Landscape control of nitrous oxide emissions during the transition from conservation reserve program to perennial grasses for bioenergy

DEBASISH SAHA[1,2], BENJAMIN M. RAU[3,a], JASON P. KAYE[1], FELIPE MONTES[2], PAUL R. ADLER[3] and ARMEN R. KEMANIAN[2]

[1]*Department of Ecosystem Science and Management, The Pennsylvania State University, University Park, PA 16802, USA,* [2]*Department of Plant Science, The Pennsylvania State University, University Park, PA 16802, USA,* [3]*Pasture Systems and Watershed Management Research Unit, USDA Agricultural Research Service, University Park, PA 16802, USA*

Abstract

Future liquid fuel demand from renewable sources may, in part, be met by converting the seasonally wet portions of the landscape currently managed for soil and water conservation to perennial energy crops. However, this shift may increase nitrous oxide (N_2O) emissions, thus limiting the carbon (C) benefits of energy crops. Particularly high emissions may occur during the transition period when the soil is disturbed, plants are establishing, and nitrate and water accumulation may favor emissions. We measured N_2O emissions and associated environmental drivers during the transition of perennial grassland in a Conservation Reserve Program (CRP) to switchgrass (*Panicum virgatum* L.) and *Miscanthus x giganteus* in the bottom 3-ha of a watershed in the Ridge and Valley ecoregion of the northeastern United States. Replicated treatments of CRP (unconverted), unfertilized switchgrass (switchgrass), nitrogen (N) fertilized switchgrass (switchgrass-N), and *Miscanthus* were randomized in four blocks. Each plot was divided into shoulder, backslope, and footslope positions based on the slope and moisture gradient. Soil N_2O flux, soil moisture, and soil mineral nitrogen availability were monitored during the growing season of 2013, the year after the land conversion. Growing season N_2O flux showed a significant vegetation-by-landscape position interaction ($P < 0.009$). Switchgrass-N and *Miscanthus* treatments had 3 and 6-times higher cumulative flux respectively than the CRP in the footslope, but at other landscape positions fluxes were similar among land uses. A peak N_2O emission event, contributing 26% of the cumulative flux, occurred after a 10.8-cm of rain during early June. Prolonged subsoil saturation coinciding with high mineral N concentration fueled N_2O emission hot spots in the footslopes under energy crops. Our results suggest that mitigating N_2O emissions during the transition of CRP to energy crops would mostly require a site-specific management of the footslopes.

Keywords: conservation reserve program, energy crops, land use change, landscape position, *Miscanthus*, switchgrass

Received 28 March 2016; revised version received 30 June 2016 and accepted 7 July 2016

Introduction

Renewable fuels are an increasing portion of the liquid fuels portfolio of the United States and some analyses suggest that to fulfill federal mandates, the nation should produce ≈80 billion liters of ethanol from cellulosic sources by 2022 (Kim *et al.*, 2009). This will require planting up to 21 million ha with cellulosic crops (McLaughlin *et al.*, 2002) like switchgrass (*Panicum virgatum*) and *Miscanthus* (*M. × giganteus*). Land seemingly suitable for energy crops is that currently enrolled in the Conservation Reserve Program (CRP), which

amounts to ≈12 million hectares of agriculturally marginal and environmentally sensitive land (Farm Service Agency, 2012).

Energy crops like switchgrass and *Miscanthus* can provide crucial ecosystem services when placed in environmentally sensitive lands across the landscape. When planted in floodplains or in lower landscape positions within watersheds, these grasses can serve as riparian buffers to reduce nutrient and sediment load to surface water and groundwater (Perez-Suarez *et al.*, 2014; Smith *et al.*, 2014). Furthermore, due to the low soil disturbance and perennial rooting systems, they can store C in the soil due to their large below-ground C allocation (Lemus & Lal, 2005; Follett *et al.*, 2012).

A critical component of the societal benefit of energy crops is that they produce fuel with a low C footprint (Tilman *et al.*, 2006; Adler *et al.*, 2007; Gelfand *et al.*, 2013). The United States Environmental Protection

[a]Present address: Savannah River Forestry Sciences Lab, USDA Forest Service, 241 Gateway Drive, Aiken, SC 29803, USA

Correspondence: Debasish Saha, tel. 814 865 8449, fax 814 863 7043, e-mails: dxs1005@psu.edu and debasish992@gmail.com

Agency's revision to the National Renewable Fuel Standard requires that to qualify as renewable, advanced biofuels lifecycle greenhouse gas (GHG) emissions must be 50% of those from fossil fuel (EPA, 2010). To achieve this goal, emissions of nitrous oxide (N_2O) must be low during the feedstock production phase, because N_2O is the largest source of GHG for feedstock production (Adler *et al.*, 2012). There are arguments to posit that converting historically managed CRP lands to agricultural crops may increase N_2O emissions (Ruan & Robertson, 2013).

In the Ridge and Valley physiographic province of the Allegheny Plateau in the northeastern United States, many lands are considered marginal due to being seasonally wet. These landscapes have characteristically shallow, coarse, and rocky ridge top soils as well as fractured subsoils that drain water to the back and footslope positions (Fig. S1). The footslope soils are derived from mixed colluvial sandstone and shale, often with fragipans at shallow depth that limit drainage (Ciolkosz *et al.*, 1995). Restricted drainage in the footslope causes a shallow, temporary water table, and extended periods of soil water content above field capacity or near saturation during spring snowmelt and rainstorm events (Buda *et al.*, 2009). The steep soils with a semi-impermeable subsoil favor nitrate (NO_3^-) transport to stream water (Kleinman *et al.*, 2006; Zhu *et al.*, 2011). The simultaneous occurrence of well drained upper lands and poorly drained footslope positions may create biogeochemical hot spots for denitrification and N_2O emissions (Vilain *et al.*, 2010).

The N_2O emissions from soil predominantly originate from nitrification and denitrification (Firestone & Davidson, 1989). Soil oxygen, NO_3^-, ammonium (NH_4^+), and labile organic C concentration determine the contribution of nitrification and denitrification to the total N_2O flux (Weier *et al.*, 1993; Gillam *et al.*, 2008). We hypothesize that in seasonally wet lands of the northeastern United States, N_2O emissions could be severe during the transition from CRP to energy crops due to accelerated C and nitrogen (N) cycling of above and below-ground residues from the former CRP vegetation, soil disturbance during the land conversion (Zenone *et al.*, 2011; Nikiema *et al.*, 2012; Ruan & Robertson, 2013), and relatively low crop growth rate in the first two years of stand establishment. Furthermore, if the energy crops are fertilized, co-locating N fertilizer with decomposable organic residues along water flow paths will create conditions for increased N_2O emissions. Thus, managing N and N_2O emissions from energy crops in this region requires understanding the interactive controls of landscape, crop growth, and hydrology on soil N cycling.

In this research, we measured soil N_2O emission during land transition from CRP to energy crops *Miscanthus* and switchgrass in a watershed in the Ridge and Valley region. The lower part of the watershed was under CRP since 1999. In 2012, we divided the landscape into replicated plots of: (i) unconverted CRP, (ii) *Miscanthus*, (iii) switchgrass, and (iv) fertilized switchgrass. The N_2O fluxes from the CRP and establishing switchgrass and *Miscanthus* were monitored during the 2013 growing season, the second year after land conversion. In June of 2013, 10.8 cm of rain from hurricane 'Andrea' caused sudden soil saturation in parts of the watershed. This event gave us an opportunity to measure the event-based response of N_2O emissions during the transition from CRP to energy crops. To the best of our knowledge, this is the first time that N_2O emissions from CRP, switchgrass, and *Miscanthus* have been simultaneously measured to assess the landscape by land management interaction during land use transition. Our research questions were: (i) what is the effect of converting CRP lands to switchgrass and *Miscanthus* on soil N_2O emissions; (ii) what is the effect of N fertilization in switchgrass on N_2O emissions; and (iii) how do landscape heterogeneity and land conversion interact to control N_2O emissions?

Materials and methods

Site description

The experimental area, hereafter called Mattern (40°42′N, 76°36′W), is located near the town of Leck Kill in east-central Pennsylvania (PA). It is part of a long-term monitoring site of the USDA-Agricultural Research Service (Sharpley *et al.*, 2008). The site has a temperate humid climate with annual mean temperature and precipitation of ≈9.2° C and ≈106 cm, respectively. Mattern is an 11-ha sub-watershed of the 726-ha watershed (WE-38) that drains to Mahantango Creek, a tributary of the Susquehanna River (Sharpley *et al.*, 2008). The site is representative of the Ridge and Valley physiographic province.

Mattern has mixed land use with 57% cropland, 30% forest, 4% pasture, 9% meadow, and <1% buildings. The upper valley lands have rotations of soybean (*Glycine max* L.), wheat (*Triticum aestivum* L.), and corn (*Zea mays* L.). Slope ranges from 1% to 20%. The elevation above sea level varies from 267 m in the valley floor to 285 m near the summit. The topsoil typically has a silt loam texture with 20–40% rock volume (Table 1) that grades to a loam and/or silty clay loam texture at depth (≈100 cm). Albrights soils are distributed along stream and valley floor and have a fragipan and argillic horizon beginning at a depth of 50–70 cm (Needelman *et al.*, 2004). These soils experience prolonged soil saturation during spring snowmelt and after rain events. In contrast, Berks soils in the shoulder and backslope positions are relatively shallow and well drained.

The plots were established in the lower portion of the watershed, in an area of approximately 3-ha that includes the watershed outlet (Fig. 1). Mattern has an ephemeral stream that is

Table 1 Soil properties in the top 20 cm soil layer at each landscape position

Landscape position	Total C g kg^{-1} soil	Total N g kg^{-1} soil	Bulk density g cm^{-3}	Rock fraction m^3 m^{-3}	Clay g kg^{-1} soil	Silt g kg^{-1} soil
Shoulder	20 ± 5	2.2 ± 0.4	1.18 ± 0.12	0.35 ± 0.05a	170 ± 30b	480 ± 28
Backslope	19 ± 5	2.1 ± 0.3	1.15 ± 0.11	0.32 ± 0.05b	190 ± 34b	480 ± 27
Footslope	19 ± 5	2.0 ± 0.4	1.21 ± 0.10	0.28 ± 0.04c	210 ± 29a	490 ± 30

Each value represents mean ± standard deviation (n = 16). Different letters within a column indicate a statistically significant difference among the landscape positions at $P < 0.05$.
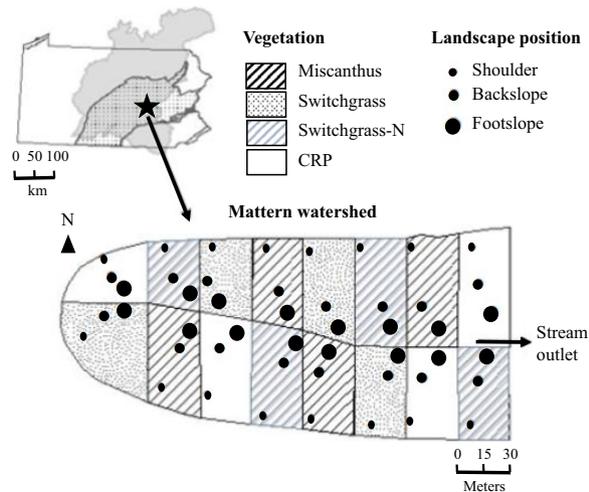
Fig. 1 Upper panel showing the location of the Mattern watershed (black star) within the Susquehanna River basin (grey shaded) and Ridge and Valley physiographic province (dotted region) of Pennsylvania. The lower panel shows treatment plots and measurement locations in shoulder, backslope, and footslope (increasing size of black circle) positions within each plot.

active most of the year except during dry summers. Both the lowland and upland were under conventionally tilled corn, soybean, wheat, and alfalfa (*Medicago* sp.) rotation with poultry manure applied at the rate of 5 Mg ha^{-1} yr^{-1}, corresponding to 205 kg N ha^{-1} yr^{-1} until 1999 (Kleinman et al., 2006). The lowland was considered marginal due to seasonal wetness and high slope that impairs annual cropping, and was brought under CRP in 1999. The CRP vegetation comprises the perennial cool-season grasses orchard grass (*Dactylis glomerata* L.), tall fescue (*Schedonorus arundinaceus* (Schreb.) Dumort.), timothy (*Phleum pratense* L.), and legumes including alfalfa (*Medicago sativa* L.) and clovers (*Trifolium* spp.).

Experimental design

The lower portion of the watershed was divided in four blocks with relatively uniform slope and aspect. Each block contained four plots measuring ≈60 × 30 m each (Fig. 1) one each of the following treatments: (i) unconverted CRP, (ii) N-fertilized switchgrass (switchgrass-N), (iii) unfertilized switchgrass (switchgrass), and (iv) unfertilized *Miscanthus*. In the 12 plots designated for energy crops, CRP vegetation was killed with

glyphosate [N-(phosphonomethyl) Glycine] in the summer of 2011, and the aboveground biomass baled and removed from the field. The glyphosate-treated area was no-till planted with winter rye (as a cover crop) in the fall of 2011, which was in turn killed with glyphosate prior to planting the energy crops in the spring of 2012. The switchgrass plots were no-till drilled in rows 20-cm apart. Rhizomes of *Miscanthus* plants were hand planted 76 cm apart in chisel-made furrows. Thus, the *Miscanthus* plots had a higher level of soil disturbance. Throughout 2012, the plots of both species were hand replanted, using plants, in areas with poor establishment, especially in wet footslope positions. By 2013, plot establishment was satisfactory except in the footslopes, especially in *Miscanthus*. In 2012, broadleaf weeds and annual grasses were controlled with herbicide; weed pressure was low in 2013. The switchgrass-N plots received 50 kg ha^{-1} of N as broadcasted urea on May 29th, 2013, a year after planting.

The upland portion of each plot borders cropland; the bottom portion merges into the ephemeral stream that drains the watershed. Based on the increasing soil wetness from top to bottom, each plot was divided into three segments: shoulder, backslope, and footslope (Fig. 1). This is customary when studying topographic effects on soil N$_2$O emissions (e.g. Pennock et al., 1992; Vilain et al., 2010). The combination of four treatments, three landscape positions, and four replications (blocks) yielded a total of 48 monitoring points.

Measurement of soil water content and air filled soil volume

We continuously monitored volumetric soil water content (θ_V, m^3 m^{-3}) with CS-616 soil moisture sensors (Campbell Scientific Inc., Logan, UT, USA). The sensors were installed at three depths (0–20, 20–40, and 40–60 cm) in each of the 48 monitoring points, for a total of 144-sensors. Each sensor was connected to one of four dataloggers through a network of buried cables.

The θ_V was used to calculate the volumetric air content in the soil layer (θ_A, m^3 m^{-3}):

$$\theta_A = \theta_S - \theta_V \tag{1}$$

where θ_S is the total porosity of a layer after correcting for rock volume (m^3 m^{-3}).

Measurement of N$_2$O emissions

We measured N$_2$O emissions from May to September of 2013. The sampling frequency varied from weekly to biweekly, and

increased after fertilization and precipitation events. The soil-atmosphere N_2O flux was measured by the static, non-steady state, vented, aluminum-foil insulated chamber method (Hutchinson & Mosier, 1981). In 2012, PVC collars of 30-cm diameter were inserted 5 cm in the soil in each of the 48 monitoring points. Each collar supports a gas-tight chamber of 10-cm height. The chamber interior was free of any vegetation.

At measurement time, chambers were placed on top of the collars and left there for 45 min. Gas samples of 20 ml were drawn from each chamber through a rubber septum connected to a manifold inside the chamber. Samples were taken 15, 30, and 45 min after chamber closure. Soil temperature near the chamber was measured during gas sampling.

The 20-ml gas samples were transferred to 12-ml pre-evacuated Labco exetainer vials (Labco Limited, Lampeter, UK). The N_2O concentration in the gas samples was measured with a Varian CP3800 (Varian, Walnut Creek, CA, USA) gas chromatograph (with Compi-Pal autosampler) equipped with a ^{63}Ni electron capture detector that operates at 300 °C to detect N_2O. The ideal gas law was used to calculate the µg N_2O-N and the flux was calculated from the rate of increase in N_2O concentration in the chamber headspace.

Cumulative N_2O flux (May 9th to September 13th) was calculated by interpolation and linear integration. We refer to this as the growing season flux as it roughly corresponds to the period when the grasses were green and soils were not frozen. The N_2O flux on the days in between two sampling days was estimated as:

$$F_L = F_o + \frac{(F_f - F_o) \times (d_f - d_i)}{d_f - d_o} \quad (2)$$

where, F_L is the estimated flux of N_2O, F_o and F_f are the measured fluxes bracketing the days interpolated, d_o and d_f are the days corresponding to F_o and F_f, and d_i is the ith day in between d_o and d_f.

Soil sampling

Soil samples (0–20 cm) were taken on every other gas flux measurement day to determine NH_4^+ and NO_3^- concentration (five sampling days during the growing season). We were not able to sample soil for mineral N on the day immediately after the cessation of 'Andrea' on June 11th because the soils were flooded. Fresh soil samples were extracted with 100 ml 2M KCl and the inorganic N species were determined by colorimetric analysis (Lachat Quick Chem 8000). All values were corrected for gravimetric water content measured on a 10 g subsample oven dried at 105 °C for 48 h.

Soil cores of 50–120 cm in length, depending on the location, were collected from each sampling point in spring 2012. The cores were taken with a SIMCO Earthprobe 200 (SIMCO Drilling Equipment, Inc. Osceola, IL, USA) using plastic tube liners of 4.5 cm in diameter and a tip diameter of 3.8-cm. The soil core was used for geomorphic description, determination of bulk density, particle size distribution (USDA-pipette method; Day, 1965), total soil C and N concentration (Elemental Combustion System auto-analyzer, Costech Analytical Technologies, Inc., Valencia, CA, USA), and rock volume (water displacement method).

Statistical analysis

We used parametric and non-parametric statistical methods for data analysis. All statistical analyses were performed with the R statistical software (R Development Core Team, 2012). First, we used an analysis of variance (ANOVA) with block, vegetation type, and landscape position effects. The residuals of the daily N_2O fluxes were not always normally distributed and were log-transformed for ANOVA. The residuals of the cumulative N_2O fluxes were not normally distributed and the original fluxes were transformed using the reciprocal square root transformation based on the ladder of powers method (Tukey, 1977) to achieve normality (Shapiro-Wilk, $W = 0.96$, $P = 0.17$) and variance homogeneity. Data were back transformed for tabular presentation. Marginal means were compared using Tukey-adjusted P-values at a significance level of $P < 0.05$. The main effect and the interactions on daily and cumulative N_2O flux were assessed with the following linear model:

$$Y_{ijk} = \mu + \alpha_i + \gamma_k + (\alpha\gamma)_{ik} + \beta_j + (\alpha\beta)_{ij} + (\beta\gamma)_{jk} + e_{ijk} \quad (3)$$

where, Y_{ijk} represents the response variable N_2O flux; α, β, and γ represent the main effect of vegetation type, landscape position, and block, respectively; e is the error term, and i, j, k denote the respective levels of the main factors.

Second, we used Random Forest method to analyze which variables best explain the observed variation in $\log_{10}$ transformed N_2O flux (Breiman, 2001). Random Forest was applied to the pooled data including only the days when soil mineral N was measured along with soil N_2O flux, θ_A, and weather variables. We used the function randomForest from the package randomForest in R (Liaw & Wiener, 2002). The control parameters for random forest were *seed* = 500 (set random number) and *ntree* = 1000 (number of trees). The control parameter *mtry* indicates the number of variables available for splitting at each node and was calculated as square root of total number of variables (Strobl *et al.*, 2009). The variable importance was plotted by using the function varImpPlot. The variables used for this analysis are: vegetation type, landscape position, soil NO_3^- and soil NH_4^+ concentration in the top 20 cm layer (mg N kg^{-1} dry soil), volumetric soil air content at the 0–20, 20–40, and 40–60 cm soil depth (θ_{A20}, θ_{A40}, and θ_{A60}; m^3 m^{-3}), and cumulative precipitation in the last two days (PPT_2, cm).

Finally, using the tree package in R (seed = 500), we constructed a conditional inference tree of N_2O emissions using observations from the five dates in which mineral N was measured. Each tree terminal node has an average N_2O flux and a number of observations (n).

Results

Weather, soil properties, and biomass yield

During the study period, the mean daily air temperature was 19.1 °C and the cumulative precipitation was 40.2 cm, with a large, 10.8 cm rain event during hurricane 'Andrea' on June 10th. The landscape positions had similar C and N distribution and bulk density in the top 20 cm soil layer ($P > 0.05$); all the treatments

started with the same organic C and N in the top 20 cm of soil (Table 1). Soils had mean C and N concentration of 19 and 2.1 g kg^{-1} soil. The soil bulk density (free of rocks) varied from 1.0 to 1.5 g cm^{-3}, with a mean of 1.2 g cm^{-3}. Rocks occupy a substantial soil volume (mean 0.32 m^3 m^{-3}, range 0.19 to 0.43 m^3 m^{-3}), with a significantly higher rock fraction in the shoulder position that decreases down the slope ($P < 0.05$). The clay concentration varied from 130 to 290 g kg^{-1}, with the highest figures in the footslopes (Table 1).

The aboveground biomass yield of the energy crops harvested in fall 2013, after the second year of growth, exceeded 10 Mg ha^{-1}, and was 2–4 times higher than that of the CRP (Table 2). While the figure for the CRP reflects the harvestable biomass in fall, it does not represent total aboveground biomass produced because a large part is produced in spring, senesces in early summer and is not harvestable in fall. There was no statistically significant effect of the landscape position and N-fertilization on biomass yield.

Soil ammonium and nitrate concentration

Mean soil NH$_4^+$ concentration during the growing season was 10 ± 12 mg N kg^{-1} soil (Fig. 2), lowest in *Miscanthus* (6 ± 5 mg N kg^{-1} soil) and highest in switchgrass-N (14 ± 20 mg N kg^{-1} soil). The variation in NH$_4^+$ concentration among landscape positions was very narrow (8.8 to 10.4 mg N kg^{-1} soil). The N-fertilization in switchgrass-N increased the mean NH$_4^+$ concentration from 0.8 ± 0.5 mg N kg^{-1} soil before the fertilization to 48 ± 22 mg N kg^{-1} soil on June 7th, a week after fertilization (Fig. 2). However, this peak NH$_4^+$ concentration faded away after the hurricane. A substantial increase in NH$_4^+$ concentration was also observed in unfertilized grasses (and higher in CRP than energy crops) during summer and tended to decrease over the growing season. No plot showed N stress as vegetation growth was thick and vigorous, but the N-fertilized plots had a darker green color and the plants lodged in mid-July.

Mean growing season soil NO$_3^-$ concentrations were 19 ± 14 mg N kg^{-1} soil (Fig. 2). In contrast to NH$_4^+$, the NO$_3^-$ concentrations were highest in *Miscanthus* plots (25 ± 17 mg N kg^{-1} soil), which were twice as high as that of CRP (13 ± 13 mg N kg^{-1} soil). Again, the variation among landscape positions was narrow (footslope 17 and shoulder 20 mg N kg^{-1} soil, respectively). In the switchgrass-N plots, the N-fertilization had a minor effect on NO$_3^-$ dynamics in shoulder and backslope positions, while the footslope position showed an increase in soil NO$_3^-$ concentration (30 mg N kg^{-1} soil) during early June. This NO$_3^-$ concentration was five-times higher than that in CRP (Fig. 2). On June 7th, just before the hurricane, *Miscanthus* plots had the highest NO$_3^-$ concentration in all landscape positions (mean 43 ± 20 mg N kg^{-1} soil), while CRP plots had the lowest NO$_3^-$ concentration (8 ± 3 mg N kg^{-1} soil). These differences were not discernible after the hurricane and NO$_3^-$ concentration became comparable among treatments.

Soil air content

Soil profile air content ranged from 0 m^3 m^{-3} (soil water saturation) to 0.32 m^3 m^{-3} (Fig. 3). The greatest variation in θ_A among the treatments was in the footslope. Mean θ_A in the profile was lowest in the 20–40 cm layer (0.14 ± 0.03 m^3 m^{-3}) and highest in the top 20 cm (0.19 ± 0.04 m^3 m^{-3}). The start of the 2013, θ_A flux measurements coincided with a rain event that reduced θ_A in the soil profile. There was a steady increase in θ_A from May 9th onwards until the onset of the hurricane in June 10th.

The hurricane driven rain saturated the soil and decreased θ_A in the top soil layer of the footslope (0.02 ± 0.02 m^3 m^{-3}), which was significantly lower than that in the backslope (0.08 ± 0.07 m^3 m^{-3}) and shoulder (0.12 ± 0.06 m^3 m^{-3}) positions on June 11th ($P < 0.05$). A prolonged period of low θ_A was noticeable in the footslope positions, especially in the subsurface

Table 2 Above-ground dry biomass production by CRP and energy crops in different landscape positions

	CRP	Switchgrass	Switchgrass-N	*Miscanthus*	Mean
Landscape position			Mg ha^{-1}		
Shoulder	3.5 ± 0.1	10.7 ± 0.4	10.5 ± 1.4	9.7 ± 1.4	8.6
Backslope	3.8 ± 0.2	11.1 ± 0.4	10.3 ± 0.6	12.5 ± 3.2	9.4
Footslope	5.2 ± 0.8	11.2 ± 0.8	11.6 ± 1.1	10.2 ± 2.1	9.6
Mean	4.2b	11.0a	10.8a	10.8a	

Each value represents mean ± standard error of mean ($n = 4$). Mean biomass yields followed by same letter within a row are not significantly different at $P < 0.05$. The above-ground biomass yields are based on post-senescence manual harvesting of 3 m × 1 m quadrats at 10 cm height from the ground surface at each monitoring point. The CRP biomass was harvested in September, while switchgrass and *Miscanthus* were harvested in early November.
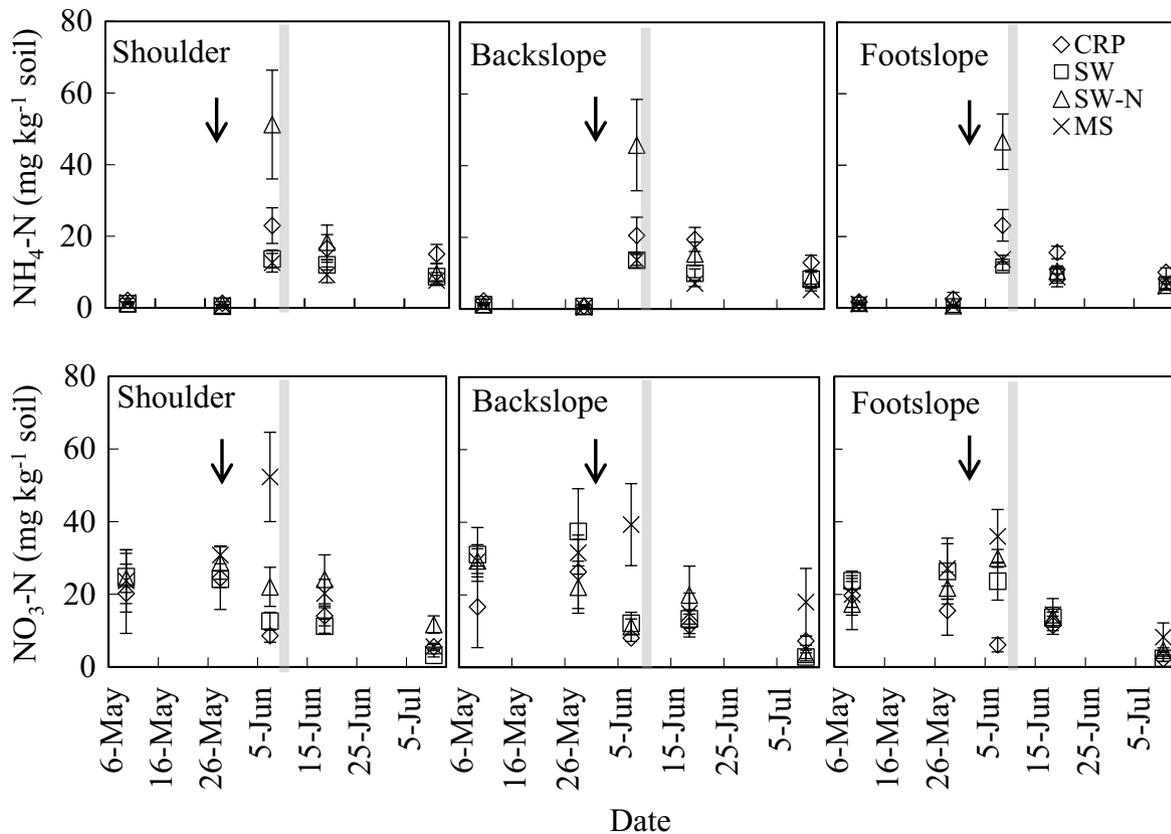
Fig. 2 Dynamics of soil NH$_4$-N (upper panel) and NO$_3$-N (lower panel) concentration in the top 20 cm soil layer under CRP and energy crops (SW, switchgrass; SW-N, fertilized switchgrass; MS, *Miscanthus*) at different landscape positions during 2013 growing season. Each point is a mean of four replicates. Error bars represent ± standard error of the mean. The solid arrow indicates the timing of N-fertilization in the switchgrass-N treatment and the vertical gray bar indicates hurricane 'Andrea'.

soil layers (Fig. 3c). Soil aeration started to increase after June 14th as drainage progressed. Subsequent rain events decreased soil aeration, but never to the extent or length of the hurricane driven storm.

N$_2$O emissions

The N$_2$O flux from soil to atmosphere widely varied among the vegetation and landscape positions, ranging from 4 to 305 g N ha^{-1} day^{-1} among vegetation types (Fig. 4). The mean flux was lowest in CRP and highest in *Miscanthus* (8 vs. 16 g N ha^{-1} day^{-1}). The footslope positions were the hot spots, with greater variability of N$_2$O emissions than other landscape positions, and a mean flux (18 g N ha^{-1} day^{-1}, range of 60 g N ha^{-1} day^{-1}) that was more than two-times higher than the shoulder positions (8 g N ha^{-1} day^{-1}). Footslope positions under *Miscanthus* had the highest mean growing season N$_2$O emission (26 g N ha^{-1} day^{-1}) followed by switchgrass-N, switchgrass, and CRP (23, 16, and 7 g N ha^{-1} day^{-1}, respectively).

During early May, emissions from the footslope positions were significantly higher than that from the shoulder positions (55 vs. 19 g N ha^{-1} day^{-1}, $P < 0.05$); emissions from backslope positions were intermediate and not significantly different from the other landscape positions (30 g N ha^{-1} day^{-1}, Fig. 4). In addition, during the same period, the average N$_2$O emission from energy crops of 41 g N ha^{-1} day^{-1} was 2.6-times higher than that from CRP. The N-fertilization did not have an immediate effect on N$_2$O flux from switchgrass-N in the shoulder and backslope positions; however, a small peak of 35 g N ha^{-1} day^{-1} occurred in the footslope position (Fig. 4).

Peak N$_2$O emissions were triggered by the hurricane rains on June 10th (Fig. 4). The rain saturated the soil and reduced θ_A (Fig. 3), coinciding with a period of high mineral N concentration in soil (Fig. 2). Averaged over all plots, the N$_2$O flux was 84 g N ha^{-1} day^{-1} on June 11th, a day after the large precipitation event. This flux was roughly four-times higher than the pre-hurricane flux of 22 g N ha^{-1} day^{-1} on June 7th. Furthermore, emissions from the footslope (156 g N ha^{-1} day^{-1}) and backslope (76 g N ha^{-1} day^{-1}) positions were significantly higher than those from the shoulder
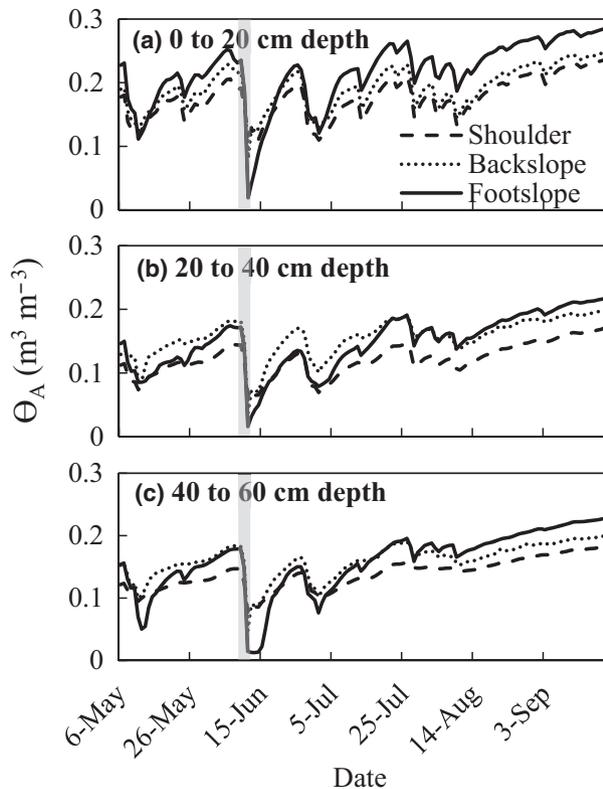
Fig. 3 Temporal and spatial variation of soil air content (θ_A) in (a) 0–20, (b) 20–40, and (c) 40–60 cm soil depths in different landscape positions during 2013 growing season N$_2$O flux monitoring period. Values were averaged across vegetation types ($n = 16$) at each depth in each landscape position. The vertical gray bar indicates hurricane 'Andrea'.

positions (20 g N ha^{-1} day^{-1}, $P < 0.05$). Immediately after the hurricane rains, the N$_2$O emissions from the grasses were in the order of: *Miscanthus* > switchgrass-N > switchgrass > CRP (130, 103, 69, and 34 g N ha^{-1} day^{-1}, respectively). A significant interaction between vegetation type-by-landscape position was only observed during this hot moment ($P = 0.03$). The emissions from lower landscape positions of *Miscanthus* (305 g N ha^{-1} day^{-1}) and switchgrass-N (233 g N ha^{-1} day^{-1}) was significantly higher than that in CRP (20 g N ha^{-1} day^{-1}, $P < 0.05$). The hurricane induced peak N$_2$O emission waned to background level after June 18th as the water drained and oxic conditions prevailed in the landscape (Fig. 3).

Growing season cumulative N$_2$O flux

The ANOVA of cumulative N$_2$O flux shows a significant vegetation-by-landscape position interaction ($P = 0.009$, Table 3). The differences in cumulative N$_2$O emissions between the CRP and energy crops only expressed in

the footslope positions (Table 3). While in CRP emissions were similar across landscape positions ($\approx$1 kg N ha^{-1}), these emissions were higher in the footslope for the energy crops, in particular for *Miscanthus* ($\approx$5.5 kg N ha^{-1}).

Analysis of conditions leading to N$_2$O emissions

The Random Forest analysis identified landscape position, cumulative precipitation in the two days before N$_2$O flux measurement (PPT$_2$), and soil NO$_3^-$ concentration as the most important factors influencing N$_2$O emissions (Fig. 5). It is the soil aeration (θ_A) in subsurface layers (20–40 and 40–60 cm) that seem to be related to N$_2$O emission, rather than the aeration in the top layer. Nonetheless, the Random Forest model explained only 28% of the variation in N$_2$O flux. Clearly, there are other controls of N$_2$O emissions that we did not measure and can include microsite properties that are difficult to characterize.

Using a regression tree, the predictor variables as identified by the Random Forest were used to classify the N$_2$O fluxes in groups that can be identified by specific properties. The regression tree contains seven terminal nodes. The primary node shows a split based on $\theta_{A40} = 0.03$ m^3 m^{-3}, with the highest emission when $\theta_{A40} < 0.03$ m^3 m^{-3} (Fig. 6). The observations that belong to the primary node are associated with high NO$_3$-N concentration (mean 19 mg N kg^{-1} soil) and poor aeration status ($\theta_{A40} < 0.03$ m^3 m^{-3}) in the soil profile, and are mostly found in the footslope positions. The shoulder positions never sustained $\theta_{A40} < 0.03$ m^3 m^{-3}. Accordingly, node 4, which is the node with lowest average emission, is composed only of measurements in the shoulder positions. When $\theta_{A40} > 0.03$ m^3 m^{-3}, moderately high emissions (mean 28 g N ha^{-1} day^{-1}) occur only in the footslope positions when soil NO$_3$-N concentration is >10 mg N kg^{-1} soil (node 7). Since the construction of the regression tree excluded the highest N$_2$O emission period after the hurricane event, the potential emissions can be much higher than the values predicted by the tree. However, the tree clearly points to the landscape position and the subsoil air content as the drivers of N$_2$O emissions.

Discussion

Converting CRP lands to energy crops only increased N$_2$O emissions significantly in the footslopes during the second year of the land use transition (Table 3). At that position, N$_2$O emissions from switchgrass, switchgrass-N, and *Miscanthus* were 2×, 3×, and 6× larger than emissions from CRP. For comparison, Gelfand *et al.* (2011) reported 4.5 times higher N$_2$O emissions from
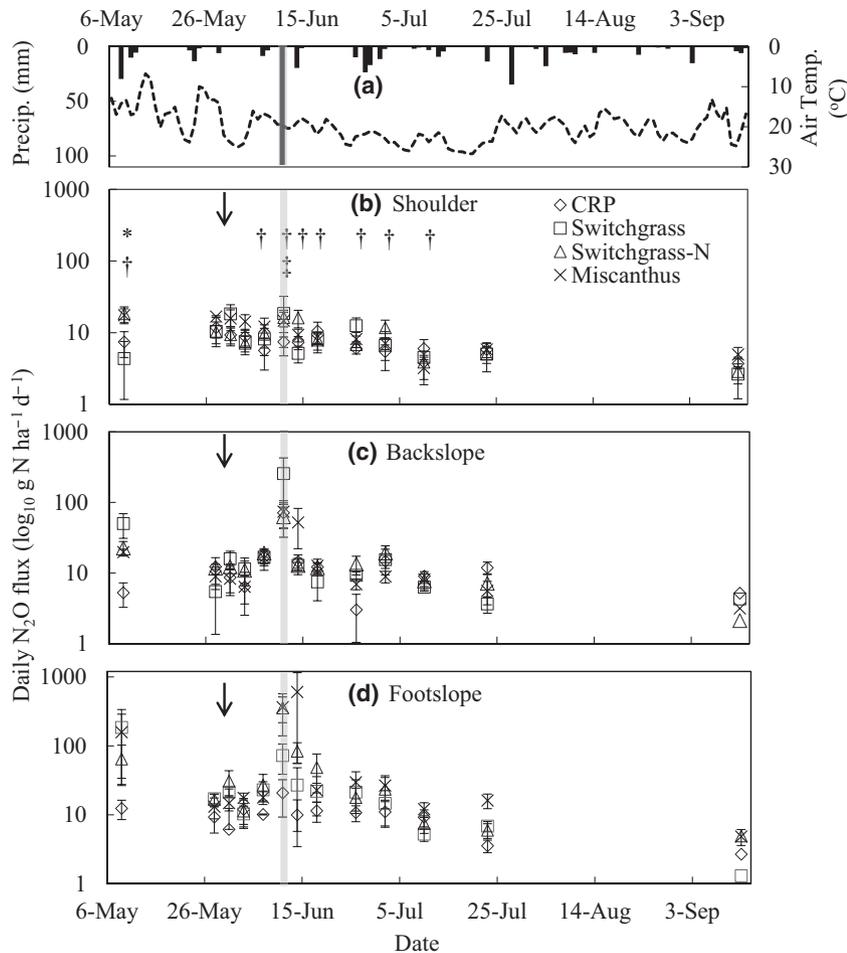
Fig. 4 Daily precipitation, air temperature (a) and $\log_{10}$ transformed daily N_2O fluxes from CRP and energy crops under (b) shoulder, (c) backslope, and (d) footslope position during 2013 growing season. Each point is a mean of four replicates. Error bars represent ± standard error of mean ($n = 4$). The solid arrow indicates the timing of N-fertilization in the switchgrass-N treatment and the vertical gray bar indicates hurricane 'Andrea'. Significant ($P < 0.05$) effects of vegetation (*), Landscape position (†), and/or their interaction (‡) on the measurement day were presented in top of panel b.

no-till soybean converted from CRP grassland. In our case, the lower landscape positions occupy at most a third of the lower part of the watershed, and therefore at least more than two thirds of the area had N_2O emissions comparable to those of CRP, hereby answering our first research question.

The N_2O emission differences among treatments built up over three distinctive periods: during early season growth prior to the hurricane, the week of the hurricane in mid-June, and the post hurricane period until the end of the growing season. These three periods have distinctive evolutions of soil mineral N and soil water in the different treatments. In the early season, the cool-season CRP vegetation starts growing before the warm season energy crops, which would reflect in comparatively more mineral N depletion in CRP. Accordingly, in early June, the soil NO_3^- concentration in CRP was lower than

that of *Miscanthus* in all landscape positions; however, the switchgrass soil NO_3^- concentration was similar to *Miscanthus* in the footslope, but similar to CRP in the shoulder and backslope (Fig. 2). Furthermore, with the obvious exception of fertilized switchgrass, CRP had slightly higher NH_4^+ than unfertilized switchgrass and *Miscanthus* at all landscape positions. Thus, the behavior of mineral N in the early season is more nuanced than expected.

Several factors may have contributed to relatively high NO_3^- accumulation under energy crops, particularly *Miscanthus*. First, in the years prior to planting the CRP in 1999, the soils received > 200 kg N ha^{-1} yr^{-1} as manure. In addition, the CRP vegetation had a visible, but not dominant, proportion of legumes. Killing the pre-existing CRP vegetation during land conversion created fresh above and belowground pools of dead grass

Table 3 Analysis of variance for significance of differences in growing season cumulative N₂O emission in different landscape positions under CRP and energy crops. The cumulative N₂O flux was reciprocal square root transformed for ANOVA, and the means were back-transformed for presentation in the table

Analysis of variance				
Sources of variance	df	Mean square	F value	P
Vegetation (V)	3	0.14	6.3	0.004
Block (B)	3	0.02	1.2	0.333
Landscape position (LP)	2	0.59	26.9	<0.001
V × LP	6	0.09	4.1	0.009
B × LP	6	0.02	0.9	0.514
V × B	9	0.04	2.0	0.106
Error	18	0.02		

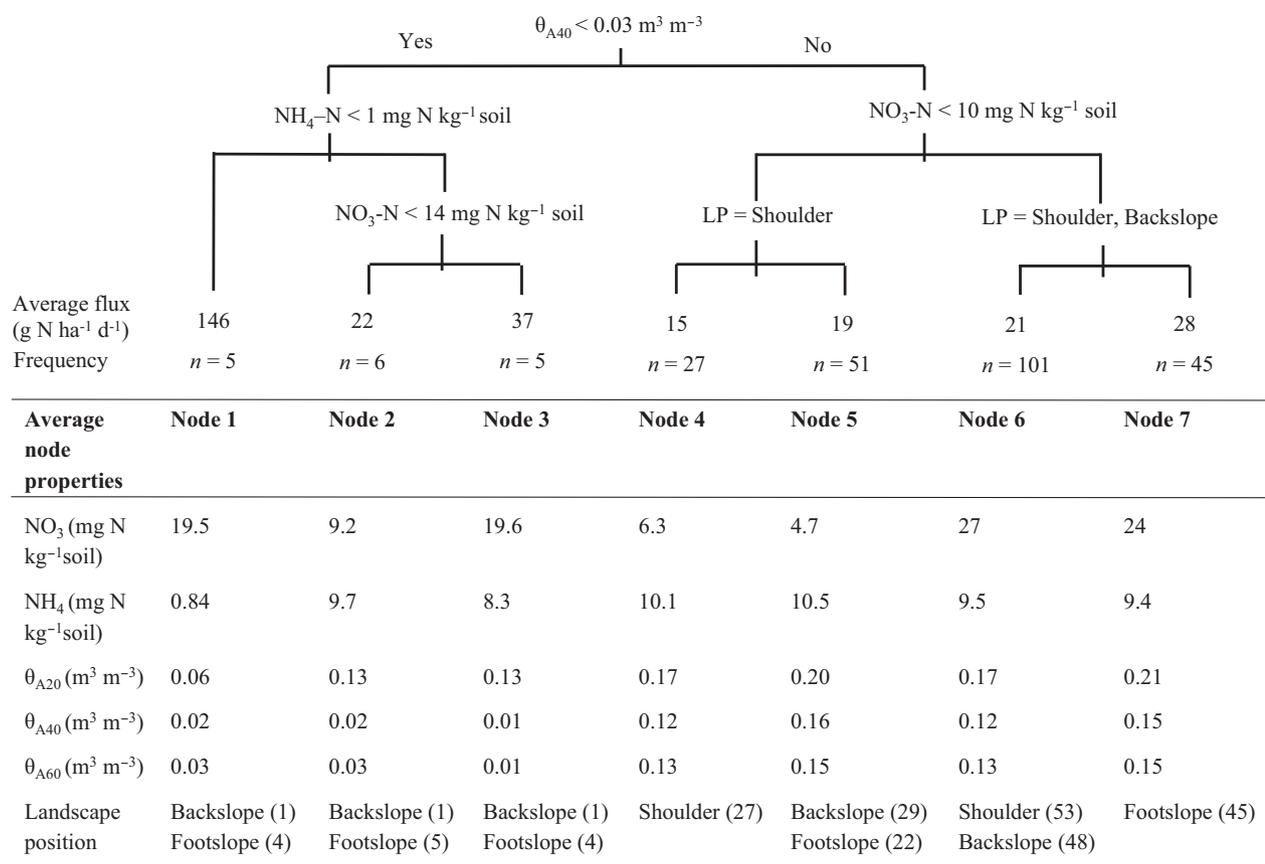| Cumulative N₂O flux					
	CRP	Switchgrass	Switchgrass-N	Miscanthus	Mean
Landscape position	kg N ha⁻¹				
Shoulder	0.8	0.8	0.9	1.1	0.9
Backslope	1.4	1.6	1.4	1.4	1.4
Footslope	**0.9**	**2.2**	**2.9**	**5.5**	2.1
Mean	1.0	1.3	1.5	1.8	

The bold figures imply significantly higher cumulative N₂O fluxes from the energy crops than the CRP in the footslope positions only.

and legume root biomass that may have mineralized N during decomposition, adding to N mineralization from soil organic matter (Zenone *et al.*, 2011; Ruan &
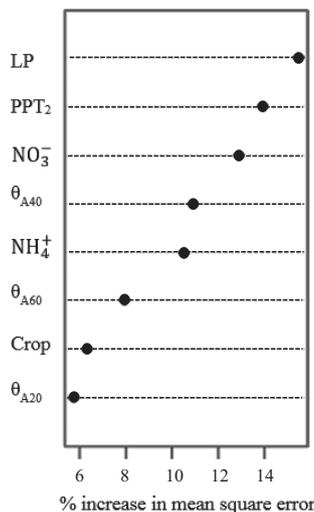
Fig. 5 Random forest based variable importance plot for N₂O flux (log₁₀ transformed). The % increase in the mean square error represents the mean increase in classification error due to random permutation of the variable indicated. Higher values of percent increase in mean squared error indicate higher importance of the variable to explain N₂O emissions in the random forest model (variance explained: 28%). LP, landscape position; PPT₂, cumulative precipitation in preceding two days; θ_{A20}, θ_{A40}, and θ_{A60}, volumetric soil air content (m³ m⁻³) at 0–20, 20–40, and 40–60 cm depth, respectively.

Robertson, 2013). Killing the rye cover crop added additional decomposable residues, albeit in low quantities (<2 Mg ha⁻¹). Second, chisel plowing prior to rhizome establishment caused a greater level of soil disturbance in *Miscanthus* compared to no-till switchgrass seeding, which may have accelerated soil organic matter decomposition (Grandy & Robertson, 2006; Mazzilli *et al.*, 2015). Third, due to the different techniques used to establish the energy crops, the switchgrass stands were denser than that of *Miscanthus* early in the growing season, allowing switchgrass an earlier canopy closure and higher N uptake. This might have resulted in more N available for losses in *Miscanthus* plots. In short, killing the established CRP vegetation in C and N rich soils, can cause high concentration of soil mineral N, favoring N₂O emissions even under no-till (switchgrass); the effect was more pronounced under *Miscanthus* possibly due to additional factors such as chisel plowing and slower establishment of the wide-spaced *Miscanthus* rhizomes (Table 3). A similar case was reported by Gauder *et al.* (2012), who found higher N₂O emission from *Miscanthus* compared with shrub willow (*Salix* spp.) during early summer and attributed the difference to the partial soil cover by *Miscanthus*, in addition to high soil mineral N after fertilization. An alternative hypothesis for the lack of NO₃⁻ accumulation in CRP can be a limited nitrification potential due to the low disturbance, as suggested by the moderate accumulation of NH₄⁺ (Fig. 2); it has been shown that the nitrification potential remarkably increased when long-term undisturbed

Fig. 6 — Regression tree:

- Root: $\theta_{A40} < 0.03\ m^3\ m^{-3}$ — Yes (left) / No (right)
  - Yes branch: $NH_4–N < 1\ mg\ N\ kg^{-1}\ soil$
    - 146 (n = 5)
    - $NO_3\text{-}N < 14\ mg\ N\ kg^{-1}\ soil$
      - 22 (n = 6)
      - 37 (n = 5)
  - No branch: $NO_3\text{-}N < 10\ mg\ N\ kg^{-1}\ soil$
    - LP = Shoulder
      - 15 (n = 27)
      - 19 (n = 51)
    - LP = Shoulder, Backslope
      - 21 (n = 101)
      - 28 (n = 45)

Average node properties	Node 1	Node 2	Node 3	Node 4	Node 5	Node 6	Node 7
Average flux (g N ha⁻¹ d⁻¹)	146	22	37	15	19	21	28
Frequency	$n = 5$	$n = 6$	$n = 5$	$n = 27$	$n = 51$	$n = 101$	$n = 45$
NO_3 (mg N kg⁻¹soil)	19.5	9.2	19.6	6.3	4.7	27	24
NH_4 (mg N kg⁻¹soil)	0.84	9.7	8.3	10.1	10.5	9.5	9.4
θ_{A20} (m³ m⁻³)	0.06	0.13	0.13	0.17	0.20	0.17	0.21
θ_{A40} (m³ m⁻³)	0.02	0.02	0.01	0.12	0.16	0.12	0.15
θ_{A60} (m³ m⁻³)	0.03	0.03	0.01	0.13	0.15	0.13	0.15
Landscape position	Backslope (1) Footslope (4)	Backslope (1) Footslope (5)	Backslope (1) Footslope (4)	Shoulder (27)	Backslope (29) Footslope (22)	Shoulder (53) Backslope (48)	Footslope (45)

Fig. 6 Regression tree to group N_2O emissions during the transition from CRP to energy crops. Upon satisfaction of the splitting condition, the tree is routed to the left. Values in parentheses beside each landscape position (LP) show the number of observations (*n*) from each landscape position.

pasture land was cleared and cultivated for short-rotation poplar (*Populus* spp.) and shrub willow (Nikiema *et al.*, 2012; Palmer *et al.*, 2014).

According to our non-parametric statistical analysis, potentially higher N_2O emissions from these energy crops are realized only when high mineral N and soil saturation converge in the landscape, which occurs predominantly in the footslopes (Figs 5 and 6). Furthermore, the analysis identified greater influence of subsoil aeration on N_2O emissions in these landscapes, a fact that is often overlooked. At our site, limited drainage through the fragipans and argillic subsoil layers within the colluvial footslopes (Ciolkosz *et al.*, 1995; Needelman *et al.*, 2004) causes extended periods of water saturation, even when the top layer is relatively well drained (Fig. 3). Thus, we hypothesize that the high N_2O emission are explained by the juxtaposition of an oxic top layer above an anoxic subsurface layer that creates a hot spot for N_2O production from denitrification when NO_3^- is not limiting.

The hot moment and the hot spots for N_2O emissions were triggered by hurricane Andrea (June 10th to 13th),

when soils under energy crops had high soil NO_3^-, and the landscape was conducive to accumulation of water in the footslopes. In this time period differences among treatments built up significantly, mostly in the footslopes (Fig. 4). Given the high level of soil NO_3^- before the event, denitrification was most likely the dominant contributor of peak N_2O emissions under low soil aeration conditions following the hurricane (Weier *et al.*, 1993; Gillam *et al.*, 2008). This single peak emission event contributed on average 26% of the growing season cumulative N_2O flux in 2013. This is similar to the findings of Parkin & Kaspar (2006), who reported that two peak events of 29 days-long accounted for 45% of annual N_2O flux from corn in the Midwest. The remainder N_2O emissions, which are grouped mostly in the right branch of the regression tree (Fig. 6), are either from nitrification or denitrification in anoxic microsites.

The comparison of unfertilized and N-fertilized switchgrass in this period also reflects the concurrence of hot spots and hot moments. The response of N_2O flux to N fertilization was not very prominent or immediate because the soil was dry for more than a week after

N-fertilization (May 29th to June 9th) (Fig. 3), limiting N transformations (Bateman & Baggs, 2005; Davidson et al., 2008). However, a small peak from the footslopes may be attributed to favorable soil water content for nitrification. A similar lag period between fertilization and peak emission due to a dry period has been reported by Baggs et al. (2003). Addressing our second research question regarding the effect of N-fertilization on N_2O emission, we found that N_2O emissions in this N-rich soils are similar for both switchgrass-N and switchgrass treatments (Table 3); nonetheless, switchgrass-N had significantly higher N_2O emissions than CRP in the footslopes.

During and after the hurricane, N_2O emissions were more responsive in both Miscanthus and switchgrass-N in the footslopes (Fig. 4). The hurricane mobilized NO_3^- in all treatments (Fig. 2). In addition, shortly after the hurricane, N uptake and transpiration due to vigorous growth decreased the high NO_3^- and anoxia co-occurrences, which likely decreased N_2O emissions later in the growing season.

Previous studies of landscape scale N_2O emissions also identified the footslope positions as the hot spots for N_2O emissions (van Kessel et al., 1993; Castellano et al., 2010; Vilain et al., 2010). The same processes seem to operate in this watershed, with localized zones of water accumulation causing spatially variable N_2O emissions. Even after receiving a 10.8-cm of rainfall during the hurricane, fast drainage and redistribution of water from the convex shoulder positions precluded aeration limitations that favor denitrification. In fact, the critical θ_A of 0.03 m^3 m^{-3} threshold identified through the regression tree analysis is rarely, if ever, reached in the backslope and shoulder positions. However, the sources of NO_3^- for denitrification and N_2O emission in the footslope may originate from upslope, with NO_3^- transferred by interflow to the footslopes. Regardless, and answering our third research question, while footslopes in the Ridge and Valley region are at risk of high N_2O emissions, backslope and shoulder positions seem to posit a much lesser risk of emissions, even in the transitional years and in N-rich soils. Because the biomass yield did not vary significantly across the landscape, the N_2O emission per unit of biomass harvested was higher in the footslopes (0.41 ± 0.15 kg N_2O-N Mg biomass^{-1}), in particular under Miscanthus (0.86 ± 0.09 kg N_2O-N Mg biomass^{-1}).

Interannual variability of N_2O emissions as reported by many studies (Burchill et al., 2014; Oates et al., 2016), and the representativeness of the study period, limit the generalization of these results. The study period had a wet early summer (Fig. 4a) coinciding with high mineral N availability in the energy crop plots (Fig. 2), the perfect storm for a transitional system when N_2O emissions are the concern. Thus, our results may represent an upper estimate of N_2O emissions during a transition from CRP to energy crops in this landscape.

Implications for management of the transition to energy crops

Our results suggest that N_2O emissions from energy crops during the transitional period, i.e. the first and second year after killing CRP, are contingent on land conversion method, landscape properties, and management strategies. The major insight of this research is that in the Ridge and Valley region, transitioning CRP land to energy crops presents a minor risk of increasing N_2O emissions in well drained portions of the watersheds, except on the footslopes. As shown in Figs 2 and 4, once the mineral N concentrations drop due to crop uptake (and N losses), N_2O emissions are low and comparable to that of CRP.

A potential outline of N management emerges from this research. First, to minimize N_2O fluxes in N-rich environments, soil disturbance should be minimized to prevent an increase in organic matter mineralization. When switchgrass was no-till established and not fertilized, N_2O emissions were comparable to CRP. Second, Miscanthus had higher N_2O emissions during the establishment phase on footslopes when compared to switchgrass. This is likely due to a combination of tillage disturbance and slow establishment from wide-spaced plants. Higher biomass yield from Miscanthus in subsequent years (Arundale et al., 2014) may compensate for initial N_2O emissions when considering lifecycle emissions of the crop. Thus, while our data point to the transition as a hot moment, longer term studies are also needed. Third, while it is not common to apply N fertilizer to Miscanthus or switchgrass in the first year of planting due to slow growth during establishment and to prevent favoring weed growth, later fertilization requires monitoring soil mineral N in spring to avoid over fertilization. In the second growing season of our study (2013), fertilizing switchgrass did not increase biomass yield. While our original concern was the need to increase N supply through fertilization, we did not foresee that soils at Mattern, which is rocky and marginal for agriculture, would continue to mineralize substantial amounts of N upon land conversion (Fig. 2).

Fourth, the risk of soil N_2O emissions is particularly large only in footslope positions. Drainage from shoulders and backslopes is swift, which minimizes the risk of anoxic conditions. Detailed site specific delineation of seasonally saturated areas will be required to avoid management (e.g. fertilization) that could exacerbate N_2O fluxes from footslope hotspots. However, while well drained landscape positions can be fertilized with

lesser risks of enhancing emissions, NO_3^- can be transported to poorly drained areas prone to higher emissions, and it is unknown how much of the N_2O emission in the footslope positions originated from the N transported from upslope areas.

In conclusion, managing the transition from CRP to energy crops maintaining a low N_2O emission per unit of biomass produced in relation to the original vegetation might be optimized by designing a transition process that minimizes the co-occurrence of high mineral N and wet soils (e.g. no-till, minimum tillage, and minimum fertilization), particularly wet subsoils. Our research suggests that a relatively small portion of the watershed is prone to significant N_2O emissions in the Ridge and Valley landscapes, and that perennial energy crops planted in well-drained portions of the landscape in current CRP land can be an important component of the portfolio of sustainable production options.

Acknowledgements

References

Adler PR, Del Grosso SJ, Parton W (2007) life-cycle assessment of net greenhouse-gas flux for bioenergy cropping systems. *Ecological Applications*, **16**, 675–691.

Adler PR, Del Grosso SJ, Inman D, Jenkinson RE, Spatan S, Zhang Y (2012) Mitigation opportunities for life-cycle greenhouse gas emissions during feedstock production across heterogeneous landscapes. In: *Managing Agricultural Greenhouse Gases* (eds Liebig MA, Franzluebbers AJ, Follett RF), pp. 203–219, Coordinated agricultural research through GRACEnet to address our changing climate. Elsevier Inc., New York. DOI: 10.1016/B978-0-12-386897-8.00012-7.

Arundale RA, Dohleman FG, Heaton EA, Mcgrath JM, Voigt TB, Long SP (2014) Yields of *Miscanthus x giganteus* and *Panucum virgatum* decline with stand age in the Midwestern USA. *Global Change Biology Bioenergy*, **6**, 1–13.

Baggs EM, Stevenson M, Pihlatie M, Regar A, Cook H, Cadisch G (2003) Nitrous oxide emissions following application of residues and fertilizer under zero and conventional tillage. *Plant and Soil*, **254**, 361–370.

Bateman EJ, Baggs EM (2005) Contributions of nitrification and denitrification to N_2O emissions from soils at different water-filled pore space. *Biology and Fertility of Soils*, **41**, 379–388.

Breiman L (2001) Random forests. *Machine Learning*, **45**, 5–32.

Buda AR, Kleinman PJA, Srinivasan MS, Bryant RB, Feyereisen GW (2009) Factors influencing surface runoff generation from two agricultural hillslopes in central Pennsylvania. *Hydrological Processes*, **23**, 1295–1312.

Burchill W, Li D, Lanigan GJ, Williams M, Humphreys J (2014) Interannual variation in nitrous oxide emissions from perennial ryegrass/white clover grassland used for dairy production. *Global Change Biology*, **20**, 3137–3146.

Castellano MJ, Schmidt JP, Kaye JP, Walker C, Graham CB, Lin H, Dell CJ (2010) Hydrological and biogeochemical controls on the timing and magnitude of nitrous oxide flux across an agricultural landscape. *Global Change Biology*, **16**, 2711–2720.

Ciolkosz EJ, Waltman WJ, Thurman NC (1995) Fragipans in Pennsylvania soils. *Soil Survey Horizons*, **36**, 5–20.

Davidson EA, Nepstad DC, Ishida FY, Brando PM (2008) Effects of an experimental drought and recovery on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest. *Global Change Biology*, **14**, 2582–2590.

Day PR (1965) Particle fractionation and particle-size analysis. In: *Methods of Soil Analysis*. (ed. Black CA), Part I. *Agronomy* 9, 545–567.

EPA, 2010. Available at: http://www.epa.gov/oms/renewablefuels/420f09023.htm

Farm Service Agency (FSA) (2012), CRP Contract Summary and Statistics. Available at: http://www.fsa.usda.gov/FSA/webapp?area=home&subject=copr&topic=rns-cs (accessed December, 2012).

Firestone MK, Davidson EA (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere* (eds Andreae MO, Schimel DS), pp. 7–21. John Wiley and Sons, New York.

Follett RF, Vogel KP, Varvel GE, Mitchell RB, Kimble J (2012) Soil carbon sequestration by switchgrass and no-till maize grown for bioenergy. *Bioenergy Research*, **5**, 866–875.

Gauder M, Butterbach-Bahl K, Graeff-Honninger S, Claupein W, Wiegel R (2012) Soil-derived trace gas fluxes from different energy crops – results from a field experiment in Southwest Germany. *Global Change Biology Bioenergy*, **4**, 289–301.

Gelfand I, Zenone T, Jasrotia P, Chen J, Hamilton SK, Robertson GP (2011) Carbon debt of Conservation Reserve Program (CRP) grasslands converted to bioenergy production. *Proceedings of National Academy of Science*, **108**, 13864–13869.

Gelfand I, Sahajpal R, Zhang X, Izaurralde RC, Gross KL, Robertson GP (2013) Sustainable bioenergy production from marginal lands in the US Midwest. *Nature*, **493**, 514–517.

Gillam KM, Zebarth BJ, Burton DL (2008) Nitrous oxide emissions from denitrification and the partitioning of gaseous losses as affected by nitrate and carbon addition and soil aeration. *Canadian Journal of Soil Science*, **88**, 133–143.

Grandy AS, Robertson GP (2006) Initial cultivation of a temperate-region soil immediately accelerates aggregate turnover and CO_2 and N_2O fluxes. *Global Change Biology*, **12**, 1507–1520.

Hutchinson GL, Mosier AR (1981) Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal*, **45**, 311–316.

van Kessel C, Pennock DJ, Farrell RE (1993) Seasonal variations in denitrification and nitrous oxide evolution at the landscape scale. *Soil Science Society of America Journal*, **57**, 988–995.

Kim H, Kim S, Dale BE (2009) Biofuels, land use change, and greenhouse gas emissions: some unexplored variables. *Environmental Science and Technology*, **43**, 961–967.

Kleinman PJA, Srinivasan MS, Dell CJ, Schmidt JP, Sharpley AN, Bryant RB (2006) Role of rainfall intensity and hydrology in nutrient transport via surface runoff. *Journal of Environmental Quality*, **35**, 1248–1259.

Lemus R, Lal R (2005) Bioenergy crops and carbon sequestration. *Critical Review in Plant Science*, **24**, 1–21.

Liaw A, Wiener M (2002) Classification and regression by randomForest. *R News*, **2**, 18–22.

Mazzilli SR, Kemanian AR, Ernst OR, Jackson RB, Piñeiro G (2015) Greater humification of belowground than aboveground biomass carbon into particulate soil organic matter in no-till corn and soybean crops. *Soil Biology and Biochemistry*, **85**, 22–30.

McLaughlin SB, de la Torre Ugarte DG, Garten CT, Lynd LR, Sanderson MA, Tolbert VR, Wolf DD (2002) High-value renewable energy from prairie grasses. *Environmental Science and Technology*, **30**, 2122–2129.

Needelman BA, Gburek WJ, Peterson GW, Sharpley AN, Kleinman PJA (2004) Surface runoff along two agricultural hillslopes with contrasting soils. *Soil Science Society of America Journal*, **68**, 914–923.

Nikiema P, Rothstein DE, Miller RO (2012) Initial greenhouse gas emissions and nitrogen leaching losses associated with converting pastureland to short-rotation woody bioenergy crops in northern Michigan, USA. *Biomass and Bioenergy*, **39**, 413–426.

Oates LG, Duncan DS, Gelfand I, Millar N, Robertson GP, Jackson R (2016) Nitrous oxide emissions during establishment of eight alternative cellulosic bioenergy cropping systems in the North Central United States. *Global Change Biology Bioenergy*, **8**, 539–549.

Palmer MM, Forrester JA, Rothstein DE, Mladenoff DJ (2014) Conversion of open lands to short-rotation woody biomass crops: site variability affects nitrogen cycling and N_2O fluxes in the US Northern Lake States. *Global Change Biology Bioenergy*, **6**, 450–464.

Parkin TB, Kaspar TC (2006) Nitrous oxide emissions from corn-soybean systems in the Midwest. *Journal of Environmental Quality*, **35**, 1496–1506.

Pennock DJ, van Kessel C, Farrell RE, Sutherland RA (1992) Landscape-scale variations in denitrification. *Soil Science Society of America Journal*, **56**, 770–776.

Perez-Suarez M, Castellano MJ, Kolka RK, Asbjournsen HM (2014) Nitrogen and carbon dynamics in prairie vegetation strip across topographical gradients in

mixed central Iowa Agroecosystems. *Agriculture, Ecosystem and Environment*, **188**, 1–11.

R Development Core Team (2012) R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. Available at: http://www.R-project.org/.

Ruan L, Robertson GP (2013) Initial nitrous oxide, carbon dioxide, and methane costs of converting conservation reserve program grassland to row crops under no-till vs. conventional tillage. *Global Change Biology*, **19**, 2478–2489.

Sharpley AN, Kleinman PJA, Heathwaite AL, Gburek WJ, Folmar GJ, Schimidt JP (2008) Phosphorus loss from an agricultural watershed as a function of storm size. *Journal of Environmental Quality*, **37**, 362–368.

Smith TE, Kolka RK, Zhou XB, Helmers MJ, Cruse RM, Tomer MD (2014) Effects of native perennial vegetation buffer strips on dissolved organic carbon in surface runoff from an agricultural landscape. *Biogeochemistry*, **120**, 121–132.

Strobl C, Malley J, Tutz G (2009) An introduction to recursive partitioning: rational, application, and characteristics of classification and regression trees, bagging, and random forests. *Psychological Methods*, **14**, 323–348.

Tilman D, Hill J, Lehman C (2006) Carbon-negative biofuels from low-input high diversity grassland biomass. *Science*, **314**, 1598–1600.

Tukey JW (1977) *Exploratory Data Analysis*. Addison-Wesley, Reading, MA, USA.

Vilain G, Garnier J, Tallec G, Cellier P (2010) Effect of slope position and land use on nitrous oxide (N_2O) emissions (Seine Basin, France). *Agriculture and Forest Meteorology*, **150**, 1192–1202.

Weier KL, Doran JW, Power JF, Walters DT (1993) Denitrification and the dinitrogen to nitrous oxide ratio as affected by soil water, available carbon and nitrate. *Soil Science Society of America Journal*, **57**, 66–72.

Zenone T, Chen J, Deal MW *et al.* (2011) CO_2 fluxes of transitional bioenergy crops: effect of land conversion during the first year of cultivation. *Global Change Biology Bioenergy*, **3**, 401–412.

Zhu Q, Schmidt JP, Buda AR, Bryant RB, Folmar GJ (2011) Nitrogen loss from a mixed land use watershed as influenced by hydrology and seasons. *Journal of Hydrology*, **405**, 307–315.

Supporting Information

Additional Supporting Information may be found online in the supporting information tab for this article:

Figure S1 Schematic diagram of a typical Ridge and Valley hillslope scale soil and hydrological processes.