Modeling biogeochemical impacts of bioenergy buffers with perennial grasses for a row-crop field in Illinois

GAYATHRI GOPALAKRISHNAN*, MARIA CRISTINA NEGRI* and WILLIAM SALAS†
*Energy Systems Division, Argonne National Laboratory, 9700 S Cass Avenue, Argonne, IL 60439, USA, †Applied Geosolutions LLC., 87 Packers Falls Road, Durham, NH 03824, USA

Abstract

Current research on the environmental sustainability of bioenergy has largely focused on the potential of bioenergy crops to sequester carbon and mitigate greenhouse gas emissions and possible impacts on water quality and quantity. A key assumption in these studies is that bioenergy crops will be grown in a manner similar to current agricultural crops such as corn and hence would affect the environment similarly. In this study, we investigate an alternative cropping system where bioenergy crops are grown in buffer strips adjacent to current agricultural crops such that nutrients present in runoff and leachate from the traditional row-crops are reused by the bioenergy crops (switchgrass, miscanthus and native prairie grasses) in the buffer strips, thus providing environmental services and meeting economic needs of farmers. The process-based biogeochemical model Denitrification-Decomposition (DNDC) was used to simulate crop yield, nitrous oxide production and nitrate concentrations in leachate for a typical agricultural field in Illinois. Model parameters have been developed for the first time for miscanthus and switchgrass in DNDC. Results from model simulations indicated that growing bioenergy crops in buffer strips mitigated nutrient runoff, reduced nitrate concentrations in leachate by 60–70% and resulted in a reduction of 50–90% in nitrous oxide emissions compared with traditional cropping systems. While all the bioenergy crop buffers had significant positive environmental benefits, switchgrass performed the best with respect to minimizing nutrient runoff and nitrous oxide emissions, while miscanthus had the highest yield. Overall, our model results indicated that the bioenergy crops grown in these buffer strips achieved yields that are comparable to those obtained for traditional agricultural systems while simultaneously providing environmental services and could be used to design sustainable agricultural landscapes.

Keywords: bioenergy crops, biogeochemical modeling, buffers, DNDC, nitrogen cycle, sustainability

Received 29 August 2011 and accepted 28 September 2011

Introduction

Agro-ecosystems are complex systems where human requirements and the environment intersect. To feed the increasing human population, artificial fertilizers, particularly inputs of nitrogen, are produced and applied to agricultural fields to maintain high crop yields. However, the environmental costs of nutrient pollution from fertilizer use are significant, including degradation of water quality, eutrophication of coastal marine systems, and increased greenhouse gas (GHG) emissions resulting from the production of nitrous oxide (N_2O) (Vitousek *et al.*, 2000).

Water quality impacts are registered both locally, with runoff and percolation of nitrate from fertilizers into local surface water and groundwater, and on a larger scale, such as the increase in the anoxic zone in the Gulf of Mexico attributed to nitrate from the Mississippi

River (Turner *et al.*, 2008). In studies of nitrate concentrations in the Mississippi River Basin, nutrient loading was found to be the highest in sub-basins of watersheds where the percentage of corn is high and the fraction of perennials is low (Crumpton *et al.*, 2006; Booth & Campbell, 2007). It is anticipated that these nutrient loads will only increase in the future, as the area of corn planted increases to meet energy demands for biofuels in addition to food and feed needs (Turner *et al.*, 2008).

Impacts to the global climate from increased production of N_2O as a result of increased fertilization are equally significant. N_2O is a GHG with a warming potential that is ca. 300 times greater than CO_2 and contributes significantly to GHG emissions (IPCC, 2006; Crutzen *et al.*, 2008). N_2O is a natural by-product of soil nitrification and denitrification that occurs when nitrogen is applied to the soil (Smeets *et al.*, 2009) and the conditions for full conversion to N_2 are not present. N_2O is emitted directly from the soil and indirectly due to runoff, leaching and volatilization of the nitrogen from the field (Bouman, 1996; IPCC, 2006). In the United

Correspondence: Gayathri Gopalakrishnan, tel. + 1 630 252 7051, fax + 1 630 252 1342, e-mail: ggopalakrishnan@anl.gov

States, agricultural soil management practices such as fertilizer application and other cropping practices accounted for 67% of the nation's emissions of N_2O in 2007, estimated at 200.3 Tg CO_2 equivalent [United States Environmental Protection Agency (USEPA), 2010]. N_2O emissions from soils have been found to be a function of various environmental and soil factors (e.g., pH, redox conditions, soil water content, organic carbon, temperature, bulk density, microbial communities, and vegetation type; Hefting *et al.*, 2003; Yu & Patrick, 2004; Hernandez-Ramirez *et al.*, 2009; Kim *et al.*, 2009; DeSimone *et al.*, 2010) and management practices (e.g., no-till cultivation, type and amount of fertilizer application, spring or fall fertilizer application; Mosier *et al.*, 1998; Venterea *et al.*, 2005; Smeets *et al.*, 2009).

A number of countries, including the United States, Australia, Canada, Japan, Norway, Switzerland, and European Union countries, have established guidelines and practices to help mitigate the negative environmental impacts of excess nitrogen fertilization from farms. These practices include establishment of conservation buffers to preserve environmentally fragile land (e.g., easily flooded land, erodible land, or land with high biodiversity), landscape maintenance fees, and agricultural support payments in combination with environmental regulations [Organization for Economic Cooperation & Development (OECD), 2001]. In particular, efforts such as the Chesapeake Bay buffers program have focused on the use of buffer strips along riparian land to provide water quality, conservation, and soil erosion control benefits [Dosskey *et al.*, 2006; United States Department of Agriculture (USDA), 2010]. The success of buffer systems at the landscape scale is debatable because of the limited adoption of these practices by the farming community, possibly due to cultural and economic factors related to removing land from active production (Lovell & Sullivan, 2006).

A solution that has been proposed to integrate environmental benefits and economic returns to the farmer is the production of second-generation perennial bioenergy crops in buffer strips (Gopalakrishnan *et al.*, 2009; Karlen, 2010). In this proposed system, perennial bioenergy crops would be grown in buffer strips on marginally productive land adjacent to conventional row-crops such that nutrients present in runoff and leaching into groundwater from row-crops growing in the fields would be taken up by the deep-rooted energy crops in the buffer. This would enable production of the energy crops without the need for additional inputs of fertilizers. These buffer strips would differ from traditional conservation buffer strips as biomass (and a fraction of the absorbed nitrogen) is removed from the system by harvesting the bioenergy crop. Productivity and crop use of nitrogen may be significantly different from unharvested conservation buffers and thereby influence N_2O emissions from the buffers as well as capture of nitrate present in runoff and leachate from the adjacent row-crop.

Research on the environmental impacts of bioenergy crops production has focused on GHG reductions, carbon sequestration, and the effects of land use change, both direct and indirect (Lemus & Lal, 2005; Hill *et al.*, 2006; Righelato & Spracklen, 2007; Fargione *et al.*, 2008; Searchinger *et al.*, 2008). A recent study suggested that increased N_2O emissions from additional fertilizer input could offset any GHG reductions achieved by bioenergy crops through carbon sequestration and fossil-fuel replacement (Crutzen *et al.*, 2008). Davis *et al.* (2010) simulated N_2O emissions at the field scale when the bioenergy crops switchgrass and miscanthus, replaced corn on fertile agricultural land and determined that switchgrass, corn, and prairie grasses were net sources of GHG emissions to the atmosphere when N_2O emissions were included, while miscanthus was a sink. Most studies have focused on growing bioenergy crops such as switchgrass and miscanthus in traditional agricultural cropping systems (Heaton *et al.*, 2008). Integrated landscapes with bioenergy crop buffers could have very different impacts on water quality in terms of nitrate concentrations in runoff and leachate and N_2O emissions. These impacts have not been studied previously.

The primary objective of this study is to model the potential effects on nitrate concentrations in groundwater (leachate) and N_2O emissions when bioenergy crop buffers are used in typical row-crop agricultural fields. However, direct measurements of N_2O emissions in these systems are lacking. A number of agro-ecosystem models have been developed that incorporate the interactions between climate, soil, plant growth, and management practices (Farahbakhshazad *et al.*, 2008) and could be used when field data are limited or lacking. Among these models, the process-based biogeochemistry model, Denitrification-Decomposition or DNDC, was first developed to estimate GHG emissions from agricultural lands in the United States (Li *et al.*, 1992) and was further improved to predict crop growth and yields, simulate discharge flow from tile-drains and quantify nitrate leaching and the soil buffering effect of ammonium (Li *et al.*, 2006; Farahbakhshazad *et al.*, 2008). As mentioned by Farahbakhshazad *et al.*, 2008, these modifications 'have made the model capable of simultaneously predicting crop yield, nitrate-N leaching and trace gas emissions under a wide range of farm management conditions, especially row-crop fields in the US Midwest'. Hence, we have utilized this model in our study to understand how bioenergy crop buffers impact water quality and N_2O emissions and the

sensitivity of these impacts when selected management strategies are used. Bioenergy crops considered here are the perennial grasses – switchgrass (*Panicum virgatum*), miscanthus (*Miscanthus giganteus*) and native prairie grasses. As bioenergy crops are relatively new, data on parameters for these crops in models such as DNDC are lacking. A secondary objective of this article is to estimate crop parameters in DNDC for miscanthus and switchgrass; native prairie grasses have been parameterized previously in the model.

A typical row-crop field in Illinois, with a long-term database and field measurements of bioenergy crop yields was selected as the target site for this study. First, crop parameters were developed and calibrated with observations at the target site. Second, model parameters were later validated against observations at two other row-crop field sites in Illinois where data were available for bioenergy crops. Third, the impacts of an integrated landscape with bioenergy crop buffers on nitrate-N leaching, N_2O emissions, and crop yields under different management strategies were modeled for the target site.

Materials and methods

The DNDC model

DNDC is a complex simulation model that describes carbon and nitrogen cycling processes in soils (Li *et al.*, 1992) and was developed to predict N_2O fluxes from arable soils and later extended to agroecosystems. DNDC uses climate, crop growth and soil environmental factors (e.g., pH, soil temperature, water content, soil carbon) to determine N_2O emissions based on denitrification and nitrification pathways. N_2O emitted during nitrification is a function of the ammonium concentration and the microbial biomass and is calculated on a daily time-step (Chen *et al.*, 2008). Denitrification is activated when soil moisture increases, soil oxygen availability decreases, or when freezing occurs and thus inhibits the diffusion of oxygen into the soils (Beheydt *et al.*, 2007). The model further assumes that soil nitrifiers or denitrifiers can utilize ammonium or nitrate and methanogens will be activated to produce methane based on soil dissolved organic carbon concentrations. As summarized by Chen *et al.* (2008), 'the predicted diffusion rate of the gases is a function of soil porosity, soil water content, soil temperature, and soil clay content and the exchange of N gases between soil layers is not simulated'. The processes governing nitrate-N leaching into the groundwater were modified by using the Langmuir equation to quantify the adsorption and desorption of ammonium ions on clay and organic matter (Li *et al.*, 2006).

DNDC has been tested at multiple sites, both in the United States and internationally and simulated results were usually found to have a good agreement with measured N_2O fluxes (Li *et al.*, 1992). In a study by Beheydt *et al.* (2007), model results were compared with data from field experiments at over 22 sites and regression coefficients of 0.85 were obtained for croplands and 0.16 for grasslands, suggesting that DNDC simulated cropping systems accurately where sufficient management data were available but was not very accurate for grasslands with insufficient management data (Beheydt *et al.*, 2007). DNDC (v9.3) was tested against field data sets on nitrate-N leaching in Illinois and Iowa and the model successfully predicted nitrate-N concentrations with regression coefficients of 0.75–0.95 compared with the field data (Li *et al.*, 2006; Tonitto *et al.*, 2007a,b).

Site specifications

The target site is located in a farm field in Urbana, Illinois (latitude 40.08°N, longitude 88.23°W) with average annual precipitation being 104 cm (30-year average). The local soils are fine-silty, mixed, mesic typic Endoaquolls and are characterized by high clay and soil organic carbon (SOC) content (silty clay loam; soil pH = 6.3; bulk density 1.58 g cm^{-3}; initial SOC content 0.015 kg C kg^{-1} at the 0–0.15 cm soil depth). For the purposes of validating bioenergy crop parameters in DNDC, two other sites in Illinois where bioenergy crop yields have been recorded were selected. The first validation site is located in Shabbona, Illinois (latitude 41.85°N, longitude 88.85°W) with average annual precipitation being 95 cm (30-year average). The local soils are fine-silty, mixed, mesic typic Endoaquolls (silty clay loam, soil pH = 6.6, bulk density 1.45 g cm^{-3}; initial SOC content 0.014 kg C kg^{-1} at the 0–0.15 cm soil depth). The second validation site is located in Simpson, Illinois (latitude 37.45°N, longitude 88.67°W) with average annual precipitation being 123 cm (30-year average). The local soils are fine-silty, mixed mesic Oxyaquic Fragiudalfs (silty clay loam, soil pH = 5.4, bulk density 1.58 g cm^{-3}; initial SOC content 0.008 kg C kg^{-1} at the 0–0.15 cm soil depth). Daily meteorological data for all three sites, including maximum and minimum temperature, solar radiation, and precipitation are available online at the Illinois Climate Network (http://www.isws.illinois.edu/warm/datatype.asp). The concentration of nitrogen in rainfall at the sites is assumed to be 1.8 mg N L^{-1} based on data published by Li *et al.* (1992) for Illinois. The three sites have been described in detail by Heaton *et al.* (2008), and include management regimes for miscanthus and switchgrass and crop yields obtained at the sites. Model results were compared to crop yields for switchgrass and miscanthus recorded at the three sites by Heaton *et al.* (2008) for calibration and validation purposes.

Baseline and selected management practices scenarios

The baseline scenario assumes that row-crops are grown in the typical farm field in Urbana, Illinois using conventional farming practices with no buffer. A fallow field is modeled to evaluate the impacts of atmospheric nitrogen on nitrate concentrations and N_2O emissions compared to runoff and leachate from fertilizing conventional row-crops. The following management practices are assumed for the row-crops: (i) continuous corn and (ii) corn–soybean rotation. An average fertilization rate of 160 kg N ha^{-1} of anhydrous ammonia for corn grown

in Illinois is assumed (USDA National Agricultural Statistics Service, 2007). The fertilizer is applied either in the spring or in the fall to evaluate effects of fertilizer application timing. The crops are assumed to be planted on 1 May and harvested on 1 October each year. We assumed that all crop residues were left on the field after harvest and incorporated into the soil following the next tillage practice. No-till and conventional moldboard tilling to 10 cm are simulated to determine the effects, if any, of tilling practices.

The buffer scenario assumes that the bioenergy crops are grown in a buffer adjacent to the row-crops at the typical farm field in Urbana, Illinois. We assume that a single bioenergy crop is grown in the buffer for each scenario and that the width and topography of the buffer strip is sufficient to maintain nutrient control. The width of vegetated buffer strips along rivers and roads is a function of the required level of treatment of runoff, rainfall characteristics, available land and the plant species used. Here, we assume a width of 50 m for the buffer to achieve 50–95% reduction in the concentrations of nutrients, pesticides and sediments from runoff (Gopalakrishnan *et al.*, 2009). Bioenergy crops are typically planted in early spring in the first year and minimal weed control is required during the first year to maintain crop productivity. Researchers have suggested that the crops would mature in 2–3 years and then could potentially be harvested every year in winter after senescence occurs (Heaton *et al.*, 2004, 2008; Tilman *et al.*, 2006). We follow the management practices outlined by Heaton *et al.* (2008) for switchgrass and miscanthus and assume that (i) notill is practiced and (ii) the grasses are harvested every year on 21 December after the first 2 years of establishment. Heaton *et al.* (2008) used weed-free seeds, followed by mowing and pesticide application to ensure weed control during the establishment period and we follow their approach in this study. As switchgrass is a prairie grass native to Illinois, we further assume that management and harvesting practices would be similar for native prairie grasses. Finally, we assume that only the nutrients present in leachate and runoff from the row-crops are taken up by the bioenergy crops growing in the buffer and no other fertilizers are applied. As DNDC is a site model, the geospatial connection between the bioenergy crop buffers and the row-crops were simulated by treating the buffers and the row-crops as a dual system, with the output from one system (row-crops) used as the input for the other system (bioenergy crop buffers). Here, the nitrate concentrations present in the leachate and runoff from the row-crops are the output from the row-crop system. These concentrations are then simulated in the fertilization module for the bioenergy crop buffers in DNDC as the nutrient source injected at a depth of 15 cm, which is then taken up by the bioenergy crops. The depth of the nutrient source is assumed below the plowing depth to better simulate the utilization of subsurface nutrients from leachate and runoff by the energy crops and changes in the depth could impact nutrient availability and hence crop yields for the bioenergy buffer. In addition, the availability of nutrients is likely to vary across the buffer strip, with higher nutrient loading at the interface between the buffer and the annual crop and then decreasing over the buffer. However, as DNDC is a site model, this variability cannot be simulated in the current model and hence we have assumed an average nutrient load across the buffer.

Alternative scenarios were composed to represent the influences of fertilizer timing, tillage practices, row-crop rotation and bioenergy crop species growing in the buffer on N_2O emissions and nitrate concentrations in runoff, and leachate in the buffer. The detailed description of each scenario is presented in Table 1. To observe the long-term effects, each of the scenarios listed in Table 1 was simulated for a 10-year period using climate data from the previous 10-year period (1999–2009). The modeled annual crop yield, nitrate-N leaching, and N_2O flux were recorded for each year with each scenario. Multiyear averages were also calculated for comparison between the different scenarios. To compare the results from

Table 1 Baseline and alternative management scenarios

| Scenario	Row-crop	Tillage practice for row-crop	Fertilizer application for row-crop	Bioenergy crop in buffer
Baseline 1	Continuous corn	Conventional moldboard to 10 cm	Spring	None
Buffer 11	Continuous corn	Conventional moldboard to 10 cm	Spring	Switchgrass
Buffer 12	Continuous corn	Conventional moldboard to 10 cm	Spring	Miscanthus
Buffer 13	Continuous corn	Conventional moldboard to 10 cm	Spring	Native prairie grass
Baseline 2	Continuous corn	No till	Spring	None
Buffer 21	Continuous corn	No till	Spring	Switchgrass
Buffer 22	Continuous corn	No till	Spring	Miscanthus
Buffer 23	Continuous corn	No till	Spring	Native prairie grass
Baseline 3	Continuous corn	Conventional moldboard to 10 cm	Fall	None
Buffer 31	Continuous corn	Conventional moldboard to 10 cm	Fall	Switchgrass
Buffer 32	Continuous corn	Conventional moldboard to 10 cm	Fall	Miscanthus
Buffer 33	Continuous corn	Conventional moldboard to 10 cm	Fall	Native prairie grass
Baseline 4	Corn–soybean rotation	Conventional moldboard to 10 cm	Spring	None
Buffer 41	Corn–soybean rotation	Conventional moldboard to 10 cm	Spring	Switchgrass
Buffer 42	Corn–soybean rotation	Conventional moldboard to 10 cm	Spring	Miscanthus
Buffer 43	Corn–soybean rotation	Conventional moldboard to 10 cm	Spring	Native prairie grass

Table 2 DNDC crop parameters and estimated values for switchgrass and miscanthus

Parameter	Switchgrass	Source	Miscanthus	Source
Maximum production (kg dry matter ha^{-1})	650	Heaton et al. (2008)	1000	Lewandowski et al. (1995)
Leaf and stem fractions of total biomass	0.55	Heaton et al. (2008), Ma et al. (2001)	0.6	Beale & Long (1995), Heaton et al. (2008)
C/N ratio for leaf and stem	54	Johnson et al. (2007)	110	Lewandowski et al. (1995)
C/N ratio for root	66	Johnson et al. (2007)	70	Lewandowski et al. (1995)
Nitrogen fixation index (= total plant N/plant N from soil)	1		3	
Water requirement (kg water per kg dry matter of biomass)	200	Heaton et al. (2004)	300	Lewandowski et al. (1995)
Leaf Area Index	7	Heaton et al. (2008)	9	Heaton et al. (2008)
Maximum height (m)	0.5	Heaton et al. (2004)	4	Heaton et al. (2004)
Thermal degree days ( )	2500	Heaton et al. (2004)	1200	Heaton et al. (2004)
Perennial plant	Yes	Heaton et al. (2004)	Yes	Heaton et al. (2004)

the baseline practice of annual crops with the perennial bioenergy crops that are harvested from the second year, the results from the first year of establishment of the bioenergy crops are not included.

Results

Novel crops can be developed and simulated in DNDC through the 'Crop Creator' module. There are 12 crop parameters in this module that need to be determined for each novel crop. These parameters were compiled using literature values from multiple sites in Europe and the United States and the calibrated values are listed in Table 2 for switchgrass and miscanthus. Calibration of the model was required as the initial parameterization did not accurately simulate the crop yields and nitrogen use measured at the field sites by Heaton et al. (2008). The values for the biomass fractions, carbon–nitrogen ratios, and the nitrogen fixation index were adjusted within the range mentioned in published literature until the model was successfully calibrated. Calibration results for the target site at Urbana, Illinois are presented in Fig. 1 for switchgrass and miscanthus. The model parameters for switchgrass and miscanthus were validated at the two sites Shabbona, Illinois and Simpson, Illinois using the management practices described in Heaton et al. (2008) and validation results are presented in Fig. 2. To estimate the impacts on nitrate leaching and N_2O emissions in a typical agricultural field from atmospheric deposition of nitrogen, we modeled a scenario where the target site was left fallow and the biogeochemical impacts simulated. The results for the fallow field scenario are presented in Fig. 3 and Table 3. Model results for (i) standard cropping systems in the Midwest under different management practices (spring or fall fertilizer application, till or no-till) and (ii) cropping systems with bioenergy buffers incorporated are presented in Table 3 and Figs 3–6.
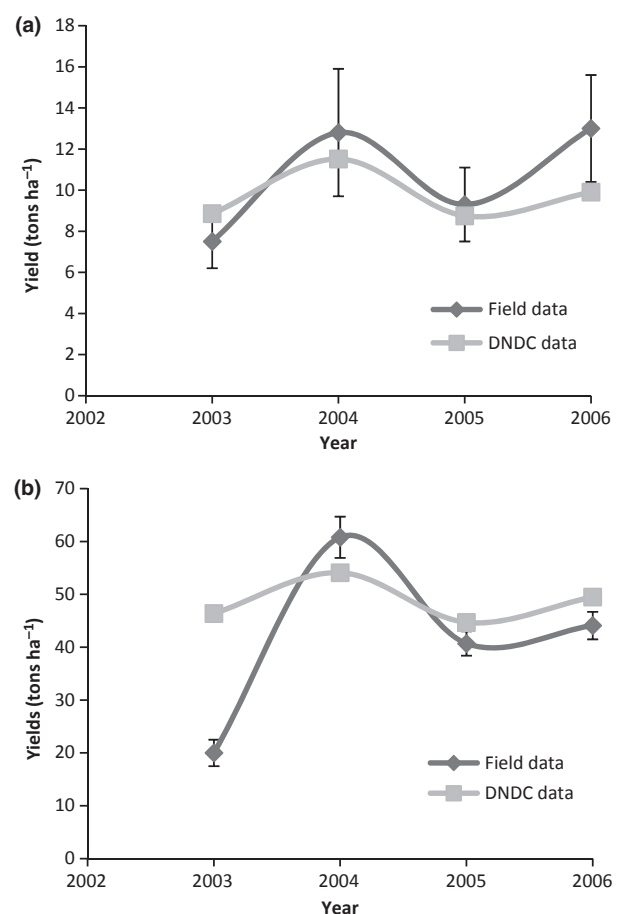
Fig. 1 DNDC model calibration results for (a) switchgrass and (b) miscanthus at the target site in Urbana, Illinois.

Discussion

Model calibration and validation for bioenergy crops

Calibration results for the target site at Urbana, Illinois are presented in Fig. 1 for switchgrass and miscanthus.
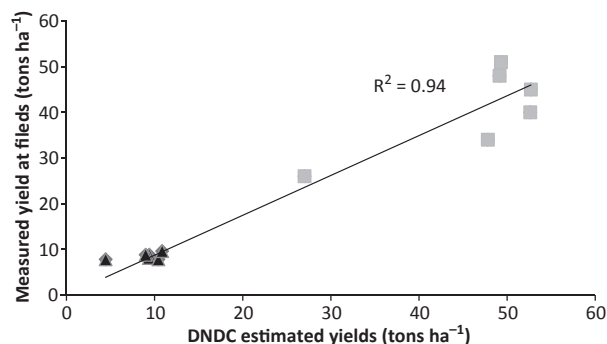
Fig. 2 DNDC model validation results for switchgrass and miscanthus grown in 2004–2006 at Shabbona, Illinois and Simpson, Illinois (■, miscanthus; ▲, switchgrass).
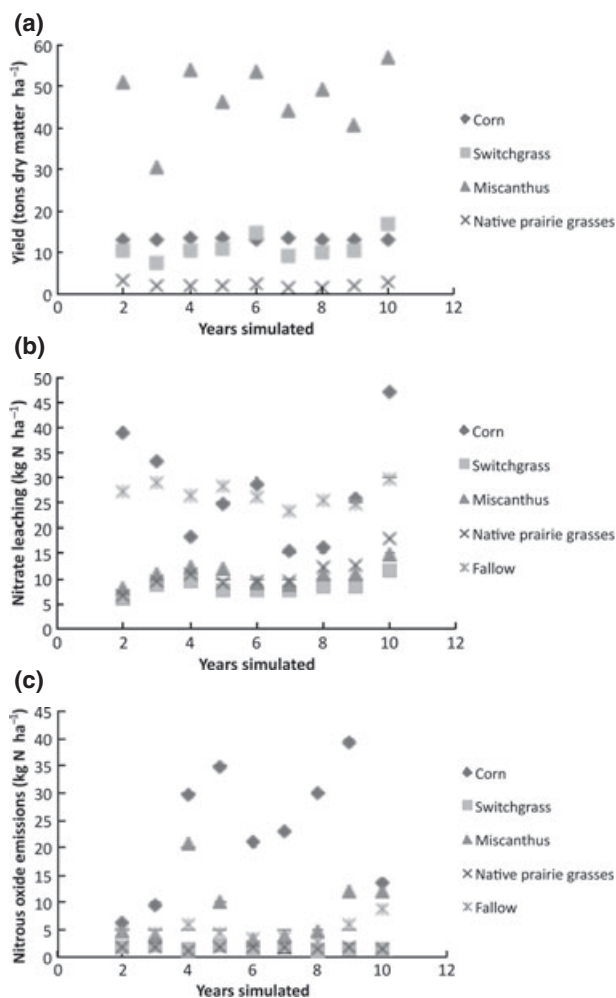

Fig. 3 Modeled multiyear yields (a), nitrate-N leaching (b), and N₂O emissions (c) for continuous corn with spring fertilization and till in a typical field in Urbana, Illinois.

As shown in Fig. 1(a), the model successfully predicted crop yields for switchgrass for the years 2003–2006, with $R^2 = 0.99$ between modeled and measured data.

Initial model simulation results for miscanthus were less successful and the model significantly underpredicted crop yields compared to values obtained in the field. The initial model parameterization for miscanthus had a nitrogen fixation index of 1, indicating that miscanthus did not fix nitrogen. However, Davis *et al.* (2010) detected nitrogenase activity in some of the bacteria associated with miscanthus, suggesting that that nitrogen fixing bacteria are present in miscanthus. To better calibrate DNDC for miscanthus, we followed Davis *et al.* (2010) in assuming that nitrogen fixation was present and included a nitrogen fixation index of 3 in the model. The results of this model calibration are shown in Fig. 1(b) for the years 2003–2006 at the target site. In general, the model successfully predicted the crop yields, with $R^2 = 0.9$ between modeled and measured data. However, the model tended to overestimate the yield for the year 2003, the first year that miscanthus was grown at the site. This overestimation is likely a function of the variability in nitrogen fixation in miscanthus and an incomplete understanding of processes governing nitrogen use in miscanthus. Davis *et al.* (2010) hypothesized that nitrogen fixation in miscanthus could occur through associative nitrogen fixation or endophytic nitrogen fixation and that biomass growth and crop yields would likely differ as a function of these processes. A better understanding of the pathways through which nitrogen is added to the miscanthus system would aid in improving model calibration.

To validate the parameterization of the crop model for miscanthus and switchgrass, the parameter values in Table 2 were entered into DNDC for the two validation sites Shabbona, Illinois and Simpson, Illinois. The model was then used to predict the crop yields for switchgrass and miscanthus grown at these sites for the years 2004–2006, under the management practices described by Heaton *et al.* (2008). The results of model validation are presented in Fig. 2. Modeled and measured data were compared and an R^2 value of 0.94 was obtained. This would suggest that the model was able to produce reasonable results, even with the current incomplete understanding of the nitrogen fixation pathway for miscanthus.

Biogeochemical effects and crop yields of bioenergy crop buffers

Nitrogen is an important limiting nutrient in ecosystems and atmospheric deposition contributes significantly to the nitrogen balance (Burns, 2002). Results from the monitoring network used by the National Atmospheric Deposition Program (http://nadp.sws. uiuc.edu) and The USEPA's Clean Air Status and

Table 3 Modeled multiyear average annual yield, nitrate leached and nitrous oxide emissions for a typical row-crop field in Illinois

Crop	Scenario	Average			Standard deviation		
		Yield (tons ha^{-1})	NO$_3$ leached (kg N ha^{-1})	N$_2$O emitted (kg N ha^{-1})	Yield (tons ha^{-1})	NO$_3$ leached (kg N ha^{-1})	N$_2$O emitted (kg N ha^{-1})
Corn	Baseline 1	13.2	27.7	23.0	0.1	10.7	11.4
Switchgrass	Buffer 11	11.2	8.4	1.6	2.8	1.6	0.3
Miscanthus	Buffer 12	47.5	10.8	8.3	8.2	2.1	6.0
Native prairie	Buffer 13	2.3	10.9	1.7	0.6	3.2	0.2
Corn	Baseline 2	13.2	24.8	22.7	0.1	9.8	11.6
Switchgrass	Buffer 21	11.1	8.4	1.6	2.8	1.6	0.3
Miscanthus	Buffer 22	47.5	10.8	7.8	8.2	2.1	5.7
Native prairie	Buffer 23	2.2	10.8	1.7	0.5	16.4	1.3
Corn	Baseline 3	9.7	77.5	19.3	2.0	17.2	11.7
Switchgrass	Buffer 31	12.8	8.4	1.6	2.7	1.6	0.3
Miscanthus	Buffer 32	47.5	10.9	12.8	8.2	2.1	9.4
Native prairie	Buffer 33	4.0	11.4	1.9	0.7	3.6	0.4
Corn-soy	Baseline 4	4.5	25.3	20.1	3.8	7.4	15.9
Switchgrass	Buffer 41	11.0	8.4	1.6	2.8	1.6	0.3
Miscanthus	Buffer 42	47.5	10.8	8.4	8.2	2.1	6.2
Native prairie	Buffer 43	2.2	10.8	1.7	0.4	3.2	0.2
Fallow land	Fallow		26.7	4.8		2.1	1.8

Trends Network (http://www.epa.gov/castnet/) show that atmospheric deposition of nitrogen in the Midwest is significant, with parts of the Midwest including Illinois receiving more than 7 kg N ha^{-1}. Researchers, such as Wolfe *et al.* (2003) have suggested that atmospheric deposition contributes to shifts in native species, impacts on water quality, and increased GHG emissions. As shown in Fig. 3 and Table 3, while the amount of nitrate leached from the fallow field varied over the years depending on rainfall and climate, on average 26 kg N ha^{-1} were leached annually over the 10-year period modeled here. N$_2$O emissions were not as significant, perhaps due to lower soil carbon levels when plants are not present and hence lower microbial respiration rates. These results suggest that atmospheric deposition plays an important role in water quality impacts from nutrients leaching from agricultural fields. While the impacts on water quality resulting from atmospheric nitrogen fertilization have been documented in natural ecosystems such as forests and grasslands (Burns, 2002; Rankinen *et al.*, 2006; Cai *et al.*, 2011), the contribution of atmospheric deposition to the nitrogen load to water from agricultural ecosystems has not been studied as extensively. Latimer & Rego (2010) evaluated the contribution of nitrogen inputs from various sources at the watershed scale for 74 New England estuaries and found that atmospheric nitrogen was a significant source in 37% of the studied systems. Our results for a fallow agricultural field in Illinois show agreement with Latimer & Rego (2010), indicating that atmospheric sources could be important contributors to nitrogen load in water bodies in addition to runoff and leachate from agricultural fields.
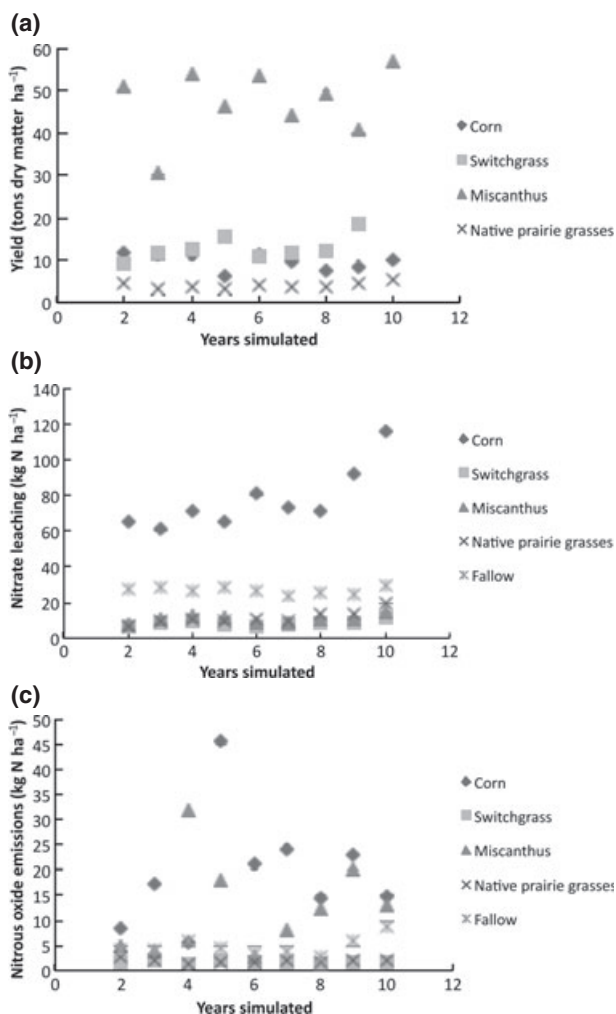
The environmental impacts from atmospheric sources are likely to be further increased as a result of fertilization and tilling practices in typical agro-ecosystems. Farmers in the Midwest often till their fields and apply fertilizers to maximize crop yield and minimize losses. We modeled the environmental impacts by including nitrogen deposition and fertilization and tilling in our agricultural field simulations using DNDC. The simulated results for corn production under these typical practices are presented in Fig. 3(a–c) and Table 3. Simulated corn yields averaged 13 tons ha^{-1} over the 10-year period (Fig. 3a) and are within the range of 9–14 tons ha^{-1} measured by the USDA and other researchers for fertile fields in Central Illinois (USDA National Agricultural Statistics Service, 2007; Khanna *et al.*, 2008). As shown in Fig. 3(b and c), the application of artificial fertilizers resulted in significant losses of nitrogen through leaching into the groundwater and production of N$_2$O. On average, ca. 27 kg N ha^{-1} was simulated as found in the leachate and 23 kg N ha^{-1} of N$_2$O emitted. N$_2$O emissions were significantly higher in the corn system compared to the fallow field, suggesting that excess nitrogen from fertilizer application is more likely degraded by the microorganisms as opposed to leaching into the water as nitrate.
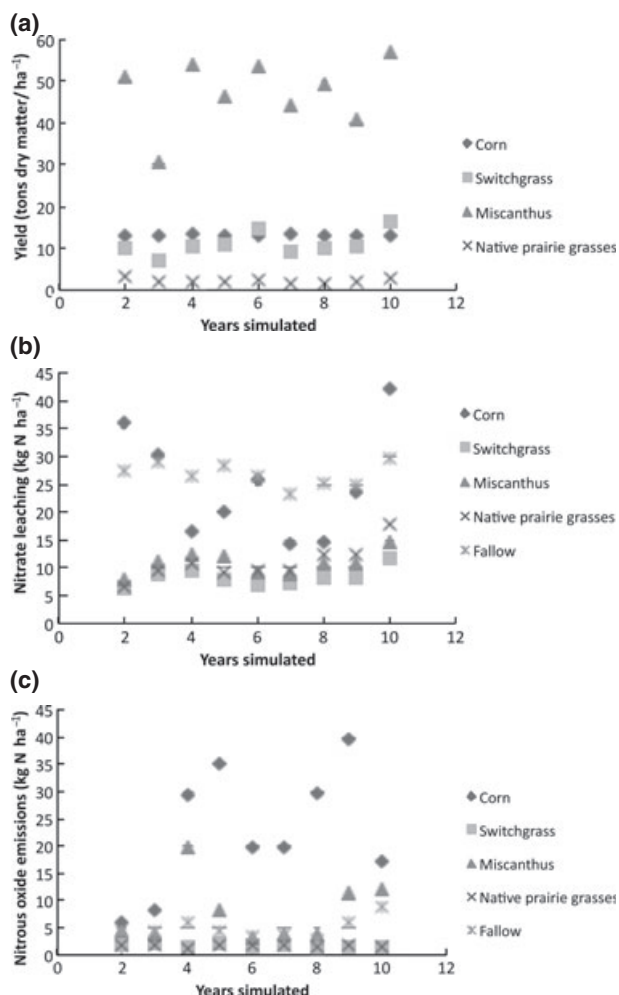
Fig. 4 Modeled multiyear yields (a), nitrate-N leaching (b), and N_2O emissions (c) for continuous corn with spring fertilization and no-till in a typical field in Urbana, Illinois.

Fig. 5 Modeled multiyear yields (a), nitrate-N leaching (b), and N_2O emissions (c) for continuous corn with fall fertilization and till in a typical field in Urbana, Illinois.

As seen in Fig. 3 and Table 3, incorporating the bioenergy buffer in the landscape appeared to reduce the environmental impacts in terms of nitrate leaching and N_2O emissions when compared to continuous corn and the fallow field system. On average, the amount of nitrate leached into the water reduced by 60–70% when the bioenergy buffers were incorporated. N_2O emissions were reduced by 65–95% compared with the continuous corn system. When switchgrass or native prairie grasses were grown in the buffer, N_2O emissions were lower than for the fallow field system. However, when miscanthus was grown in the buffer, N_2O emissions were double that seen in the fallow field. This result could be a function of the inclusion of nitrogen fixation in the miscanthus crop model compared to switchgrass or native prairie grasses. The type of N-fixation in the miscanthus system could produce very different results. As suggested by Davis *et al.* (2010), associative N-fixation

resulted in an addition of nitrogen to the soil pool and hence a possibility of increased denitrification and N_2O emissions. Endophytic N-fixation would likely not have this effect. However, DNDC utilizes a single parameter to model nitrogen fixation and the differences resulting from different N-fixation process are not evident in model results. While results presented here are encouraging, a better understanding of the nitrogen fixation in miscanthus and better incorporation of the different N-fixation processes in DNDC are needed to more accurately model the impacts on N_2O emissions when miscanthus bioenergy buffers are used in agro-ecosystems.

The annual yields of bioenergy crops in the buffer ranged from 2 tons ha^{-1} for native prairie grasses to 11 tons ha^{-1} for switchgrass and 47 tons ha^{-1} for miscanthus (Fig. 3a and Table 3). The yields for switchgrass are marginally lower than the yields obtained for
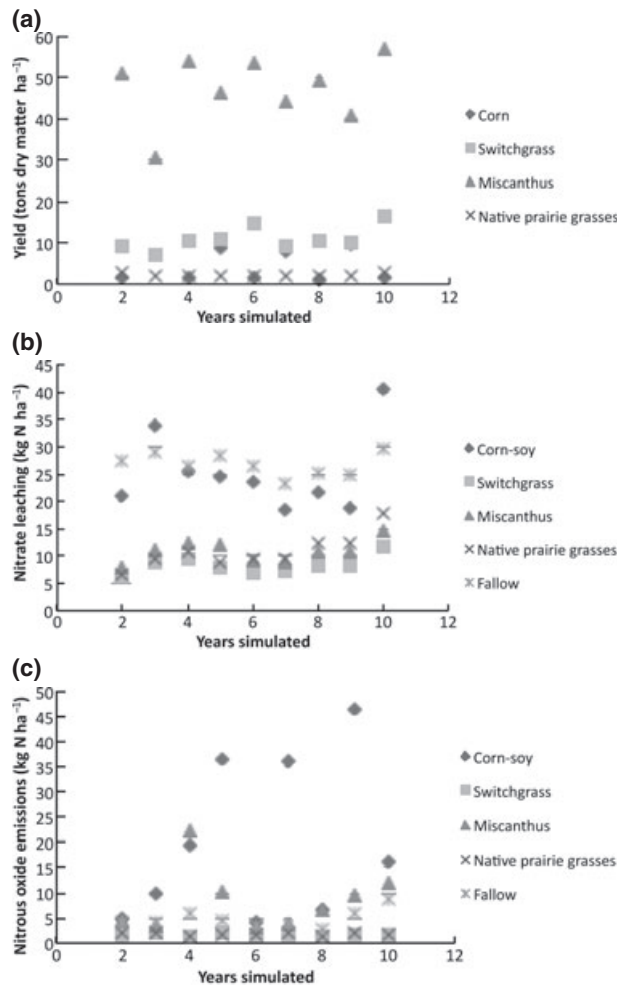
Fig. 6 Modeled multiyear yields (a), nitrate-N leaching (b), and N₂O emissions (c) for corn-soy rotation with spring fertilization and till in a typical field in Urbana, Illinois.

corn, while the yields for miscanthus are far greater than corn yields. Further, the modeled yields for switchgrass and miscanthus in the buffer systems are comparable to the yields measured by Heaton *et al.* (2008) for the same crops grown in traditional row-crop systems with application of artificial fertilizers. This result suggests that growing switchgrass and miscanthus in the buffer would enable the farmer to grow a second crop productively and mitigate the negative environmental impact of corn production. The modeled yields for the native prairie grasses are significantly lower and could be dependent on of the prairie mix assumed in the model. These results are similar to those obtained by Schmer *et al.* (2008) when native prairie grasses were found to be less productive than switchgrass in fertilized agro-ecosystems. Tilman *et al.* (2006) found that native prairie grasses grown in Minnesota had similar yields to switchgrass that was not

fertilized. Additional field data on the type of prairie community, management practices and comparisons with bioenergy crops would likely aid in better model prediction.

Impacts of alternative management practices used in combination with bioenergy crop buffers

While the results presented in the previous section for a continuous corn system with spring fertilization and tilling are encouraging, differences in management practices are likely to impact the amount of nitrate-N leached and N₂O emissions from the system. One of the management practices explored in this study is the type of tilling. Farmers have used conventional tillage to improve soil aeration and nitrogen availability for the crop. However, tilling the soil increases soil erosion and hence a no-till system is recommended to reduce the physical disturbance, mitigate soil erosion and minimize mineralization of soil nitrogen. The results of using a no-till system compared to conventional tillage are presented in Fig. 4 and Table 3. No significant differences in crop yield, nitrate-N leaching and N₂O emissions for the no-till system compared to the conventional till system were observed (Fig. 4a–c). These results are similar to field observations reported by Parkin & Kaspar (2006) when no significant impact was seen with a no-till system. However, field observations have been uneven with some studies reporting increased nitrate-N leaching and N₂O emissions (Bakhsh *et al.*, 2000; Venterea *et al.*, 2005), and others reporting reductions in nitrate-N leaching and N₂O emissions (Kanwar & Baker, 1993; Dinnes, 2004). Dinnes, 2004 suggested that rainfall patterns, fertilizer application rate and timing and type of cropping system had a greater impact than tillage practice. The results presented in Fig. 4 show greater interannual variability compared to the type of tillage practice and indicate that climatic factors have a greater influence as suggested by Dinnes, 2004.

The timing of the fertilizer application is the second management practice explored here. In this practice, the fertilizer is applied in the fall because of greater ease of application. The results of a fall application are shown in Fig. 5 and Table 3. A reduction in corn yield was observed with the average yield decreasing from 13 to 9 tons ha^{-1}. Approximately three times as much nitrate-N leached from the corn during the fall application of fertilizer compared with the spring fertilization. However, when the buffer system was incorporated into the landscape, the final amounts of nitrate-N leaching into the water after uptake by the energy crops were similar to results for the buffer system when fertilizers were applied in the spring (Fig. 3) and were much smaller than the leachate from the continuous corn

(Fig. 5a). There was a corresponding increase in the yields of switchgrass and native prairie grasses in the buffer, probably due to the increased amount of nitrate-N leaching from the corn and being taken up by the buffer crops (Table 3). No increase in miscanthus yields were observed, possibly because miscanthus is assumed to fix nitrogen and hence is less sensitive to changes in nitrogen available from other sources. Ng *et al.* (2010) obtained similar results while modeling the production of miscanthus in traditional row-cropping systems for a watershed where they found that changing the amount of fertilizer applied to miscanthus did not impact crop yields. N_2O emissions were marginally lower in the continuous corn system compared to spring fertilization. These results highlight the potential tradeoffs in environmental impacts as a result of different management practices. In the case of the fall fertilization, N_2O emissions were reduced while the amount of nitrate-N leaching into groundwater increased, highlighting the tradeoff between mitigation of GHG emissions and impacts on local water quality.

The type of cropping system used also had an impact on the environment. For example, Turner *et al.* (2008) found that a continuous corn cropping system resulted in greater nitrogen loading in watersheds compared with a corn–soybean rotation or a mix of corn and perennial grasses. In this study, simulations of the corn–soybean rotation resulted in crop yields that were lower on average compared to a continuous corn system (Fig. 6 and Table 3). However, the amount of nitrate-N leached into the groundwater and N_2O emitted were marginally lower for the rotation compared with the continuous corn system. It is interesting to observe that the yields of the bioenergy crops remained relatively unchanged when both the continuous corn and the corn–soybean rotation were used and the final amounts of nitrate-N leached and N_2O emissions were similar in both cases. This suggests that energy crop system functions as a relatively stable buffer against negative environmental impacts resulting from traditional agricultural practices. However, the economic impacts of this system need to be further evaluated before wide-scale adoption of this system is likely.

In summary, this study indicates that incorporating bioenergy crop buffers into agricultural landscapes has the potential to provide economic and environmental services. While agricultural management practices (till or no-till, fertilizer timing) change the amounts of nitrate leaching out from the corn or corn–soybean system and the N_2O emitted, bioenergy crop buffers appear to mitigate the worst environmental impacts for all practices. However, the biogeochemical model DNDC focuses on the field scale and results obtained here need to be tested at the watershed or landscape scales. Additionally, spatially explicit biogeochemical models that connect hydrology and the nitrogen cycle with energy crops and water flow are currently lacking. Watershed models such as the Soil Water Assessment Tool incorporate the nitrogen cycle, but use a more empirical approach and lack the detailed nitrogen cycling present in biogeochemical models such as DNDC. As bioenergy crop buffers are landscape-scale features that capture surface runoff and subsurface flow (leachate), models that enable scale-up of these results to the landscape or watershed would be needed to evaluate the effectiveness of such systems at larger scales. Finally, the processes governing nitrogen fixation in miscanthus are still unclear and would need to be further validated at the field scale to better understand the implications on nitrogen fluxes in bioenergy buffer strips.

Current research on the environmental sustainability of bioenergy has assumed that bioenergy crops will be grown in a manner similar to current agricultural crops such as corn and hence would affect the environment similarly. In this study, we evaluated an alternative system where bioenergy crops are grown in buffer strips adjacent to current agricultural crops such that nutrients present in runoff and leachate from the traditional row-crops are reused by the bioenergy crops in the buffer strips. Overall, our model results indicated that the bioenergy crops grown in these buffer strips achieved yields that are comparable to those obtained for traditional agricultural systems while simultaneously providing environmental services by mitigating nitrate leaching and N_2O emissions. Results from the multiyear simulations with alternative management practices suggested that the energy crops tend to mitigate the worst environmental impacts from corn and other traditional row-crops. While this study was conducted for a specific field in Illinois, and hence the modeled results may not be specifically applicable to other sites around the country, the general trends may apply and may help in designing sustainable agricultural landscapes using bioenergy crops.

Acknowledgements

References

Bakhsh A, Kanwar RS, Karlen DL, Cambardella CA, Colvin TS, Moorman TB, Bailey TB (2000) Tillage and nitrogen management effects on crop yield and residual soil nitrate. *Transactions of ASAE*, **43**, 1589–1595.

Beale CV, Long SP (1995) Can perennial C4 grasses attain high efficiencies of radiant energy conversion in cool climates? *Plant, Cell and Environment*, **18**, 641–650.

Beheydt D, Boeckx P, Sleutel S, Li C, Van Cleemput O (2007) Validation of DNDC for 22 long-term N_2O field emissions measurements. *Atmospheric Environment*, **41**, 6196–6211.

Booth MS, Campbell C (2007) Spring nitrate flux in the Mississippi River basin: a landscape model with conservation applications. *Environmental Science Technology*, **41**, 5410–5418.

Bouman AF (1996) Direct emission of nitrous oxide from agricultural soils. *Nutrient Cycling in Agroecosystems*, **46**, 53–70.

Burns DA (2002) *The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and Southern Wyoming- a synthesis and critical assessment of published results*. USGS Water Resources Investigations. Report 02-4066: 36.

Cai MJ, Schwartz JS, Robinson RB, Moore SE, Kulp MA (2011) Long-term annual and seasonal patterns of acidic deposition and stream water quality in a Great Smoky Mountains High-Elevation watershed. *Water Air and Soil Pollution*, **219**, 547–562.

Chen D, Li Y, Grace P, Mosier AR (2008) N_2O emissions from agricultural lands: a synthesis of simulation approaches. *Plant and Soil*, **309**, 169–189.

Crumpton WG, Stenback GA, Miller BA, Helmers MJ (2006) *Potential benefits of wetland filters for tile drainage systems: impact on nitrate loads to Mississippi river subbasins*. Final Project Report, project No. IOW06682, U.S. Department of Agriculture, Washington DC.

Crutzen PJ, Mosier AR, Smith KA, Winiwarter W (2008) N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmospheric Chemistry and Physics*, **8**, 389–395.

Davis SC, Parton WJ, Dohleman FG, Smith CM, Del Grosso S, Kent AD, DeLucia EH (2010) Comparative biogeochemical cycles of bioenergy crops reveal nitrogen-fixation and low greenhouse gas emissions in a Miscanthus x giganteus agro-ecosystem. *Ecosystems*, **13**, 144–156.

DeSimone J, Macrae ML, Bourbonniere RA (2010) Spatial variability in surface N2O fluxes across a riparian zone and relationships with soil environmental conditions and nutrient supply. *Agriculture, Ecosystems and Environment*, **138**, 1–9.

Dinnes DL (2004) *Assessments of Practices to Reduce Nitrogen and Phosphorus Nonpoint Source Pollution of Iowa's Surface Waters*. Iowa Department of Natural Resources, Des Moines, IA.

Dosskey MG, Helmers MJ, Eisenhauer DE (2006) An approach for using soil surveys to guide the placement of water quality buffers. *Journal of Soil and Water Conservation*, **61**, 344–354.

Farahbakhshazad N, Dinnes DL, Li C, Jaynes DB, Salas W (2008) Modelling biogeochemical impacts of alternative management practices for a row-crop field in Iowa. *Agriculture, Ecosystems and Environment*, **123**, 30–48.

Fargione J, Hill J, Tilman D, Polasky S, Hawthorne P (2008) Land clearing and the biofuel carbon debt. *Science*, **219**, 1235–1238.

Gopalakrishnan G, Negri MC, Wang M, Wu M, Snyder SW, LaFreniere L (2009) Biofuels, land, and water: a systems approach to sustainability. *Environmental Science and Technology*, **43**, 6094–6100.

Heaton EA, Voight T, Long S (2004) A quantitative r eview comparing the yields of two candidate C4 perennial biomass crops in relation to nitrogen, temperature and water. *Biomass and Bioenergy*, **27**, 21–30.

Heaton EA, Dohleman FG, Long SP (2008) Meeting US biofuel goals with less land: the potential of Miscanthus. *Global Change Biology*, **14**, 2000–2014.

Hefting M, Bobbink R, De Caluwe H (2003) Nitrous oxide emissions and denitrification in chronically nitrate-loaded riparian buffer zones. *Journal of Environmental Quality*, **32**, 1194–1203.

Hernandez-Ramirez G, Brouder S, Smith D, VanScoyoc G, Michalski G (2009) Nitrous oxide production in an eastern corn belt soil: sources and redox range. *Soil Science Society of America Journal*, **73**, 1182–1191.

Hill J, Nelson E, Tilman D, Polasky S, Tiffany D (2006) Environmental, economic and energetic costs and benefits of biodiesel and ethanol biofuels. *Proceedings of National Academy of Sciences*, **103**, 11206–11210.

IPCC (2006) IPCC guidelines for national greenhouse gas inventories, prepared by the National Greenhouse gas inventories programme. In: *N2O Emissions from Managed Soils and CO_2 Emissions from Lime and Urea Applications*, Vol 4, Chapter 11 (eds Eggleston HS, Buendia L, Miwa K, Ngara T, Tanabe K). IGES, Hayama, Japan.

Johnson JM-F, Barbour NW, Weyers SL (2007) Chemical composition of crop biomass impacts its decomposition. *Soil Science Society of America Journal*, **71**, 155–162.

Kanwar RS, Baker JL (1993) *Tillage and chemical management effects on groundwater quality. Proceedings, Agricultural Research to Protect Water Quality*, Minneapolis, MN. 21–24 February 1993, Soil Water Conservation Society, Ankeny, IA.

Karlen D (2010) *A landscape vision for integrating industrial crops into biofuel systems*. Association for the Advancement of Industrial Crops Conference, Fort Collins, CO, USA. Available at: http://www.aaic.org/10program.htm (accessed 18–22 September 2010).

Khanna M, Dhungana B, Clifton-Brown J (2008) Costs of producing miscanthus and switchgrass for bioenergy in Illinois. *Biomass and Bioenergy*, **32**, 482–493.

Kim DG, Isenhart TM, Parkin TB, Schutlz RC, Loynachan TE (2009) Nitrate and dissolved nitrous oxide in groundwater within cropped fields and riparian buffers. *Biogeosciences Discussions*, **6**, 651–685.

Latimer JS, Rego SA (2010) Empirical relationship between eelgrass extent and predicted watershed-derived nitrogen loading for shallow New England estuaries. *Estuarine Coastal and Shelf Science*, **90**, 231–240.

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

Lewandowski I, Kicherer A, Vonier P (1995) CO_2-Balance for the cultivation and combustion of Miscanthus. *Biomass and Bioenergy*, **8**, 81–90.

Li C, Frolking S, Frolking TA (1992) A model of nitrous oxide evolution from soil driven by rainfall events, 1. Model structure and sensitivity. *Journal of Geophysical Research*, **90**, 9776–9799.

Li C, Farahbakhshazad N, Dinnes DL, Jaynes DB, Salas WA, McLaughlin D (2006) Modeling nitrate leaching with a biogeochemical model modified based on observations in a row-crop field in Iowa. *Ecological Modeling*, **196**, 116–130.

Lovell ST, Sullivan WC (2006) Environmental benefits of conservation buffers in the United States: evidence, promise, and open questions. *Agricultural Ecosystems and Environment*, **112**, 249–260.

Ma Z, Wood CW, Bransby DI (2001) Impact of row spacing, nitrogen rate, and time on carbon partitioning of switchgrass. *Biomass and Bioenergy*, **20**, 413–419.

Mosier AR, Duxbury JM, Freney JR, Heinemeyer O, Minami K (1998) Assessing and mitigating N_2O emissions from agricultural soils. *Climatic Change*, **40**, 7–38.

Ng TL, Eheart JW, Cai X, Miguez F (2010) Modeling miscanthus in the Soil and Water Assessment Tool (SWAT) to simulate its water quality effects as a bioenergy crop. *Environmental Science and Technology*, **44**, 7138–7144.

Organization for Economic Cooperation and Development (OECD) (2001) *Agricultural Policies in OECD Countries: Monitoring and Evaluation*. OECD, Paris.

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

Rankinen K, Karvonen T, Butterfield D (2006) An application of the GLUE methodology for estimating the parameters of the INCA-N model. *Science of Total Environment*, **365**, 123–139.

Righelato R, Spracklen DV (2007) Environment: carbon mitigation by biofuels or by saving and restoring forests. *Science*, **317**, 902–904.

Schmer MR, Vogel KP, Mitchell RB, Perrin RK (2008) Net energy of cellulosic ethanol from switchgrass. *Proceedings of National Academy of Science, USA*, **105**, 464–469.

Searchinger T, Heimlich R, Houghton RA *et al.* (2008) Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science*, **319**, 1238–1240.

Smeets EMW, Bouman LF, Stehfest E, Van Vuuren DP, Posthuma A (2009) Contribution of N_2O to the greenhouse gas balance of first-generation biofuels. *Global Change Biology.*, **15**, 1–23.

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

Tonitto C, David MB, Drinkwater LE, Li C (2007a) Application of the DNDC Model to tile-drained Illinois agroecosystems, model calibration, validation, and uncertainty analysis. *Nutrient Cycling Agroecosystems*, **78**, 51–63, doi: 10.1007/s10705-006-9076-0.

Tonitto C, David MB, Li C, Drinkwater LE (2007b) Application of the DNDC model to tile-drained Illinois agroecosystems, Model comparison of conventional and diversified rotations. *Nutrient Cycling Agroecosystems*, **78**, 65–81, doi: 10.1007/s10705-006-9074-2.

Turner RE, Rabalais NN, Justic D (2008) Gulf of Mexico Hypoxia: alternate states and a legacy. *Environmental Science Technology*, **42**, 2323–2327.

United States Department of Agriculture (USDA) (2010) *Conservation Buffers: Design Guidelines for Buffers, Corridors and Greenways*. Available at www.unl.edu/nac/bufferguidelines/ (accessed 6 July 2011).

United States Environmental Protection Agency (USEPA) (2010) *Nitrous Oxide: Sources and Emissions*. Available at http://www.epa.gov/nitrousoxide/sources.html (accessed 6 July 2011).

USDA National Agricultural Statistics Service (2007) *Census of Agriculture*. Available at: http://www.agcensus.usda.gov/ (accessed 5 August 2008).

Venterea RT, Burger M, Spokas KA (2005) Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *Journal Environmental Quality*, **34**, 1467–1477.

Vitousek PM, Naylor R, Crews T *et al.* (2000) Nutrient imbalances in agricultural development. *Science*, **324**, 1519–1520.

Wolfe AP, Van Gorp AC, Baron JS (2003) Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): a response to anthropogenic nitrogen deposition. *Geobiology*, **1**, 153–169.

Yu K, Patrick W Jr (2004) Redox Window with minimum global warming potential contribution from rice soils. *Soil Science Society of America Journal*, **68**, 2086–2091.