these relationships may be a useful approach for sorting out the extreme variation in yield that has been observed in previous studies [*Beaulieu et al.*, 2011; *Schlesinger*, 2009].

4.4. O_2 Effects on Greenhouse Gas Fluxes

[34] In addition to understanding how soil O_2 varied, and how the variation affected denitrification rates, we also asked: How does seasonal variation in O_2 affect in situ greenhouse gas fluxes? We measured fluxes of N_2O, CO_2 and CH_4 from the wet and dry zones to test the hypothesis that gases indicative of increased anaerobic conditions (e.g., CH_4 and N_2O) would increase under decreasing field O_2. Greenhouse gas flux rates measured from the Gifford Riparian Wetland fall within the published ranges of fluxes from other riparian sites, as compiled by *Soosaar et al.* [2011]. N_2O fluxes at the Gifford site ranged from −20–820 μg N m^{-2} hr^{-1}, which is comparable to range of −25–104 μg N m^{-2} hr^{-1} from a mixed forest riparian zone [*Dhondt et al.*, 2004] and 108–566 μg N m^{-2} hr^{-1} in an Alder riparian zone [*Hefting et al.*, 2006]. CO_2 fluxes in our site ranged from 2.2–37 mg CO_2 m^{-2} hr^{-1}, within the range of 0–365 mg CO_2 m^{-2} hr^{-1} measured in a gray alder riparian zone over an eight-year period [*Soosaar et al.*, 2011]. CH_4 flux at our site ranged from −22–258 μg CH_4 m^{-2} hr^{-1}, well within the range of −38–561 μg CH_4 m^{-2} hr^{-1} in the study reported by *Soosaar et al.* [2011] and generally higher than the range of 0.06–0.15 μg CH_4 m^{-2} hr^{-1} in riparian zones of northern hardwood forests [*Hopfensperger et al.*, 2009]. Of the three gases, only CO_2 fluxes showed a clear seasonal signal with increased CO_2 in the summer compared to spring or fall probably due to the influence of increased plant respiration during the growing season. However, this was only apparent in the wet zone, whereas the CO_2 flux from the dry zone was relatively consistent over time. Neither N_2O nor CH_4 fluxes (Figure 4) correlated were correlated to O_2 patterns (Figure 1) in the wet or dry zone.

[35] Field-level N_2O fluxes often exhibit micro-scale spatial variability, which makes understanding and predicting the controls on N_2O fluxes difficult [*DeSimone et al.*, 2010; *Groffman and Gold*, 1998; *van den Heuvel et al.*, 2009]. Temporal patterns are also difficult to discern, though many studies have documented relatively large fluxes in early spring compared to other seasons [*DeSimone et al.*, 2010; *Dhondt et al.*, 2004]. The field fluxes of N_2O measured in the Gifford Riparian Wetland also fit the pattern of high spatial and temporal variation, with the highest flux occurring in May. While we hypothesized that field-level O_2 concentrations would correlate with N_2O fluxes, we did not see a corresponding pattern in the data. Therefore, while O_2 exhibits tight control on N_2O flux at some spatial scales (e.g., cores), it does not seem to translate to predicting patterns at larger spatial scales (e.g., gas chambers). However, this is not altogether surprising since data sets with much more temporal and spatial resolution than ours have also failed to link N_2O fluxes with key drivers [*van den Heuvel et al.*, 2009]. Temporal scaling may be an issue here—we measured trace gases once a month, whereas O_2 was measured hourly. Spatial factors may also be important, as macropore [O_2] may not be reflective of conditions within the much larger area of the GHG chamber and may not account for the balance of N_2O producing and consuming sites within the chamber area. Understanding the spatial and temporal complexity of these controlling factors will be necessary to build models capable of predicting N loss through denitrification and N_2O fluxes associated with this activity.

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