Environmental Research Letters

LETTER

Nitrogen fertilization challenges the climate benefit of cellulosic biofuels

Leilei Ruan1,2,3, Ajay K Bhardwaj1,2, Stephen K Hamilton1,2,4 and G Philip Robertson1,2,3

1 W.K. Kellogg Biological Station, Michigan State University, Hickory Corners, MI 49060, USA
2 Great Lakes Bioenergy Research Center, Michigan State University, East Lansing, MI 48824, USA
3 Dept. of Plant, Soil, and Microbial Sciences, Michigan State University, East Lansing, MI 48824, USA
4 Dept. of Integrative Biology, Michigan State University, East Lansing, MI 48824, USA

Current address: Central Soil Salinity Research Institute, Indian Council of Agricultural Research, Karnal, Haryana 132001, India

E-mail: robert30@msu.edu

Keywords: nitrous oxide (N\textsubscript{2}O), nitrate leaching, switchgrass, methane (CH\textsubscript{4}) oxidation, nitrogen fertilizer, life cycle analysis, IPCC emission factor

Supplementary material for this article is available online

Abstract

Cellulosic biofuels are intended to improve future energy and climate security. Nitrogen (N) fertilizer is commonly recommended to stimulate yields but can increase losses of the greenhouse gas nitrous oxide (N\textsubscript{2}O) and other forms of reactive N, including nitrate. We measured soil N\textsubscript{2}O emissions and nitrate leaching along a switchgrass (\textit{Panicum virgatum}) high resolution N-fertilizer gradient for three years post-establishment. Results revealed an exponential increase in annual N\textsubscript{2}O emissions that each year became stronger ($R^2 > 0.9, P < 0.001$) and deviated further from the fixed percentage assumed for IPCC Tier 1 emission factors. Concomitantly, switchgrass yields became less responsive each year to N fertilizer. Nitrate leaching (and calculated indirect N\textsubscript{2}O emissions) also increased exponentially in response to N inputs, but neither methane (CH\textsubscript{4}) uptake nor soil organic carbon changed detectably. Overall, N fertilizer inputs at rates greater than crop need curtailed the climate benefit of ethanol production almost two-fold, from a maximum mitigation capacity of $-5.71 \pm 0.22$ Mg CO$_2$e ha$^{-1}$ yr$^{-1}$ in switchgrass fertilized at 56 kg N ha$^{-1}$ to only $-2.97 \pm 0.18$ Mg CO$_2$e ha$^{-1}$ yr$^{-1}$ in switchgrass fertilized at 196 kg N ha$^{-1}$. Minimizing N fertilizer use will be an important strategy for fully realizing the climate benefits of cellulosic biofuel production.

1. Introduction

The global production of biofuels has increased dramatically in response to calls for greater energy security and climate change mitigation. In the US, legislation mandates production of 1.36 billion liters of ethanol biofuel by 2022 with a growing fraction from cellulosic sources (US Congress 2007). Cellulosic biofuels offer the potential for greater environmental benefits compared to grain based biofuels (Tilman et al 2006, Robertson et al 2008, 2011). Switchgrass (\textit{Panicum virgatum}), a perennial grass native to North America, is among the most promising cellulosic biofuel crops due to its ability to grow on marginal and erosive lands, sequester soil carbon (Liska and Cassman 2008), reduce nitrogen (N) leaching (Smith et al 2013), and be grown with relatively little fossil fuel input (McLaughlin and Adams Kszos 2005).

Switchgrass is often considered an inherently N-thrifty plant, especially when managed for biomass production (Parrish and Fike 2005). Nevertheless, multiple studies have documented a productivity response to added N, with most reporting maximum yields at N rates between 56 and 202 kg N ha$^{-1}$ (Vogel et al 2002, Mulkey et al 2006, Mooney et al 2009, Nikiema et al 2011). In a recent on-farm experiment (Schmer et al 2008), farmers fertilized switchgrass at rates up to 212 kg N ha$^{-1}$.

Although N fertilizer can increase biomass production, added N increases the greenhouse gas (GHG) contributions of biofuel production substantially: not only through the production, transportation, and
distribution of the fertilizer itself, but also through fertilizer-induced microbial emissions of nitrous oxide (N\textsubscript{2}O), a GHG with a global warming potential \sim 300 times that of carbon dioxide (CO\textsubscript{2}) (Solomon et al. 2007) and a major cause of stratospheric ozone depletion (Portmann et al. 2012). Moreover, fertilizer N lost to the environment as nitrate (NO\textsubscript{3}\textsuperscript{–}) leads to indirect emissions of N\textsubscript{2}O elsewhere in downstream surface waters (Beaulieu et al. 2011) as well as to degraded water quality (Robertson and Vitousek 2009). Additionally, well-aerated soils are a globally significant sink for atmospheric methane (CH\textsubscript{4}), and ammonium (NH\textsubscript{4}\textsuperscript{+}) from N fertilizers can competitively inhibit microbial CH\textsubscript{4} oxidation in soils (Gulledge and Schimel 1998, Le Mer and Roger 2001).

Earlier studies have noted the potential for N fertilizer inputs to substantially reduce and even eliminate the climate benefit of food crops grown for biofuels (Crutzen et al. 2007, Mosier et al. 2009, Smith et al. 2012). While Erisman et al. (2010) further noted that this is unlikely to be the case for purpose-grown cellulosic crops because of their lower N fertilizer needs, perennial nature, and higher C:N ratios in harvested biomass, this has not yet been empirically tested.

Here we test the potential for N fertilization to significantly reduce the climate change mitigation benefit of cellulosic biofuels. We present results from a 3 yr experiment to investigate direct and indirect N\textsubscript{2}O emissions, CH\textsubscript{4} uptake, NO\textsubscript{3}\textsuperscript{–} leaching, soil organic carbon (SOC) accumulation, and biomass production in recently established switchgrass under eight different N fertilizer rates. Our analysis allows an evaluation of the impact of N fertilization on the net GHG balance of switchgrass grown as a cellulosic biofuel feedstock.

2. Methods

The experiment was conducted at a site in southwest Michigan USA, in the northeastern portion of the US Corn Belt. The Switchgrass N Rate Experiment is part of the Great Lakes Bioenergy Research Center (GLBRC) and located at the Kellogg Biological Station Long-term Ecological Research Site (www.lter.kbs.msu.edu; 42°23'N, 85°22'W, elevation 284 m asl). Precipitation averages 1005 mm yr \textsuperscript{–1} with an average snowfall of \sim 1.3 m. Mean annual temperature is 10.1 °C ranging from a monthly mean of −3.8 °C in January to 22.9 °C in July (NCDC 2013). Soils are mesic Typic Hapludalfs of Kalamazoo loam developed on glacial outwash (Robertson and Hamilton 2015). Prior to establishing the experiments, soil pH (0–25 cm depth) was 7.47 ± 0.04 (mean ± standard error, n = 12 plots), bulk density (BD) was 1.24 ± 0.04 g cm\textsuperscript{–3}, total N was 1.25 ± 0.09 g kg\textsuperscript{–1} soil, and SOC was 10.2 ± 0.74 g kg\textsuperscript{–1} soil (http://data.sustainability.glbrc.org/).

Switchgrass (variety Cave-in-Rock) was planted at a seeding rate of 7.84 kg ha\textsuperscript{–1} on 11 July, 2008, after tillage to a depth of 25 cm. Plots were established on land that had been in alfalfa, corn, and occasional soybean production for preceding decades. Eight fertilization treatments (0, 28, 56, 84, 112, 140, 168, and 196 kg N ha\textsuperscript{–1}) were established in switchgrass plots (4.5 × 6 m) arranged in a randomized complete block design with four replicate blocks, for a total of 32 experimental plots. Nitrogen fertilizer was applied once per year in 2009–2011: granular 46% urea was broadcasted on 17 June, 2009, and liquid 28% urea ammonium nitrate was sprayed on 10 May, 2010, and 16 May, 2011. Biomass was harvested in late fall annually on each plot using a John Deere 7330 tractor with a plot harvester (Wintersteiger Inc., Salt Lake City, UT) and HarvestMaster HM800 Plot Harvest Data System (Juniper Systems Inc., Logan, UT). Dry matter percentage was determined by oven-drying subsamples from harvested plots at 50 °C until a constant weight. Harvest height was \sim 10 cm.

2.1. N\textsubscript{2}O and CH\textsubscript{4} sampling

N\textsubscript{2}O and CH\textsubscript{4} fluxes were measured using a static chamber—gas chromatography approach (Ruan and Robertson 2013) from May to December in 2009–2011. We measured fluxes 2–3 times per week during the growing season to capture the temporal dynamics of N\textsubscript{2}O and CH\textsubscript{4} fluxes as influenced by fertilization and precipitation, and then measured fluxes every 2 weeks after mid-September. A vented chamber (28 cm diameter × 26 cm height) equipped with a detachable lid and septum was installed in each treatment plot for a total of 32 chambers. Chamber bases were inserted into the soil \sim 5 cm for the duration of the study. Vegetation inside (but not surrounding) chambers was clipped to maintain plant heights lower than chamber heights. During flux samplings, chambers were tightly sealed with the lid and then headspace gas samples were collected four times with a 10 ml syringe at approximately 15 min intervals. Samples were stored over-pressurized in 5.6 ml glass vials (Labco Ltd, High Wycombe, UK). Gases were analyzed within three days by gas chromatography (Hewlett Packard 5890 Series II, Rolling Meadows, IL, USA). Gases were separated on a Porapak Q column (1.8 m, 80/100 mesh) at 80 °C; CH\textsubscript{4} was analyzed with a flame ionization detector at 300 °C and N\textsubscript{2}O was analyzed with a 63Ni electron capture detector at 350 °C.

2.2. Soil water-filled pore space (WFPS %), inorganic N, and NO\textsubscript{3}\textsuperscript{–} leaching

At each gas sampling event we measured soil temperature, gravimetric water content, and inorganic N (NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{–}) concentrations at 0–25 cm depth. Soil gravimetric water content (GWC, g water g\textsuperscript{–1} dry soil) was determined by oven-drying soil at 60 °C for 48 h until constant mass. Soil BD was measured three
times during each growing season using a fixed-volume soil core (125 cm$^3$) for each treatment plot. WFPS% was calculated as

$$\text{% WFPS} = \frac{100\% \times \frac{\text{GWC} \text{ (g g}^{-1}) \times \text{BD} \text{ (g cm}^{-3})}{\text{soil porosity}}}{1}$$

where soil porosity = 1 − [BD (g cm$^{-3}$/particle density (g cm$^{-3}$)]. Soil particle density was assumed to be the standard 2.65 g cm$^{-3}$.

For measuring NH$_4^+$ and NO$_3^-$, three 10 g soil samples (4 mm sieved) were extracted with 100 ml of 1 M KCl. Filtrates from soil extracts were analyzed colorimetrically on a Flow Solution IV autoanalyzer (OI Analytical, College Station, TX, USA).

Nitrate leaching below the root zone (1.0 m depth) was determined by measuring concentrations in soil pore water and then multiplying concentrations by downward water percolation (drainage) from the overlying soil. The study site has no detectable overland runoff because of its highly permeable soils. Soil pore water was sampled at weekly to fortnightly intervals (except when the ground was frozen) using low-tension porous ceramic cup samplers (Eijkelkamp Agrisearch Equipment, California, USA) installed at a 45° angle from the soil surface. The collected and filtered (1 μm nominal pore size; Pall A/E) water samples were analyzed for NO$_3^-$ using a Dionex 600 ion chromatograph. Previous work at this site (Syswerda et al. 2012) has shown that NO$_3^-$ dominates N leaching with negligible leaching of NH$_4^+$ or dissolved organic N.

Percolation of water from the root zone was modeled at a daily time step using the systems approach for land use sustainability model well-calibrated for KBS soils (Basso and Ritchie 2015), which accounts for management practices, water balance, soil organic matter change, nitrogen and phosphorus dynamics, heat balance, and plant growth and development. The soil water balance module is based on CERES models (Ritchie et al. 1998) with revisions for infiltration, soil water export (Suleiman and Ritchie 2004), evaporation (Suleiman and Ritchie 2003), and runoff. Daily leaching losses of nitrate were estimated from modeled water percolation plus linear interpolation of the measured nitrate concentrations.

### 2.3. SOC sampling

One intact soil core (7.6 cm diameter × 100 cm depth) was taken from each of the 32 experimental plots in June 2008 and May 2013 with a hydraulic sampler (Geoprobe model 540MT, Salina, KS). Each core was then cut into three profile segments: 0–25 cm (to represent the Ap layer), 25–50 cm (E layer), and 50–100 cm (Bt layer) (Syswerda et al. 2011). Each segment was sieved (4 mm), oven-dried, and weighed for BD. Dry soil samples were then finely ground in a roller mill and three 10 mg samples were analyzed for C using a Costech elemental combustion system (Costech Analytical Technologies, Valencia, California).

### 2.4. Net GHG balance

To estimate the global warming impact (GWI) of GHG fluxes, we multiplied fluxes of CH$_4$ and N$_2$O by their 100 yr horizon global warming potential factors of 25 and 298, respectively, to yield CO$_2$ equivalents (CO$_2$e) (Solomon et al. 2007).

We assumed that all CO$_2$ taken up from the atmosphere as net primary production by switchgrass was stored in harvested biomass and SOC. SOC change in CO$_2$e was calculated as the product of the difference of SOC (Mg ha$^{-1}$ yr$^{-1}$) over the 4 yr study and the conversion factor of C to CO$_2$ (44/12).

Fossil fuel offset credit (Mg CO$_2$e ha$^{-1}$ yr$^{-1}$) is defined as the avoided CO$_2$ emissions due to the displacement of fossil fuel use by biofuels during production, transportation, distribution, combustion, and coproducts allocation (Plevin 2009). Avoided CO$_2$e emissions were calculated from a comparison of life cycle analyses of petroleum gasoline versus ethanol from switchgrass. Gasoline releases 94 g CO$_2$e per MJ petroleum gasoline produced, distributed, and combusted (Farrell et al. 2006, Wang et al. 2012). Net CO$_2$e emissions per MJ of switchgrass ethanol were calculated as the product of net CO$_2$e emissions (Mg CO$_2$e ha$^{-1}$) from ethanol production, transportation, distribution and combustion and the total energy equivalent of biomass yield (MJ ha$^{-1}$). Net CO$_2$e emissions were calculated using the GREET model (Huo et al. 2009) to calculate fossil fuel offset credits for the fossil fuel CO$_2$ emissions that would be displaced by the production of both ethanol and biorefinery coproducts (Farrell et al. 2006, Gelfand et al. 2013), with all farming inputs equal to 0. Farming inputs were calculated separately using actual values from the study site as presented in table S3. Total energy equivalent (MJ ha$^{-1}$) was calculated as the product of harvestable dry-weight biomass (Mg ha$^{-1}$), biorefinery ethanol yield (380 Mg$^{-1}$ biomass) (Schmer et al. 2008, Gelfand et al. 2011) and ethanol energy content (21.1 MJ l$^{-1}$; low heating value) (Gelfand et al. 2011, 2013). Finally, the fossil fuel offset credit (Mg CO$_2$e ha$^{-1}$) was calculated as the product of the CO$_2$e difference from life cycle analyses of petroleum gasoline and ethanol from switchgrass (g CO$_2$e MJ$^{-1}$) and the ethanol energy content.

### 2.5. Data analysis

Cumulative fluxes of gases over annual periods were calculated by linear interpolation of daily fluxes between sample days. Data were analyzed using the PROC MIXED procedure in SAS 9.2 (SAS Institute, Cary, NC, USA). Treatment means were compared for significance using t-tests at $\alpha = 0.05$ level. The relationships between daily N$_2$O emissions and environmental factors such as soil temperature, soil
moisture, and soil total N were assessed by multiple linear regressions (stepwise) using PROC REG. Quadratic-plateau curves for switchgrass yields versus N fertilization rates were calculated using PROC NLIN, with switchgrass yields at successive fertilizer rates weighted by the inverse of its rank order along the N gradient (1/1 to 1/8). To determine the relationship between annual N$_2$O emissions or leached nitrogen and N fertilization rate we performed exponential regression using PROC NLIN and linear regression using PROC REG. Likelihood ratio-based stepwise linear regressions using PROC NLIN and linear regression for the exponential model, respectively (table S1). Additionally, $R^2$ values for the exponential model (0.90–0.94) were consistently higher than were $R^2$ values for the linear model (0.84–0.88) (table S1).

From 2009 to 2011, mean daily N$_2$O emissions ranged from 1.28 ± 0.14 g N ha$^{-1}$ d$^{-1}$ in the low (0 kg N ha$^{-1}$) fertilization treatment to 25.8 ± 1.9 g N ha$^{-1}$ d$^{-1}$ in the high (196 kg N ha$^{-1}$) fertilization treatment (figure S1). The maximum daily N$_2$O emission was 270 ± 25 g N ha$^{-1}$ d$^{-1}$ in the highest N treatment and the minimum daily emission was undetectable in treatments that received less than 56 kg N ha$^{-1}$ yr$^{-1}$. Most of the fertilizer-associated N$_2$O emissions occurred within 40 days following fertilization, coincident with soil wetting by rainfall. N$_2$O emissions were strongly correlated with soil inorganic N concentrations (mg N kg$^{-1}$) and % soil WFPS (N$_2$O emission = $-34.8 + 0.83 \times$ inorganic N + 81.9 \times$ WFPS, $R^2 = 0.48, n = 2112, P < 0.001$). At all soil inorganic N levels, N$_2$O emissions were highly dependent on WFPS (figure S2).

Modeled soil water drainage was 275, 399 and 515 mm yr$^{-1}$ in 2009, 2010 and 2011, respectively, representing 37%, 39% and 46% of annual precipitation. Annual NO$_3^-$ leaching rates ranged from 2.65 ± 1.29 kg N ha$^{-1}$ yr$^{-1}$ for unfertilized switchgrass to 56.0 ± 2.7 kg N ha$^{-1}$ yr$^{-1}$ for switchgrass fertilized at 196 kg N ha$^{-1}$, and also increased exponentially (table S2) in response to increasing N inputs, with no significant difference in the increase among years (figure 3).

3. Results and discussion

Switchgrass yields were responsive to N fertilizer in 2009, but were less responsive in 2010 and 2011 (figure 1). Based on a quadratic plateau model ($R^2_{2009} = 0.86, P < 0.01; R^2_{2010} = 0.69, P < 0.01; R^2_{2011} = 0.21, P < 0.05$), maximum yields of 4.2, 8.9 and 10.6 Mg ha$^{-1}$ yr$^{-1}$ occurred at 147 kg N ha$^{-1}$ in 2009, at 72 kg N ha$^{-1}$ in 2010, and at only 34 kg N ha$^{-1}$ in 2011, respectively. Yields for 2010 and 2011 are consistent with average regional yields of 8.7 ± 4.2 Mg ha$^{-1}$ yr$^{-1}$ for post-establishment switchgrass (Wullschleger et al 2010).

We observed an exponential increase in annual N$_2$O emissions with increasing N fertilization rates in each year (figure 2). The AIC and the BIC values were consistently lower for the exponential model for each study year and as well for all 3 years together: for individual years AIC and BIC values for the linear model were 52%–121% and 76%–173% higher than those for the exponential model, respectively (table S1). Additionally, $R^2$ values for the exponential model (0.90–0.94) were consistently higher than were $R^2$ values for the linear model (0.84–0.88) (table S1).

Switchgrass yields in response to N fertilization for the first three harvest years (2009–2011) are consistent with average regional yields of 5.9 ± 1.2 Mg ha$^{-1}$ yr$^{-1}$ for established switchgrass, 4.2 ± 0.8 Mg ha$^{-1}$ yr$^{-1}$ for post-establishment switchgrass (Wullschleger et al 2010).
The exponential increases in N$_2$O emissions and NO$_3^-$ leaching are likely due to surplus soil N at levels above which plant N demands are met, resulting in more available N for the nitrifiers and denitrifiers that produce N$_2$O, as well as for leaching. The exponential increase for N$_2$O also implies that the N$_2$O emission factor used for most national GHG inventories (De Klein et al. 2006) varies with N fertilizer rate, in agreement with other recent studies for annual crops but yet untested for perennial crops (Shcherbak et al. 2014). In this study the emission factor increased from 0.6% to 2.1% across the range of added N (figure 4). A constant emission factor, as called for by IPCC Tier 1 methodology (De Klein et al. 2006), would underestimate 3 year N$_2$O emissions by 30% at lower levels of N fertilizer and up to 107% at higher levels.

Mean daily CH$_4$ uptake rates ranged from $-1.49 \pm 0.31$ to $-0.82 \pm 0.27$ g CH$_4$·C ha$^{-1}$·d$^{-1}$ across all eight fertilizer levels (figure S3). There were no significant N treatment differences detected ($P > 0.1$), although mean CH$_4$ uptake rates in highly fertilized soils (>56 kg N added ha$^{-1}$) were only 55%–74% of those in the unfertilized treatment. We also found no significant SOC accumulation in any of our N treatments over the 3 year study period (figure S4). Likely this is due to lost soil C on conversion of the field to switchgrass in 2008, although spatial variability makes it difficult to detect SOC change in fewer than

**Figure 2.** Exponentially increasing annual N$_2$O emission in response to increasing N fertilization rates for the first three harvest years (2009–2011) ($P < 0.001$, bands represent 95% confidence intervals).

**Figure 3.** Exponentially increasing annual NO$_3^-$ leaching in response to increasing N fertilization rates for the first three harvest years (2009–2011) ($R^2 = 0.74$, $P < 0.0001$, band represents 95% confidence intervals).
10 years in many soils (Kravchenko and Robertson 2011), including ours (Syswerda et al 2011).

We combined our field measurements with published carbon costs for agricultural inputs (Robertson et al 2000, Farrell et al 2006, Schmer et al 2008, Gelfand et al 2011, 2013) to estimate overall GWI in units of CO₂ equivalents (CO₂e) for each of our N treatments (table S3). Measurements of NO₃⁻ loss allow us to include a major portion of indirect N₂O production, missing from most empirical GWI assessments. Estimated indirect N₂O emissions from the loss of leached NO₃⁻ ranged from 22.1 ± 7.8 for unfertilized switchgrass to 157 ± 12.3 kg CO₂e ha⁻¹ yr⁻¹ for switchgrass fertilized at 196 kg N ha⁻¹. Calculated 3 year averages of fossil fuel offsets for our eight N treatments ranged from –4.84 ± 0.12 Mg CO₂e ha⁻¹ yr⁻¹ in our

Figure 4. Relationships between soil N₂O emission factors (% of N fertilizer input that was ultimately emitted as N₂O) and N fertilization rates for the first three harvest years (2009–2011), including linear regression fits.

Figure 5. Annual global warming impacts (GWI; based on overall GHG balances) for switchgrass production across the N fertilizer gradient. (a) GWI components including fossil fuel offset credits for displacement of gasoline by biofuel; (b) net GWI. GHG emissions from agricultural inputs include farm machinery, switchgrass seed production, and N fertilizer production, transportation and distribution. Indirect N₂O emissions represent N₂O produced off-site by leached NO₃⁻. Direct N₂O and CH₄ fluxes are from field measurements during 2009–2011. CH₄ uptake rates were negligible and are not visible in the graph. Error bars represent standard errors based on n = 4 replicate plots.
unfertilized treatment to $-6.42 \pm 0.38 \text{Mg CO}_2\text{e ha}^{-1} \text{yr}^{-1}$ in our treatment with the highest yield per unit N added (56 kg N ha$^{-1}$) (figure 5(a)).

Including all GHG sources and credits in the GWI analysis, each N treatment shows net climate change mitigation (i.e., negative net CO$_2$e), with maximum net mitigation capacities as high as $-5.71 \pm 0.22 \text{Mg CO}_2\text{e ha}^{-1} \text{yr}^{-1}$ in the treatment fertilized at 56 kg N ha$^{-1}$ (figure 5(b)). However, at fertilization rates above 56 kg N ha$^{-1}$ net mitigation decreased monotonically with each increment of added N to only $-2.97 \pm 0.18 \text{Mg CO}_2\text{e ha}^{-1} \text{yr}^{-1}$ for the 196 kg N ha$^{-1}$ treatment (figure 5(b)).

Greater N$_2$O emissions in N fertilized compared to non-fertilized switchgrass has been noted in Nova Scotia Canada (Wile et al 2014), Nebraska USA (Schmer et al 2012), northern Michigan USA (Nikïèma et al 2011), and southern Michigan and Wisconsin USA (Oates et al 2016). Two studies Nikïèma et al (2011) and Wile et al (2014) included three fertilizer rates, and while N$_2$O responses were in some site years consistent with an exponential response, three rates are insufficient to statistically test for nonlinearity. We are not familiar with any N leaching studies that have tested the effects of fertilizer rates on nitrate loss in switchgrass or any other perennial biofuel crop.

That the mitigation potential of switchgrass fertilized at high N rates is only about half of its mitigation potential at yield-optimizing N rates points to a significant challenge for realizing the environmental potential of cellulosic biofuels. Knowledge of and careful management for crop N needs appear to be crucial. In many cases, such as for the maturing switchgrass crops in this study, fertilizer needs may be close to nil: some varieties of switchgrass are known to be unresponsive to fertilizer N (Christian et al 2002), presumably because of a high N use efficiency and/or the presence of other N acquisition mechanisms, possibly including biological N fixation.

4. Conclusions

Breeding for low N needs, and then fertilizing only as needed—if at all—to meet these needs will be an important strategy for meeting the full climate mitigation benefits of cellulosic biofuels. In the meantime, incentives to grow N-conserving crop varieties and to apply as little fertilizer N as necessary will be needed to meet the climate benefit claims of this emerging industry (Robertson et al 2008). Incentives to reduce N fertilizer use would have an additional advantage of reducing unnecessary N pollution of ground- and surface waters and lowering the cost of biofuel crop production.

Acknowledgments

We thank M Barrows, S Bohm, P Jasrotia, K Kahmark, C McMinn, E Robertson, J Simmons, S Sippel, S VanderWulp and many others for assistance in the field and lab. We also thank A N Kravchenko, A J M Smucker, and I Gelfand for helpful comments on an earlier version of the manuscript and J Schuette and C Kremer for help with figures. Financial support was provided by the US DOE Office of Science (DE-FC02-07ER64494) and Office of Energy Efficiency and Renewable Energy (DE-AC05-76RL01830), the National Science Foundation LTER Program (DEB 1027253), and Michigan State University AgBioResearch.

References


Farrell A E, Plevin R J, Turner B T, Jones A D, O’Hare M and Kammen D M 2006 Ethanol can contribute to energy and environmental goals Science 311 506–8


NCDC (National Climatic Data Center) 2013 Summary of Monthly Normals 1981–2010, Gull Lake Biological Station, MI, USA (http://ncdc.noaa.gov/cdo-web/search)


Ruan L and Robertson G P 2013 Initial nitrous oxide, carbon dioxide, and methane costs of converting conservation reserve program grassland to row crops under no-till versus conventional tillage. Glob. Change Biol. 19 2478–89


Suleiman A and Ritchie T J 2004 Modifications to the DSSAT vertical drainage model for more accurate soil water dynamics. Soil Sci. 169 745–57


Supplementary data for “Nitrogen fertilization challenges the climate benefit of cellulosic biofuels”

Leilei Ruan\(^1,2,3\), Ajay K Bhardwaj\(^2,5\), Stephen K Hamilton\(^1,2,4\), and G Philip Robertson\(^1,2,3\)*

\(^1\) W.K. Kellogg Biological Station, Michigan State University, Hickory Corners, MI 49060 USA
\(^2\) Great Lakes Bioenergy Research Center, Michigan State University, East Lansing, MI 48824 USA
\(^3\) Dept. of Plant, Soil, and Microbial Sciences, Michigan State University, East Lansing, MI 48824 USA
\(^4\) Dept. of Integrative Biology, Michigan State University, East Lansing, MI 48824 USA
\(^5\) Current address: Central Soil Salinity Research Institute, Indian Council of Agricultural Research, Karnal, Haryana 132001 India

Contains:

- Supplementary tables S1-S3
- Supplementary references
- Supplementary figures S1-S4

* Corresponding author: robert30@msu.edu; 269.671.2267
### Table S1. Model comparisons for the response of annual N$_2$O emissions to N fertilization rate. AIC = Akaike information criterion and BIC = Bayesian information criterion. In this comparison the best model has the lowest criteria; % AIC and % BIC represent the percentage increases for the linear models compared with the better exponential models that are indicated with “√”.

<table>
<thead>
<tr>
<th>Year</th>
<th>Model</th>
<th>R$^2$</th>
<th>AIC</th>
<th>% AIC</th>
<th>BIC</th>
<th>% BIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>Linear</td>
<td>0.88</td>
<td>-3.02</td>
<td>52%</td>
<td>1.37</td>
<td>173%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.90</td>
<td>-6.3</td>
<td>√</td>
<td>-1.87</td>
<td>√</td>
</tr>
<tr>
<td>2010</td>
<td>Linear</td>
<td>0.84</td>
<td>43.7</td>
<td>90%</td>
<td>48.1</td>
<td>76%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.91</td>
<td>23.0</td>
<td>√</td>
<td>27.4</td>
<td>√</td>
</tr>
<tr>
<td>2011</td>
<td>Linear</td>
<td>0.86</td>
<td>54.0</td>
<td>121%</td>
<td>58.4</td>
<td>103%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.94</td>
<td>24.4</td>
<td>√</td>
<td>28.7</td>
<td>√</td>
</tr>
<tr>
<td>All 3 yr</td>
<td>Linear</td>
<td>0.73</td>
<td>176</td>
<td>13.5%</td>
<td>184</td>
<td>12.9%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.75</td>
<td>155</td>
<td>√</td>
<td>163</td>
<td>√</td>
</tr>
</tbody>
</table>

### Table S2. Model comparisons for the response of annual N leaching to N fertilization rate. See Table S1 legend for further information.

<table>
<thead>
<tr>
<th>Year</th>
<th>Model</th>
<th>R$^2$</th>
<th>AIC</th>
<th>% AIC</th>
<th>BIC</th>
<th>% BIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>Linear</td>
<td>0.60</td>
<td>174</td>
<td>1%</td>
<td>178</td>
<td>1%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.65</td>
<td>172</td>
<td>√</td>
<td>176</td>
<td>√</td>
</tr>
<tr>
<td>2010</td>
<td>Linear</td>
<td>0.73</td>
<td>182</td>
<td>4%</td>
<td>185</td>
<td>4%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.80</td>
<td>175</td>
<td>√</td>
<td>178</td>
<td>√</td>
</tr>
<tr>
<td>2011</td>
<td>Linear</td>
<td>0.65</td>
<td>190</td>
<td>15%</td>
<td>194</td>
<td>14%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.87</td>
<td>166</td>
<td>√</td>
<td>170</td>
<td>√</td>
</tr>
<tr>
<td>All 3 yr</td>
<td>Linear</td>
<td>0.64</td>
<td>547</td>
<td>4%</td>
<td>554</td>
<td>4%</td>
</tr>
<tr>
<td></td>
<td>Exponential</td>
<td>0.74</td>
<td>525</td>
<td>√</td>
<td>532</td>
<td>√</td>
</tr>
</tbody>
</table>
**Table S3.** Estimation of CO$_2$-equivalent emissions associated with switchgrass for cellulosic biofuel crop production. GWI = Global warming impact.

<table>
<thead>
<tr>
<th>GWI component$^a$</th>
<th>Mg CO$_2$e ha$^{-1}$ yr$^{-1}$</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeds$^b$</td>
<td>0.014</td>
<td>See footnote b</td>
</tr>
<tr>
<td>Planting</td>
<td>0.013</td>
<td>Gelfand <em>et al</em> 2013</td>
</tr>
<tr>
<td>N fertilizer production$^c$</td>
<td>$4.5 \times X \times 0.001$</td>
<td>Robertson <em>et al</em> 2000</td>
</tr>
<tr>
<td>N fertilizer application</td>
<td>0.026</td>
<td>Gelfand <em>et al</em> 2013</td>
</tr>
<tr>
<td>Harvesting (baling)</td>
<td>0.019</td>
<td>Gelfand <em>et al</em> 2013</td>
</tr>
<tr>
<td>Direct N$_2$O emissions</td>
<td>Field data</td>
<td>This study</td>
</tr>
<tr>
<td>Indirect N$_2$O emissions$^d$</td>
<td>Leaching N $\times 0.75%$</td>
<td>This study and IPCC 2006 N$_2$O indirect emission factor (De Klein <em>et al</em> 2006)</td>
</tr>
<tr>
<td>CH$_4$ uptake</td>
<td>Field data</td>
<td>This study</td>
</tr>
<tr>
<td>SOC change</td>
<td>Field data</td>
<td>This study</td>
</tr>
<tr>
<td>Fossil fuel offset credits$^e$</td>
<td>Field data and GREET</td>
<td>This study</td>
</tr>
</tbody>
</table>

$^a$ Phosphorus and potassium fertilizers were not applied in our study, nor were herbicides, insecticides or lime.

$^b$ Calculation for seed production (Mg CO$_2$e ha$^{-1}$ yr$^{-1}$):
- Switchgrass seeds production energy, 43.8 MJ kg$^{-1}$, was based on the analysis of Schmer _et al._ (2008). In order to convert energy (MJ kg$^{-1}$ yr$^{-1}$) to carbon emissions (Mg CO$_2$e ha$^{-1}$), we assumed that energy used in seed production consisted of a 50, 20, and 30% mix of fuel oil, natural gas, and electricity, respectively (Börjesson 1996). We also used energy conversion factors of 0.094 kg CO$_2$e MJ$^{-1}$ (Farrell _et al._ 2006), 0.056 kg CO$_2$e MJ$^{-1}$ (Farrell _et al._ 2006), and 0.21 kg CO$_2$e MJ$^{-1}$ (EPA 2014) for the conversion of gasoline, natural gas and electricity to carbon emissions, respectively. As a result:
  - Fuel: 43.8 MJ kg$^{-1}$ $\times$ 50% $\times$ 0.094 kg CO$_2$e MJ$^{-1}$ = 2.06 kg CO$_2$e kg$^{-1}$
  - Natural Gas: 43.8 MJ kg$^{-1}$ $\times$ 20% $\times$ 0.056 kg CO$_2$e MJ$^{-1}$ = 0.49 kg CO$_2$e kg$^{-1}$
  - Electricity: 43.8 MJ kg$^{-1}$ $\times$ 30% $\times$ 0.21 kg CO$_2$e MJ$^{-1}$ = 2.73 kg CO$_2$e kg$^{-1}$
  - Total carbon emissions (kg CO$_2$e kg$^{-1}$) = Fuel + natural gas + electricity = 5.28 kg CO$_2$e kg$^{-1}$
  - The seeding rate in our study is 7.84 kg ha$^{-1}$. Therefore,
  - Total carbon emissions (Mg CO$_2$e ha$^{-1}$) = 5.28 kg CO$_2$e kg$^{-1}$ $\times$ 7.84 kg ha$^{-1}$ $\times$ 0.001 Mg kg$^{-1}$ = 0.04 Mg CO$_2$e ha$^{-1}$
  - Since it is a perennial grass, switchgrass does not need to be seeded annually. Therefore, we averaged this value over the study period (3 yr), i.e., 0.014 Mg CO$_2$e ha$^{-1}$ yr$^{-1}$.

$^c$ Based on Robertson _et al._ (2000), 4.5 kg CO$_2$e released per kg of N produced and transported to field crops; X is the N fertilization rate (kg N ha$^{-1}$ yr$^{-1}$); 0.001 is the conversion factor from kg to Mg.

$^d$ Leaching N data from the field experiment in this study.

$^e$ GREET (Huo _et al._ 2009) was used to calculate fossil fuel offset credits for different yields from each N treatment, with all farming inputs set to 0 as noted in Methods. Offset credits include co-product credits, which for lignocellulosic biomass includes lignin, used to generate electricity.
Supplementary references

Börjesson P I I 1996 Energy analysis of biomass production and transportation *Biomass and Bioenergy* 11 305-18


Farrell A E, Plevin R J, Turner B T, Jones A D, O'Hare M and Kammen D M 2006 Ethanol can contribute to energy and environmental goals *Science* 311 506-8


Supplementary figures

**Figure S1.** Mean daily N₂O emissions May to December for the first three harvest years (2009-2011) following establishment in 2008 across the eight fertilization treatments. Error bars omitted for clarity (n=4 replicate chambers per treatment).
**Figure S2.** Relationship of daily N$_2$O emission to soil water content (water-filled pore space) at 0–25 cm depth across several levels of soil inorganic nitrogen (KCl-extractable NO$_3$$^-$ + NH$_4$$^+$) during the first three harvest years (2009-2011). Bands show 95% confidence intervals around linear regression fits to the data (data points not shown); all fits are significant at $\alpha=0.05$.

**Figure S3.** Average daily CH$_4$ uptake rates in each switchgrass N fertilization treatment for May to December for the first three harvest years (2009-2011). Error bars represent standard errors of the mean (n=4 replicate plots). There are no significant differences among treatments ($\alpha=0.05$).
Figure S4. Soil carbon concentrations at depths of 0-25, 25-50, and 50-100 cm across the N fertilization gradient. Error bars represent standard errors based on n=4 replicate plots. Bars to the left of the dashed line represent samples taken in 2012 versus those taken at the outset of the experiment in 2008 (to the right side of dashed line). There are no significant differences among treatments (α=0.05).