



Carbon and nitrogen dynamics in bioenergy ecosystems:

1. Model development, validation and sensitivity analysis

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Abstract

Biofuel made from conventional (e.g., maize (*Zea mays* L.)) and cellulosic crops (e.g., switchgrass (*Panicum virgatum* L.) and *Miscanthus* (*Miscanthus* × *giganteus*)) provides alternative energy to fossil fuels and has been considered to mitigate greenhouse gas emissions. To estimate the large-scale carbon and nitrogen dynamics of these biofuel ecosystems, process-based models are needed. Here, we developed an agroecosystem model (AgTEM) based on the Terrestrial Ecosystem Model for these ecosystems. The model was incorporated with biogeochemical and ecophysiological processes including crop phenology, biomass allocation, nitrification, and denitrification, as well as agronomic management of irrigation and fertilization. It was used to estimate crop yield, biomass, net carbon exchange, and nitrous oxide emissions at an ecosystem level. The model was first parameterized for maize, switchgrass, and *Miscanthus* ecosystems and then validated with field observation data. We found that AgTEM well reproduces the annual net primary production and nitrous oxide fluxes of most sites, with over 85% of total variation explained by the model. Local sensitivity analysis indicated that the model sensitivity varies among different ecosystems. Net primary production of maize is sensitive to temperature, precipitation, cloudiness, fertilizer, and irrigation and less sensitive to atmospheric CO₂ concentrations. In contrast, the net primary production of switchgrass and *Miscanthus* is most sensitive to temperature among all factors. Nitrous oxide fluxes are sensitive to management in maize ecosystems, and sensitive to climate factors in cellulosic ecosystems. The developed model should help advance our understanding of carbon and nitrogen dynamics of these biofuel ecosystems at both site and regional levels.

Keywords: biomass, denitrification, greenhouse gas, maize, *Miscanthus*, modeling, nitrification, switchgrass

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Introduction

Bioenergy is becoming increasingly attractive to many countries, but has sparked an intensive debate regarding energy, economy, society, and environment. Biofuels provide alternative energy to conventional fossil fuels. However, producing biofuels requires a large amount of biomass feedstocks, which may lead to land, water, and nutrient competitions between bioenergy crops and grain crops (Tilman *et al.*, 2009; Pimentel *et al.*, 2010), causing problems such as food insecurity (Fargione *et al.*, 2010; Diffenbaugh *et al.*, 2012). In addition, the environmental impact of producing and using biofuel is another concern to our society. In particular, to what degree, biofuel feedstock producing, biofuel conversion, and biofuel use will mitigate the climate change has

been a research focus (Farrell *et al.*, 2006; Searchinger *et al.*, 2008; Melillo *et al.*, 2009).

Biofuel crops can assimilate carbon dioxide (CO₂) from the atmosphere and accumulate C into biomass and soils. Using fossil fuels, however, releases CO₂. From the perspective of C cycling, biofuels deserve more credits for their C sequestration effect than fossil fuels (Tilman *et al.*, 2006; Clifton-Brown *et al.*, 2007). To date, many studies indicated that, substituting biofuels, especially using cellulosic crops, for fossil fuels (e.g., gasoline) would mitigate GHG emissions, and therefore benefit the environment (e.g., Farrell *et al.*, 2006; Bessou *et al.*, 2011). However, looking beyond agroecosystems and considering land availability and indirect land-use change impacts due to bioenergy expansion, the biofuel effects on the environment are not so clear. Besides using existing cropland to grow crops for bioenergy use, natural ecosystems (mainly forest and grassland) might be converted to biofuel crops to produce biomass feedstocks, which will inevitably cause land-use change.

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Studies have shown that by considering the GHG emissions caused by indirect land-use change, the C savings or C credit through developing biofuel is significantly reduced or even became negative (Searchinger *et al.*, 2008; Melillo *et al.*, 2009). The discrepancies among different studies are due to a number of uncertainty sources, including the definition of the process of interest, system boundaries of the life cycle of biofuel production, understanding of biogeochemical or physiological mechanisms, data assimilation, and methods applied. These uncertainties are unavoidable when complex systems and human behavior are included in the carbon sink and source analysis of biofuel development and use (Fargione *et al.*, 2010). The high degree of uncertainty highlights the necessity of further research on large-scale bioenergy development.

To estimate regional GHG emissions of land ecosystems, biogeochemical models that represent the C and N processes and dynamics under changing environmental conditions were used (McGuire *et al.*, 2001; Surendran Nair *et al.*, 2012). These models are either empirically based or mechanistically based. Using data from field observations, empirical models represent relationships between a dependent variable (e.g., biomass yield, CO₂ emission) and independent variables regarding climate, soil, and management (e.g., Heaton *et al.*, 2004; Jager *et al.*, 2010). This approach is relatively simple but also less accurate as it does not include the biogeochemical and physical processes of ecosystems. In contrast, most process-based models used to quantify the C and N budget of bioenergy ecosystems have been derived from models originally developed for natural ecosystems (Kucharik, 2003; Bondeau *et al.*, 2007; Di Vittorio *et al.*, 2010). These models incorporated with agroecosystem processes can simulate biomass accumulation and allocation as well as C and N dynamics of agroecosystems. For example, Agro-IBIS was developed by taking advantage of the mechanistic nature of a well-tested model, the Integrated Biosphere Simulator (IBIS), which simulates interactions among soil, plant, and the atmosphere. The Agro-IBIS has been used to simulate maize yield (Kucharik, 2003) and cellulosic biomass production (Vanloocke *et al.*, 2010). Similarly, Agro-BGC is a modified version of the Biome-BGC ecosystem model, with processes added to simulate C₄ perennial grass functionality and agricultural practices (Di Vittorio *et al.*, 2010). Another example is LPJml, a model for managed land. It was developed based on the well-established Lund–Potsdam–Jena–DGVM. The LPJml can simulate crop yield and C balance (Bondeau *et al.*, 2007). Some species-specific models, such as ALMANAC (Kiniry *et al.*, 1992; for switchgrass and *Miscanthus*), APSIM (Keating *et al.*, 1999; for sugarcane), MISCANMOD and MISCANFOR (Clifton-Brown *et al.*, 2004; Hastings

et al., 2009, for *Miscanthus*) were also developed to simulate crop growth. These models may have diverse structures and use different algorithms to describe the same biogeochemical process, but all of them can be used to simulate crop biomass production and some can also simulate C and N dynamics (e.g., Agro-BGC, LPJml).

The Terrestrial Ecosystem Model (TEM) is a global-scale biogeochemical model, among the most-used ecosystem models for estimating C, N, and water dynamics of terrestrial ecosystems (e.g., McGuire *et al.*, 1992; Zhuang *et al.*, 2003, 2013). Although many efforts were made toward modifying TEM for agricultural ecosystems, the crop physiology and agroecosystem processes have not been explicitly considered to date (McGuire *et al.*, 2001; Felzer *et al.*, 2004; Melillo *et al.*, 2009). Here, we develop an agricultural version of TEM (AgTEM) to explicitly model the C and N dynamics of agroecosystems.

AgTEM mainly incorporated two sets of processes that are related to agricultural ecosystems: one is on C accumulation and allocation, and the other is on N cycling by introducing nitrification and denitrification processes in soils. In TEM, total C sequestered through photosynthesis is allocated into two major pools of vegetation and soil of natural ecosystems. For agricultural ecosystems, photosynthesis, phenological development, and biomass allocation are crucial for determining ecosystem C fluxes and pools. In addition, agricultural management (e.g., fertilization and irrigation) affects crop development and therefore was considered in AgTEM. For agroecosystems, the N input from outside the ecosystem significantly affects crop N uptake, soil N availability, and the whole N cycle in a plant–soil–atmosphere system. Thus, special attention was paid to the N dynamics in crop soils and the interactions between soil and crop plants in AgTEM.

Materials and methods

Based on TEM, this study developed an agricultural ecosystem model (AgTEM) to simulate the C and N dynamics of crop ecosystems. The site-level observational data of C and N fluxes and pools were used to test the model performance in simulating net primary production (NPP) and nitrous oxide (N₂O) emissions. The model sensitivity responding to major input variables was also analyzed. In a companion study, we examined potential N₂O emissions from bioenergy ecosystems using the model, as presented in Qin *et al.* (2013). Below, we first introduce the TEM model, and then detail how AgTEM is developed, followed by descriptions on model parameterization, validation, and sensitivity analysis.

Terrestrial Ecosystem Model

TEM estimates C and N fluxes and pool sizes of ecosystems at a monthly time step and a given spatial resolution (e.g., 0.5°

latitude by 0.5° longitude) using spatially referenced information on climate, elevation, soil, vegetation, and water availability, as well as soil- and vegetation-specific parameters. TEM was first documented and applied for regional estimates in the early 1990s (Raich *et al.*, 1991; McGuire *et al.*, 1992), and several major improvements have been made during the past two decades as a result of advance of ecosystem understanding and available computing resources (e.g., McGuire *et al.*, 2001; Zhuang *et al.*, 2003; Felzer *et al.*, 2004). Equilibrium, as well as transient types of simulations, was introduced to TEM in the late 1990s to early 2000s, and inherited thereafter in the later versions. New modules, such as splitting N pools, ozone effects, and soil thermal and hydrological models, were incorporated into TEM to better understand terrestrial C and N dynamics under changing environmental conditions (Zhuang *et al.*, 2002, 2003; Felzer *et al.*, 2004, 2009).

Many efforts have been put into improving understanding of natural ecosystem processes. Managed ecosystems (e.g., agricultural cropland), however, were less studied using TEM. To understand the agricultural ecosystem C and N dynamics, some progress has been made toward modeling land-use change and cropping effects (McGuire *et al.*, 2001; Felzer *et al.*, 2004; Melillo *et al.*, 2009). However, a significant compromise in earlier versions of TEM for modeling agricultural ecosystems was that crop ecosystems were parameterized as grassland ecosystem (e.g., Felzer *et al.*, 2004) (Table 1). Nitrogen oxides (NO_x) emitted from agroecosystems, particularly in fertilized croplands, were not included or not mechanistically modeled in TEM (Table 1). In ecosystem models, NPP is the difference between gross primary production (GPP) and autotrophic respiration (R_A). It represents the biomass produced by plants and is used to estimate agricultural yield of the agroecosystem (Hicke *et al.*, 2004).

AgTEM development

AgTEM was developed to estimate C and N dynamics of bioenergy crop ecosystems (namely, maize, switchgrass and *Miscanthus*) at a daily time step and at any given spatial resolution. In AgTEM, the algorithms of modeling C and N fluxes and pool sizes are inherited from TEM. A majority of the algorithms describing ecosystem biogeochemical processes in TEM are still applicable in agroecosystems (Table 1). Similar to TEM, five differential equations were used to govern the dynamics of state variables and fluxes (Raich *et al.*, 1991):

$$\frac{dC_V}{dt} = GPP_t - R_{At} - L_{Ct}(-H_{Ct}) \quad (1)$$

$$\frac{dN_V}{dt} = NUPTAKE_t - L_{Nt}(-H_{Nt}) \quad (2)$$

$$\frac{dC_S}{dt} = L_{Ct} - R_{Ht}(+R_{Ct}) \quad (3)$$

$$\frac{dN_S}{dt} = L_{Nt} - NETNMIN_t(+R_{Nt}) \quad (4)$$

$$\frac{dN_{av}}{dt} = NINPUT_t + NETNMIN_t - NLOST_t - NUPTAKE_t, \quad (5)$$

where C_V , N_V , C_S , N_S , and N_{av} are pools of vegetation C, vegetation N, soil C, soil N, and available N, respectively, determined by corresponding C and N fluxes (see acronyms in Table 2). The terms in parentheses of Eqns (1) to (4) refer to biomass harvest (H) and return (R) in agroecosystems, which were not included in earlier version of TEM for natural ecosystems. In these equations, t refers to the time step used for computation. To assure stability in the integration over time, 4–5th order Runge–Kutta integration procedure (Cheney & Kincaid, 1985) or the Euler method (Atkinson, 1989; Butcher, 2008) can be used for different time steps. In this and the companion studies (Qin *et al.*, 2013), Euler method was used because of its lower computational cost. Other major modifications and new algorithms in AgTEM include temperature effects on GPP, crop phenological process and biomass accumulation, agricultural management, as well as soil N nitrification and denitrification (Table 1). Below, we detail the development.

GPP. Temperature effects on GPP are modeled in TEM as a multiplier on potential GPP utilizing minimum temperature, maximum temperature, and optimum temperature for plant photosynthesis (Raich *et al.*, 1991). For each time step, the temperature multiplier on GPP ($TEMP$) is modeled as follows:

$$TEMP = \begin{cases} 0, & (T_{air} < T_{min}) \\ \frac{(T_{air}-T_{min})(T_{air}-T_{max})}{(T_{air}-T_{min})(T_{air}-T_{max})-(T_{air}-T_{optmin})^2}, & (T_{min} < T_{air} < T_{optmin}) \\ 1.0, & (T_{optmin} < T_{air} < T_{optmax}) \\ \frac{(T_{air}-T_{min})(T_{air}-T_{max})}{(T_{air}-T_{min})(T_{air}-T_{max})-(T_{air}-T_{optmax})^2}, & (T_{optmax} < T_{air} < T_{max}) \\ 0, & (T_{air} > T_{max}) \end{cases} \quad (6)$$

where T_{air} , T_{min} , T_{optmin} , T_{optmax} , and T_{max} are parameters of transient, minimum, maximum, minimum optimum, and maximum optimum air temperatures, respectively. These parameters are crop-specific in AgTEM (Table 3).

Phenology. In TEM, plant phenology was empirically simulated using the estimated evapotranspiration and photosynthetic capacity to describe relative changes of mature vegetation (Raich *et al.*, 1991). In AgTEM, however, crop phenology describing crop growth stages can either be imported from historical observational data or modeled according to a crop's response to air temperature. Growing degree day (GDD), a measure of heat accumulation, is used to predict plant development rates (Felzer *et al.*, 2004; Deryng *et al.*, 2011). Cumulative GDD is modeled as a function of daily temperature:

$$GDD = \sum \max(0, \min(T_{air}, T_{ceil}) - T_{base}), \quad (7)$$

where T_{base} and T_{ceil} are base and ceiling temperature parameters, defined as lower and upper temperature thresholds for the process of interest, respectively. These parameters vary among species and possibly cultivars (McMaster & Wilhelm, 1997). In AgTEM (Table 4), GDD are used to predict crop emergence and maturity, using crop-specific threshold parameters.

Table 1 Agricultural modules used in AgTEM and historical TEM versions

TEM version	Agricultural module	Vegetation/Crop type	Phenology	Soil N/N ₂ O	Notes and references
TEM4.1 and earlier	N/A*	Natural ecosystems, such as forest, grass, shrub; managed ecosystems N/A	Empirical model simulates relative changes in the photosynthetic capacity of mature vegetation	Soil N mineralization, assimilation; N ₂ O simulations N/A	Earlier TEM focused on natural ecosystems only; managed ecosystems were noticed but not incorporated (Raich <i>et al.</i> , 1991; McGuire <i>et al.</i> , 1992)
TEM4.2 w/ crop module	RAP approach† of Esser (1995) was included for 'cultivated ecosystems'	Crop as a whole; model uses <i>grass</i> parameterization to describe the C and N dynamics of crop plants	Inherited from TEM4.1	Inherited from TEM4.1	Initial attempts were made to incorporate the effects of agriculture on terrestrial C and N dynamics (McGuire <i>et al.</i> , 2001; Felzer <i>et al.</i> , 2004)
TEM4.3	RAP approach improved; agricultural management discussed	Inherited from TEM4.2	GDD approach‡, using single set of parameters for CROP	Inherited from TEM4.1	TEM4.3 was initially designed to simulate ozone effects on C fluxes, and practices such as irrigation and fertilization were discussed (Felzer <i>et al.</i> , 2004); it's also used to simulate cellulosic biofuels (Melillo <i>et al.</i> , 2009)
AgTEM1.0	Based on TEM4.2, similar RAP algorithms were used	Maize, switchgrass and <i>Miscanthus</i> ; crop-specific model parameterization was adopted	Inherited from TEM4.2	Inherited from TEM4.1	First attempt to calibrate TEM for crop-specific C dynamics purposes; it was used for testing potential biomass production from bioenergy crops at ecosystem level (Qin <i>et al.</i> , 2012)
AgTEM2.0 (current version)	Agricultural version of TEM; agricultural management, such as irrigation, fertilization	Inherited from AgTEM1.0	GDD approach, using crop-specific parameters	Soil N mineralization, assimilation, nitrification, denitrification; N ₂ O simulations available	Daily version of AgTEM was designed to simulate C and N dynamics in agricultural ecosystems, especially applicable in bioenergy crop ecosystems

*N/A, not available.

†RAP approach indicated relative agricultural productivity, where agricultural productivity was simulated as a multiplier of the original natural vegetation.

‡GDD approach adopted growing degree days to simulate crop phenology development.

Table 2 Variables used in AgTEM to govern C and N fluxes and pools

Variable	Definition	Unit
State variables		
C_S	C in soil and detritus	g C m^{-2}
C_V	C in vegetation	g C m^{-2}
N_{av}	Available N in soil and detritus	g N m^{-2}
N_S	Organic N in soil and detritus	g N m^{-2}
N_V	N in vegetation	g N m^{-2}
Carbon fluxes		
E_P	Decomposition of harvested products	$\text{g C m}^{-2} \text{ day}^{-1}$
GPP	Gross primary production	$\text{g C m}^{-2} \text{ day}^{-1}$
H_C	C in harvested products	$\text{g C m}^{-2} \text{ day}^{-1}$
L_C	C in litterfall	$\text{g C m}^{-2} \text{ day}^{-1}$
NCE	Net carbon exchange	$\text{g C m}^{-2} \text{ day}^{-1}$
NPP	Net primary production	$\text{g C m}^{-2} \text{ day}^{-1}$
R_A	Autotrophic respiration	$\text{g C m}^{-2} \text{ day}^{-1}$
R_C	C in returned biomass	$\text{g C m}^{-2} \text{ day}^{-1}$
R_H	Heterotrophic respiration	$\text{g C m}^{-2} \text{ day}^{-1}$
Nitrogen fluxes		
L_N	N in litterfall	$\text{g N m}^{-2} \text{ day}^{-1}$
$NETNMIN$	Net rate of soil N mineralization	$\text{g N m}^{-2} \text{ day}^{-1}$
$NINPUT$	N inputs from outside ecosystem	$\text{g N m}^{-2} \text{ day}^{-1}$
$NLOST$	N losses from ecosystem	$\text{g N m}^{-2} \text{ day}^{-1}$
$NUPTAKE$	N uptake by vegetation	$\text{g N m}^{-2} \text{ day}^{-1}$
R_N	N in returned biomass	$\text{g N m}^{-2} \text{ day}^{-1}$

Biomass allocation. During the growth period between crop emergence and maturity, plants use solar energy to capture atmospheric CO_2 through photosynthesis. The total net chemical energy captured by plant, or cumulative NPP, forms the total biomass of a given ecosystem. In agroecosystems, crop grain (e.g., maize) or biomass (e.g., switchgrass) can then be harvested and removed from the ecosystems. Part of the biomass leftover such as residues and dead roots will be returned to the soil C and N cycling. In AgTEM, biomass of interest (YLD, e.g., yield of grain or harvestable biomass) is modeled

empirically based on total NPP (NPP_{tot}) following Hicke & Lobell (2004) and Monfreda *et al.* (2008):

$$YLD = \frac{NPP_{tot} \delta_{hi}}{\delta_c D_{hi}}, \quad (8)$$

where δ_{hi} , δ_c , D_{hi} are parameters for determining the proportion of NPP being harvested, the C content in the dry matter, and the dry proportion of YLD, respectively (Table 5). For the grain harvest of food crops (e.g., maize), δ_{hi} is a function of the harvest index and a ratio of aboveground-to-belowground biomass (R_{hi}):

$$\delta_{hi} = \left(1 - \frac{1}{R_{hi} + 1}\right) HI, \quad (9)$$

where HI refers to the harvest index, measuring the proportion of total aboveground biological yield allocated to the economic yield of the crop (Table 5). R_{hi} , also known as 'shoot-to-root ratio,' indicates the biomass allocation to aboveground and belowground and is assumed to be constant for a specific crop (Hicke & Lobell, 2004). For crops used for biomass harvest purposes, HI needs to be slightly modified such that harvestable biomass instead of grain can be accounted for in Eqn (9).

The net carbon exchange between the terrestrial biosphere and the atmosphere is described with Eqn (10) in AgTEM:

$$NCE = NPP - R_H - E_P, \quad (10)$$

where the net carbon exchange (NCE) is the remaining C flux from NPP, after heterotrophic respiration (i.e., decomposition) (R_H) and decomposition (E_P) of products harvested from ecosystems for human use (e.g., harvested for YLD) (McGuire *et al.*, 2001). A positive NCE indicates ecosystem acting as a CO_2 sink whereas a negative NCE means that ecosystem is a CO_2 source.

Management. Agricultural management practices, such as irrigation, fertilization, rotation, and cultivar selection, affect mass and energy input and output in agroecosystems. However, the original TEM designated for natural ecosystems has not considered these factors (e.g., McGuire *et al.*, 1992). Using the modified TEM to simulate agroecosystem has some difficulties in modeling C-N-management interactions and integrating time-varying spatially explicit data into regional simulations (e.g.,

Table 3 Minimum, maximum, and optimum temperatures for plant photosynthesis

TEM version	Vegetation/ Crop type	T_{min} (°C)	T_{optmin}	T_{optmax}	T_{max}^*	Notes and references
TEM	Grass	0	13.0	32.7	38.0	In early TEM (e.g., TEM4.2, 4.3), crops were parameterized under grass vegetation type (McGuire <i>et al.</i> , 2001; Felzer <i>et al.</i> , 2004)
AgTEM	Maize	0	15.0	31.0	41.0	In AgTEM2.0, crop-specific sets instead of single set parameters were used for different crop type (Bird <i>et al.</i> , 1977; Kim & Reddy, 2004; Sage & Kubien, 2007)
	Switchgrass	0	13.0	33.0	41.0	
	<i>Miscanthus</i>	0	13.0	33.0	41.0	

* T_{min} , T_{optmin} , T_{optmax} , and T_{max} are minimum, minimum optimum, maximum optimum and maximum temperatures, respectively.

Table 4 Parameters used to determine growing degree days and simulate crop phenology

Vegetation/ Crop type	T_{base} (°C)	T_{ceil}^*	GDD_{emg} (°C day)	GDD_{mat}^\dagger	Notes and references
Grass	—	—	—	—	Not incorporated in TEM4.2 and earlier version (McGuire <i>et al.</i> , 2001)
Crop	5	—	300	2000	Used in modified TEM4.3 for simulating agricultural activities (Felzer <i>et al.</i> , 2004)
Maize	10 (5–15) [‡]	30	120	1600	Used in AgTEM according to Bondeau <i>et al.</i> (2007) and Nielsen (2010)
Switchgrass	10 (10–12) [‡]	30	300	2300	Used in AgTEM according to models such as ALMANAC (Kiniry <i>et al.</i> , 1992)
<i>Miscanthus</i>	10	30	300	2500	Used in AgTEM according to models such as MISCANMOD (Clifton-Brown <i>et al.</i> , 2004)

* T_{base} and T_{ceil} are base and threshold temperatures for calculating vegetation- and/or crop-specific GDDs, respectively.

[†] GDD_{emg} and GDD_{mat} are GDD heat unites required for crop emergence and maturity, respectively.

[‡]Value used for each crop species, but subject to change for different varieties (as in parentheses).

Table 5 Values of crop-specific parameters used for biomass harvest in AgTEM

Crop type	δ_c^*	D_{hi}^\dagger	R_{hi}^\ddagger	HI^\S	
				Grain	Biomass
Maize	0.45	0.85	0.85/0.15	0.53	—
Switchgrass	0.45	0.90	0.58/0.42	—	0.90
<i>Miscanthus</i>	0.45	0.90	0.71/0.29	—	0.90

* δ_c is the carbon content in the dry matter.

[†] D_{hi} is the dry proportion of YLD.

[‡] R_{hi} is parameterized as aboveground biomass/belowground biomass here.

[§] HI refers to maize grain harvested (grain) or the proportion of aboveground biomass harvested (biomass); no biomass harvested for maize at site level and no grain available for switchgrass and *Miscanthus*. Data sources and references: Prince *et al.*, 2001; Hicke & Lobell, 2004; Mosier *et al.*, 2006; Meyer *et al.*, 2010.

Felzer *et al.*, 2004) (Table 1). In contrast, AgTEM includes two major management practices of irrigation and N fertilization. Besides precipitation percolation, irrigation is considered as an additional direct water input into the soils, which is modeled based on Zhuang *et al.* (2002). N fertilizer, mainly in the form of NH_4^+ -N and NO_3^- -N, enters soils, as nutrients to support crop biomass accumulation and soil microbial activities. The N fertilization implementation in AgTEM is modeled as N input from sources outside the ecosystem, affecting NPP, N dynamics and C–N interactions, which were described in Raich *et al.* (1991) and McGuire *et al.* (1992). N fertilizers also affect nitrification and denitrification processes in AgTEM.

Nitrification and denitrification. Atmospheric nitrogen enters agroecosystems mainly through atmospheric deposition (e.g., lightning and rainfall), synthetic N fertilizer application, manure application, and litter fall. These N inputs are further mineralized into soil available N such as NH_4^+ and NO_3^- . The gaseous NO_x emissions from soils, mostly in forms of N_2 , nitric oxide (NO) and N_2O , are mainly produced through nitrifica-

tion and denitrification processes (Fig. 1). Nitrification describes the process of the biological oxidation of ammonia with oxygen into nitrite and nitrate. Denitrification represents a process of nitrate reduction that eventually produces N_2 and N_2O (Fig. 1).

In AgTEM, NO_x emissions are simulated according to the amount of soil inorganic N, determined by the microenvironment depending on temperature, soil pH, soil water content, and soil biological activity (Fig. S1, S2). Algorithms describing nitrification and denitrification processes from other studies (e.g., Bradbury *et al.*, 1993; Henault *et al.*, 2005) and models (EOSSE, Smith *et al.*, 2010; Bell *et al.*, 2012) were adapted. Three major NO_x fluxes (namely, N_2O , NO, and also N_2) are included in AgTEM. NO_x (NOX) is the total NO and N_2O emissions from nitrification and N_2 and N_2O emissions from denitrification:

$$\begin{array}{l} NH_4^+ \xrightarrow{NO_{ntf}} N_2O_{ntf} \\ NO_3^- \xrightarrow[N_2_{dtf}]{N_2O_{dtf}} N_2O_{dtf} \end{array} \Rightarrow N_2O \Rightarrow NOX, \quad (11)$$

where N_2O_{ntf} , NO_{ntf} , N_2O_{dtf} , and N_2_{dtf} indicate fluxes of N_2O from nitrification, NO from nitrification, N_2O from denitrification and N_2 from denitrification, respectively (Table S1). Total N_2O fluxes (N_2O) account for both N_2O_{ntf} and N_2O_{dtf} (more details on nitrification and denitrification modeling can be found in Supporting Information).

Model parameterization and site-level validation

There are a number of constant, vegetation-specific, or soil-specific parameters in AgTEM. Most of them have been defined and determined in earlier studies (e.g. Raich *et al.*, 1991; McGuire *et al.*, 1992; Zhuang *et al.*, 2003). Some vegetation-specific parameters, such as those used to estimate C and N dynamics in maize, switchgrass, and *Miscanthus* ecosystems, were determined via calibration of the model driven with climate data using observed data of C and N fluxes and pool sizes (Qin *et al.*, 2011, 2012). To determine biomass allocation and biomass-yield conversion, crop-specific parameters used in Eqns (8) and (9) were defined according to previous researches (Table 5). Most parameters used in soil N

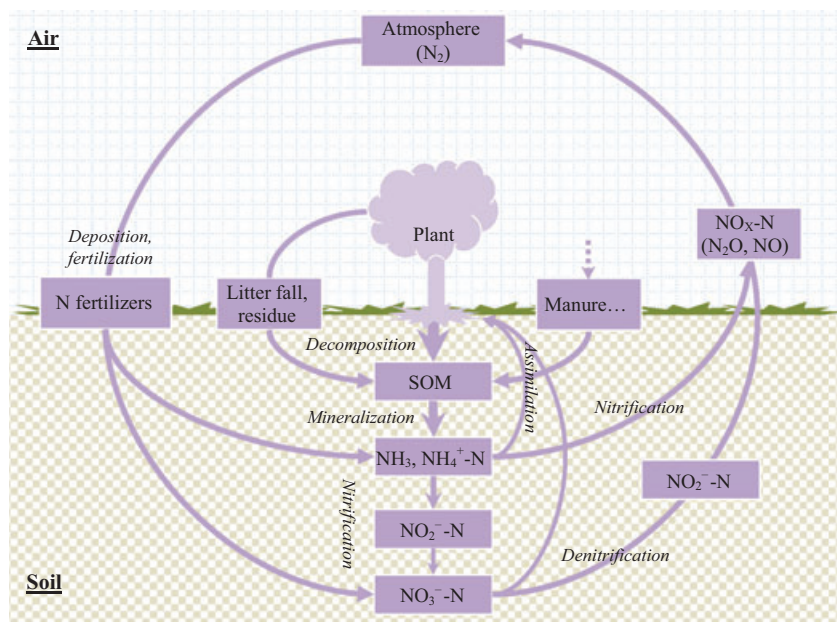


Fig. 1 N cycling among the atmosphere, biosphere, and pedosphere. Major processes were modeled in AgTEM. SOM, soil organic matter; N_2 , nitrogen; NH_3 , ammonia; NO_x , nitrogen oxides; N_2O , nitrous oxide; NO , nitric oxide.

nitrification and denitrification can be found in earlier studies (Table S2).

Validation investigates models' performance to reproduce the observations from a system within its domain of application (Rykiel, 1996). The model simulations are compared with observed data, and certain criteria are used to determine model performance (Smith *et al.*, 1997). In total, 29 field experiment sites, including 82 site-treatment (i.e., N input level) observational data sets, were organized for validating AgTEM across the United States. These sites cover three bioenergy ecosystems including maize, switchgrass, and *Miscanthus* (Table 6). For maize, only continuous maize cropping systems were included in the validation. Data of biomass yield (e.g., maize grain, cellulosic biomass) and annual N_2O fluxes were used for model and data comparison. Site location, agricultural management, soil properties, and daily climate conditions were used for model simulations. Site annual N_2O flux estimates were based on observations during the crop growing season, and accumulated through all growth stages. Possible N_2O fluxes from the nongrowing season were not estimated. For site-level data collection and processing (e.g., NPP calculation) procedures, information can be found in earlier studies (Qin *et al.*, 2011, 2012). The climate data of air temperature, precipitation, cloudiness were obtained from the ECMWF (European Centre for Medium-Range Weather Forecasts) Data Server (www.ecmwf.int). For each site-treatment, AgTEM was run for multiple years, using forcing data describing site location, elevation, climate, soil, vegetation, and management. NPP, biomass of interest (i.e., maize grain, harvestable biomass), and N_2O flux were analyzed. For all three crops, modeled NPP and N_2O were then compared with the observed data.

For comparison, the modeled data were plotted against observations, and a linear regression with a zero intercept was computed to estimate the slope and coefficient of determination (R^2). The closer the regression slope to 1, the better the model fits to the observed data. R^2 ($0 \leq R^2 \leq 1$) indicates the pattern of simulated and observed values (Smith *et al.*, 1997; Huang *et al.*, 2009). The root mean square error (RMSE) and model efficiency (EF) (Loague & Green, 1991) were also reported to show the discrepancies between simulations and observations.

We also estimated the N_2O fluxes following the Intergovernmental Panel on Climate Change (IPCC) N-input approach (Tier 1) (De Klein *et al.*, 2006). The annual direct soil N_2O emissions were empirically calculated as a factor (0.01) of total N input into soils, including N from fertilizer, manure, water, and residue. Water N was not accounted for in our study, partly because of its scarcity compared to other N sources and also due to a lack of data. Model performance was evaluated in a similar manner to AgTEM.

Model sensitivity analysis

A sensitivity analysis studies the response of the model to different sources of variance in input data (e.g., parameters, forcing data) (Loucks *et al.*, 2005). To study AgTEM sensitivity, three sites with the most accessible information, one for each ecosystem type (Table 6), were selected. Six major input variables representing the climate, management, and CO_2 conditions were included in the sensitivity analysis. For a simplified general form of AgTEM Eqn (12), an output corresponding to change in input variables can be written as Eqn (13):

$$Y = f(X_1, \dots, X_6) \quad (12)$$

Table 6 Field experiments studying biomass production and N₂O emissions of bioenergy crops, used in this study

Bioenergy crop	Location	Collection period	Experimental treatment	Available observational data	References
Maize	Fort Collins, CO [†]	2002–2004	Three nitrogen levels (0–202/224 kg N ha ⁻¹); maximum level differs for 2002 and 2003–2004	Grain yield, N ₂ O flux	Halvorson <i>et al.</i> , 2006;
	Fort Collins, CO	2005–2006	Four nitrogen levels (0–246 kg N ha ⁻¹)	N ₂ O flux	Mosier <i>et al.</i> , 2006
	Fort Collins, CO	2007–2008	Three nitrogen levels (0–246 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Halvorson <i>et al.</i> , 2008
	West Lafayette, IN	2004–2006	One nitrogen level, changed from 222 kg N ha ⁻¹ in 2004–2005 to 260 kg N ha ⁻¹ in 2006	N ₂ O flux	Halvorson <i>et al.</i> , 2010
	Hickory Corners, MI	2001–2003	Nine nitrogen levels available, from 0 to 291 kg N ha ⁻¹	Grain yield, N ₂ O flux	Omonode <i>et al.</i> , 2011
	Fairgrove, MI	2007–2008	Six nitrogen levels (0–225 kg N ha ⁻¹)	Grain yield, N ₂ O flux	McSwiney & Robertson, 2005
	Hickory Corners, MI	2007–2008	Six nitrogen levels (0–225 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Hoben <i>et al.</i> , 2011
	Mason, MI	2007	Six nitrogen levels (0–225 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Hoben <i>et al.</i> , 2011
	Reese, MI	2007–2008	Six nitrogen levels (0–225 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Hoben <i>et al.</i> , 2011
	Stockbridge, MI	2008	Six nitrogen levels (0–225 kg N ha ⁻¹)	N ₂ O flux	Hoben <i>et al.</i> , 2011
Switchgrass	Lincoln, NE	2003–2005	Recommended and intensified management, each had three nitrogen levels (180–310 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Adviento-Borbe <i>et al.</i> , 2007
	Rock Springs, PA	2006–2007	With only one nitrogen level (224 kg N ha ⁻¹)	Grain yield, N ₂ O flux	Adviento-Borbe <i>et al.</i> , 2010
	Chatham, MI [‡]	2009	Three nitrogen levels (0–112 kg N ha ⁻¹)	Harvested biomass, N ₂ O flux	Nikiema <i>et al.</i> , 2011
	Shabbona, IL	2004–2006	No nitrogen applied	Harvested biomass, limited [*]	Heaton <i>et al.</i> , 2008
	Simpson, IL	2004–2006	No nitrogen applied	Harvested biomass, limited	Heaton <i>et al.</i> , 2008
	Urbana, IL	2004–2006	No nitrogen applied	Harvested biomass, limited	Heaton <i>et al.</i> , 2008
	Manhattan, KS	2011	One nitrogen level (156 kg N ha ⁻¹)	N ₂ O flux	Propheter <i>et al.</i> , 2010;
					McGowan <i>et al.</i> , 2012
	Raleigh, NC	1999–2001	Four switchgrass cultivars were planted at eight sites (1–8); Nitrogen was applied to all plots at an annual rate of 100 kg N ha ⁻¹ , site 1 Same as above, but for site 2	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Princeton, KY	1999–2001	Same as above, but for site 3	Harvested biomass	Fike <i>et al.</i> , 2006a, b
<i>Miscanthus</i>	Knoxville, TN	1999–2001	Same as above, but for site 4	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Jackson, TN	1999–2001	Same as above, but for site 5	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Blacksburg, VA	1999–2001	Same as above, but for site 6	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Blacksburg, VA	1999–2001	Same as above, but for site 7	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Orange, VA	1999–2001	Same as above, but for site 8	Harvested biomass	Fike <i>et al.</i> , 2006a, b
	Morgantown, WV	1999–2001	Three nitrogen levels (0–120 kg N ha ⁻¹)	Harvested biomass, N ₂ O flux	Behnke <i>et al.</i> , 2012
	Urbana, IL [§]	2010	One nitrogen level (156 kg N ha ⁻¹)	N ₂ O flux	Propheter <i>et al.</i> , 2010;
	Manhattan, KS	2011			McGowan <i>et al.</i> , 2012
	Shabbona, IL	2004–2006	No nitrogen applied	Harvested biomass	Heaton <i>et al.</i> , 2008
	Simpson, IL	2004–2006	No nitrogen applied	Harvested biomass	Heaton <i>et al.</i> , 2008
	Urbana, IL	2004–2006	No nitrogen applied	Harvested biomass	Heaton <i>et al.</i> , 2008

*No data for the first year.

[†]Maize site selected for model sensitivity analysis.[‡]Switchgrass site selected for model sensitivity analysis.[§]*Miscanthus* site selected for model sensitivity analysis.

$$E(Y_i^j) = E_{X_i}(Y|X_i^0), \quad (13)$$

where X_i denotes the i -th input variables, and X_1 to X_6 are daily air temperature (*TAIR*), daily precipitation (*PREC*), daily cloudiness (*CLDS*), daily N fertilizer application (*FTLZ*), daily irrigation (*IRGT*), and annual atmospheric CO₂ concentrations (*KCO2*), respectively. Y indicates the model output whose sensitivity to environment will be evaluated, and here j can refer to NPP and N₂O fluxes in AgTEM. Y_i corresponds to input X_i . As for Eqn (13), $(Y|X_i^0)$ is the model simulation under changing variable X_i , while other variables are fixed (X_i^0). Therefore, the change of model output due to a given changing input can be expressed as follows:

$$V(Y_i) = \frac{E(Y_i)}{E(Y_0)} - 1, \quad (14)$$

where $V(Y_i)$ is the change of output Y responding to changing input X_i , relative to a reference scenario where all input variables are fixed (as in Y_0). In this study, all input forcing data collected for each site were used for the reference scenario. In particular, the N fertilizer application rate in the reference scenario was set as 134 kg N ha⁻¹ for maize and 56 kg N ha⁻¹ for switchgrass and *Miscanthus*. A certain perturbation was exerted to the forcing data to represent input changes:

$$X^T C = \begin{pmatrix} \text{TAIR} & \text{PREC} & \text{CLDS} & \text{FTLZ} & \text{IRGT} & \text{KCO2} \end{pmatrix}^T \begin{pmatrix} -1 & 0 & +1 \end{pmatrix} \quad (15)$$

As in Eqn (15), for each variable X , negative (−1) and positive (+1) changes (C) were added on to the reference (0) forcing data to calculate output sensitivity to increases and decreases of inputs, respectively. For each model simulation regarding the changing variable X , NPP and N₂O outputs were analyzed, and a decadal average $V(Y)$ was reported to demonstrate the magnitude of sensitivity for a given Y .

Results

Site-level biomass production and nitrous oxide emissions

The field experiment sites (i.e., maize, switchgrass, and *Miscanthus*) selected for model validation spread across a majority portion of the maize-producing areas in the conterminous United States, covering a variety of climate zones such as semiarid steppe climate, humid continental climate, and humid subtropical climate (Fig. 2a). Of the 82 site-treatment datasets collected from 29 sites, 65 of them contain N₂O observational data (maize: 57, switchgrass: 4, *Miscanthus*: 4), and 62 have NPP data (maize: 45, switchgrass: 10, *Miscanthus*: 7). These data were used as dependent variables for comparisons between model simulations and observations. N input at the site-level ranges from 0 to 310 kg N ha⁻¹ for maize and 0 to 156 kg N ha⁻¹ for switchgrass and *Miscanthus* (Table 6), representing a wide diversity of N treatments.

AgTEM simulations of crop NPP are consistent with the observations (Fig. 2b). The observed NPP of maize has an average of 680 g C m⁻², with a range from 287 to 1400 g C m⁻². Crop productivity tends to increase with increasing N application. Observed NPP of switchgrass and *Miscanthus* are relatively higher than maize, about 850 and 1400 g C m⁻², respectively. However, the biomass production is not necessarily related to the N input level. For all sites ($n = 62$), the regression between modeled and observed NPP yields an R^2 of 0.74 with a slope of 0.95 ($P < 0.001$). However, two observations (Fig. 2b, circled) evidently deviate from the 1 : 1 line, showing an underestimation in AgTEM. These two observations of *Miscanthus* from central and southern Illinois show an extremely high biomass production (Heaton *et al.*, 2008), with an average annual NPP flux of about 2150 g C m⁻², about three times the average NPP of the rest of the 60 observations. The peak biomass production may be because of favorable climate, management, and proper harvest time during the experiment time (Heaton *et al.*, 2008). To better illustrate the model performance at the majority of sites, observations beyond the range of [mean ± 2SD (standard deviation)] were removed for the comparison. For these sites within 2SD, the indices indicate that fitness of simulations is improved. The slope of regression approximates 1, with a R^2 of 0.85; the RMSE decreases from 0.20 to 0.14 and EF increases from 0.83 to 0.88 (Fig. 2b).

N₂O fluxes from maize, switchgrass, and *Miscanthus* were modeled using both AgTEM and an IPCC empirical model. Observations from maize ecosystems show that N₂O emitted from croplands with high N application rates are mostly larger than those with lower N input levels (Fig. 2c). As for all sites ($n = 65$), the average N₂O flux is 1.8 kg N ha⁻¹ (1 kg N ha⁻¹ = 0.1 g N m⁻²), with the maximum flux reaching 13.5 kg N ha⁻¹ observed in a continuous maize field in Indiana (Omonode *et al.*, 2011). Normally, N fertilizers are not applied to switchgrass and *Miscanthus*, and the highest N application rate tested in the field experiments is 156 kg N ha⁻¹. N₂O emissions from soils of these cellulosic crops are comparable with those from maize cropland under similar N input levels (Fig. 2c). The model simulations using AgTEM well estimate the N₂O change, at least for fluxes within a reasonable range (e.g., less than 5.0 kg N ha⁻¹). The comparison between modeled and observed N₂O results in a slope of 0.83 and R^2 of 0.78, for all sites. By moving two maize observations outside the 2SD range (Fig. 2c, circled), one from Stockbridge, MI (Hoben *et al.*, 2011) and the other from West Lafayette, IN (Omonode *et al.*, 2011), the regression generates a higher slope of 0.94 with a greater R^2 of 0.86. The RMSE declined from 0.37 to 0.25,

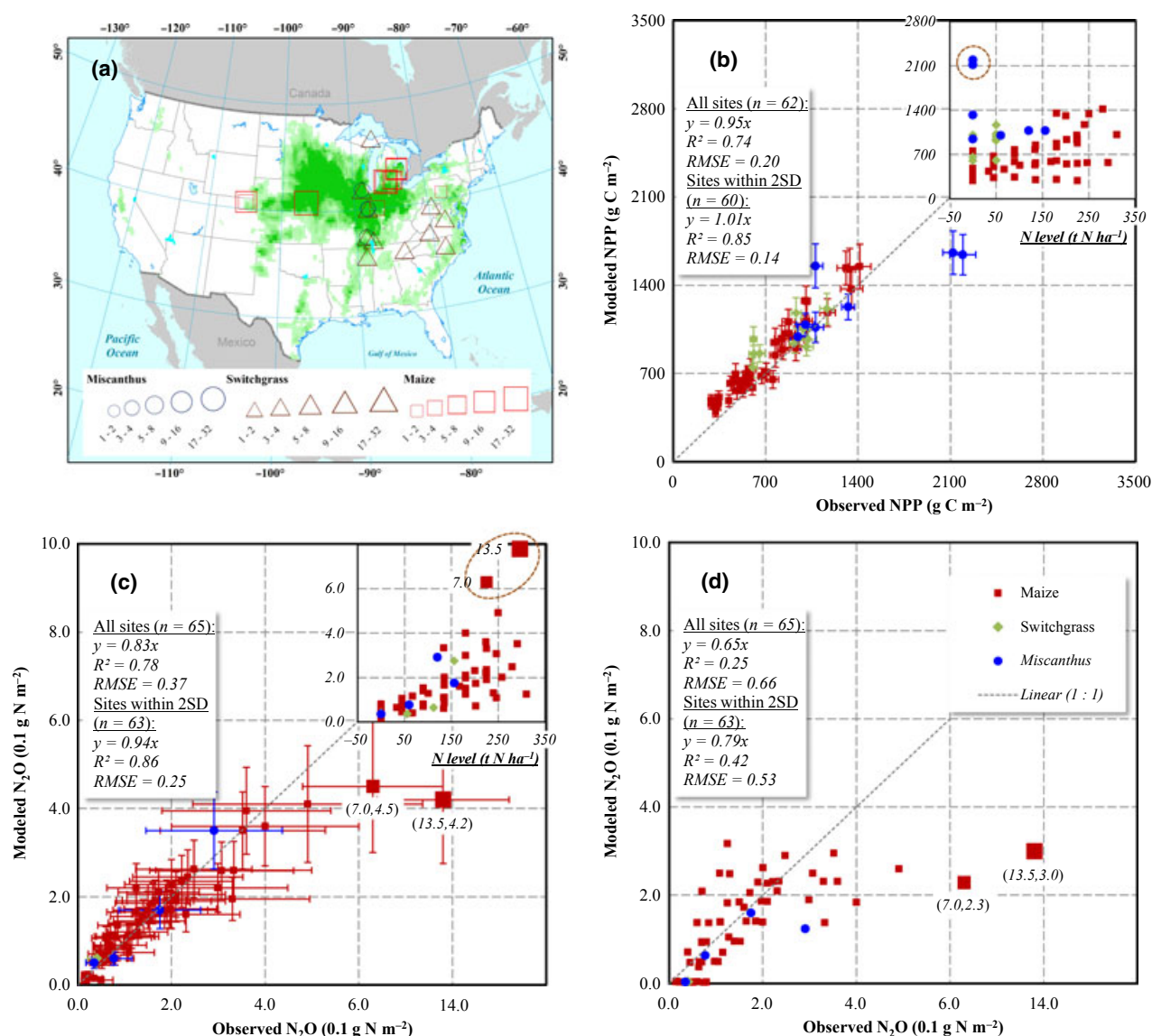


Fig. 2 Modeled vs. observed NPP and N₂O fluxes in bioenergy ecosystems at site-level. (a) Maize, switchgrass, and *Miscanthus* sites cover a majority of the maize-producing areas (shadowed in deep green) across the conterminous United States (Monfreda *et al.*, 2008), (b) AgTEM modeled vs. observed NPP, with illustration of NPP change over N input level in the upper right inset, (c) AgTEM modeled vs. observed N₂O, with illustration of N₂O change over N input level in the upper right inset, (d) IPCC modeled vs. observed N₂O.

and EF slightly improved from 0.81 to 0.88. The discrepancies between modeled and observed fluxes are partly explained by high soil organic matter content (Hoben *et al.*, 2011). Possible maize residues and residual mineral N gains from N fixation by the previous crop (Omonode *et al.*, 2011) contributed to N₂O emissions, while AgTEM did not capture these changes.

The IPCC approach relates N₂O emissions solely to N input, such as N fertilizer and residue, but fails to consider environmental factors that also significantly affect N dynamics (Grassini & Cassman, 2012). In our study,

the predictions from the IPCC model capture a proportion of the observations, with more persuasive indices supporting the fitness for sites within 2SD than for all available sites (Fig. 2d). However, high variances still existed; the RMSE and EF were 0.66 and 0.41, respectively, for all sites ($n = 65$), and 0.53 and 0.46, respectively, for limited sites ($n = 63$). The emission factor of 0.01 may not fit all ecosystems. Based on the observations collected in this study, the emission factor of N₂O for maize is 0.010 ($R^2 = 0.44$, $P < 0.001$, $n = 63$) or 0.013 ($R^2 = 0.33$, $P < 0.001$, $n = 65$); for switchgrass, it is 0.013

($R^2 = 0.62$, $P = 0.2$, $n = 4$) and for *Miscanthus* it is 0.016 ($R^2 = 0.56$, $P = 0.2$, $n = 4$).

Compared with the IPCC empirical model in most cases, AgTEM is a better tool to estimate N_2O fluxes from maize, switchgrass and *Miscanthus* ecosystems. The IPCC approach is a good substitute when process-based models are not used due to lacking data or when the estimation accuracy requirement is not high. AgTEM will work under more complicated circumstances, especially when N_2O accounting has higher accuracy requirement while the environment conditions are complex. For example, regional, national, or even global large-scale estimates require process-based modeling for better accounting for the complex climate–soil–atmosphere interactions (Bondeau *et al.*, 2007; Del Grosso *et al.*, 2010).

Model sensitivity to environmental and management factors

A sensitivity analysis quantifies the impact of changes in input data on model outputs. Usually, only a subset of input variables dominates outputs in process-based models (Loucks *et al.*, 2005). To identify those input variables, AgTEM simulations were conducted by varying six input variables at three separate locations, one site for each type of crop. The sensitivity of NPP and N_2O in terms of percentage change relative to the reference simulation is reported separately for maize, switchgrass, and *Miscanthus*.

In AgTEM, climate, soil and CO_2 conditions, and agricultural management including irrigation and fertilization which determine photosynthesis and autotrophic

respiration will ultimately affect NPP. The sensitivity analysis shows that the perturbations to input variables affect NPP for all three crops. However, the magnitudes of sensitivity differ among variables and crops (Fig. 3). For all crops, KCO_2 , TAIR, PREC, FTLZ, and IRGT (except no IRGT available for cellulosic crops) have positive effects on NPP, where a positive change of input results in a positive change of output, while CLDS has a negative effect on NPP. All crops are comparably sensitive to CO_2 and air temperature, but cellulosic crops (i.e., switchgrass and *Miscanthus*) are much less sensitive than maize to precipitation, cloudiness, and fertilizer application (Fig. 3). In maize ecosystems, NPP is most sensitive to air temperature, where about 20% of the NPP increase was due to a 10% temperature increase and a 16% NPP decrease was due to a 10% temperature decrease, and least sensitive to CO_2 , where only about a 7% NPP change was due to a 10% CO_2 input change (Fig. 3a). In switchgrass and *Miscanthus* ecosystems, air temperature is still the dominant factor affecting NPP, and a 10% input change caused a 20% NPP change. However, NPP responses are much less noticeable in response to changes in precipitation, cloudiness, and fertilization, only a 1–5% change resulted from a 10% input change (Fig. 3b and c).

These responses may be partly explained by the fact that environmental and management factors directly or indirectly affect the plant photosynthesis and respiration. The atmospheric CO_2 positively affects GPP production via photosynthesis. Elevated CO_2 significantly increases leaf photosynthetic CO_2 uptake rate (Leakey *et al.*, 2004; Oliver *et al.*, 2009). Higher temperature means a longer growth period and higher GDD, which

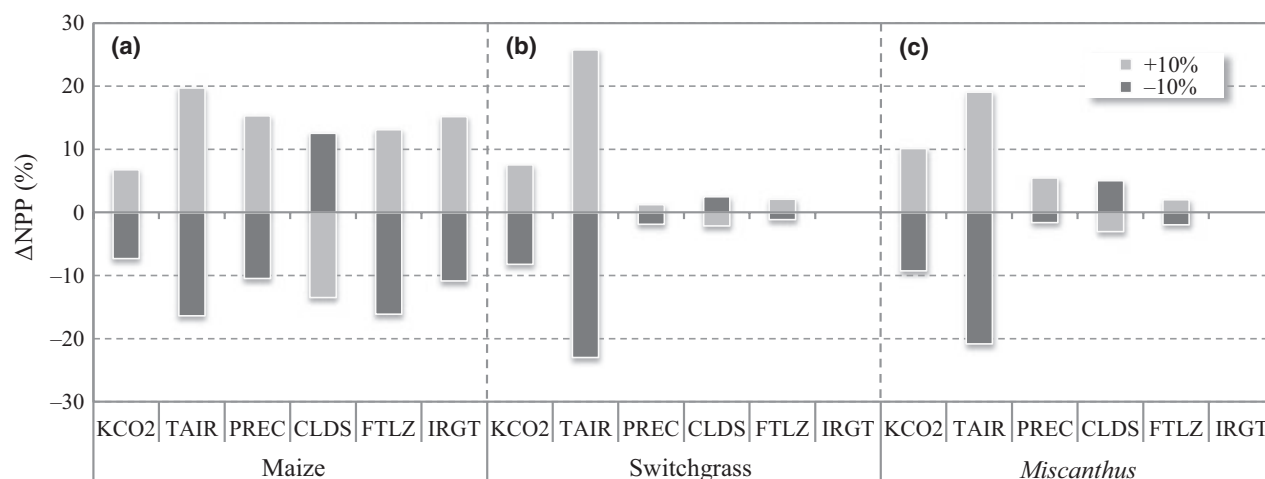


Fig. 3 Sensitivity of Net primary production (NPP) responding to model input ($\pm 10\%$ change) in different ecosystems. Estimates were made for (a) maize at site Fort Collins, CO, (b) switchgrass at site Chatham, MI and (c) *Miscanthus* at site Urbana, IL. KCO_2 , atmospheric CO_2 concentration; TAIR, temperature; PREC, precipitation; CLDS, cloudiness; FTLZ, fertilizer amount; IRGT, irrigation amount.

may benefit crops, especially those grown in the relatively colder areas. An example is the selected switchgrass site in the central Upper Peninsula of Michigan, USA. (46.55°N, 86.92°W, 266.1 m a.s.l.) (Nikiema *et al.*, 2011). Abundant but not excessive precipitation can protect crops from drought, providing sufficient water for evaporation and transpiration. Lower cloudiness allows more solar radiation to be absorbed by plants, and therefore more energy to be stored in vegetation. Favorable management practices could always benefit crop production, for example, irrigation for water inputs and fertilization for nutrient inputs. However, switchgrass and *Miscanthus* seemed to benefit less from increased water and nutrient inputs or less harmed due to less input (Fig. 3b and c). This is because that these biofuel crops have a relatively higher efficiency for using solar radiation, water, and nutrients (e.g., N) compared with maize. Studies reported that switchgrass and *Miscanthus* could intercept large proportions of the photosynthetically active radiation (Heaton *et al.*, 2008), use much less irrigation than food crops (Fargione *et al.*, 2010), and have no or only slight responses to N fertilization (Lewandowski *et al.*, 2003).

Among the six factors, CO₂ generally has the least impact on N₂O output in AgTEM among all three ecosystems (Fig. 4). N₂O output is negatively related to CO₂ input; less than a 0.5% N₂O flux change was estimated in response to a 10% CO₂ change. For maize ecosystems, the model is more sensitive to fertilization and irrigation, and less responsive to climate factors (Fig. 4a). For switchgrass and *Miscanthus* ecosystems, the model shows a much higher sensitivity to climate factors than management. A 4–9% change in N₂O is observed as a result of a 10% change of temperature or

precipitation, and a 2–3.5% N₂O change has occurred in response to a cloudiness change (Fig. 4b and c). Low N input level (56 kg N ha⁻¹) partly explains the insensitivity of modeling response to fertilization.

Additional tests using $\pm 20\%$ input change confirmed the pattern of local responses of NPP (Fig. S3) and N₂O (Fig. S4) to input perturbations. However, the relative output changes vary among different input variables and ecosystems. It should be noted that the local sensitivity analysis here is not for quantifying the regional impacts of input on outputs. The sensitivity results may change due to change of input data and the sites for conducting the analysis. A global sensitivity analysis at regional levels would be needed to allow full exploration of the input space, accounting for high-dimensionality, interactions, and spatial heterogeneity. However, the global sensitivity analysis requires more information to build probability distributions for the input variables and parameters and expects higher computational complexity (Tang & Zhuang, 2009).

Discussion

Impacts of N input on biomass production and N₂O emissions

Nitrogen, an indispensable nutrient for plants, is often the limiting factor for both crop growth and N₂O production. Generally, crop yields and NPP depend on N availability; higher productivity normally requires considerable N inputs, especially for soils with poor nutrient contents (Millar *et al.*, 2010). Many earlier recommendations on crop N application were made based on a positive N-yield relationship (e.g., Stanford, 1973).

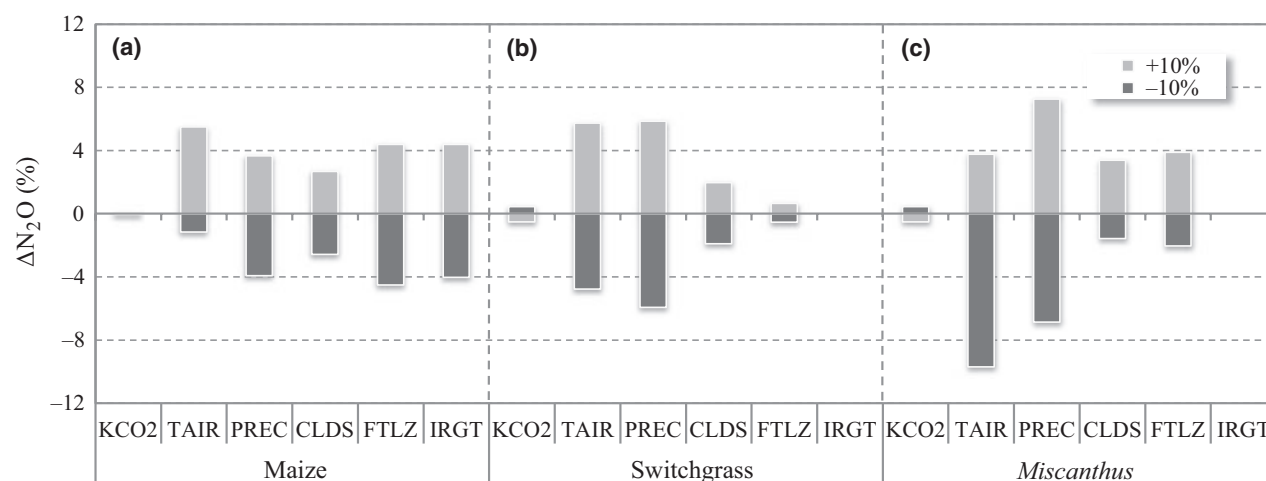


Fig. 4 Sensitivity of N₂O responding to model input ($\pm 10\%$ change) in different ecosystems. Estimates were made for (a) maize at site Fort Collins, CO, (b) switchgrass at site Chatham, MI, and (c) *Miscanthus* at site Urbana, IL. Abbreviations are same as in Fig. 3.

However, later N response trials and observations questioned the poor N-yield relationship because crop yield may not necessarily increase at excessive N input levels (Nafziger *et al.*, 2004; Millar *et al.*, 2010). N input may enhance crop growth at lower N levels, but may reach a crop yield threshold when the N application is sufficient (Nafziger *et al.*, 2004). For example in the three-year trials in Michigan, McSwiney & Robertson (2005) observed that maize grain yields increased in response to N additions from 0 to 101 kg N ha⁻¹, but then leveled off when more N was added.

When N availability exceeds the needs by plant and competing biota, N₂O emissions can be substantial and exhibit exponential responses to the magnitude of N inputs. It has been found in this study (Fig. 2c) and others (McSwiney & Robertson, 2005; Hoben *et al.*, 2011) that the relationship between N₂O flux and N input is nonlinear, with a lower emission rate at relatively low N application levels, and a much higher rate when N input increases. N₂O emissions are often simulated as an exponential function of the N input rate with empirical models (McSwiney & Robertson, 2005; Van Groenigen *et al.*, 2010), instead of simply applying a linear model like the IPCC tier 1 approach (De Klein *et al.*, 2006). That is, with increasing N, the marginal gain of crop yields decreases while the marginal N₂O emissions increase. The recommended rate of N application can only be reached at such a point that the marginal benefit from crop production balances marginal loss or cost via resource input (e.g., N fertilization) and environment pollution (e.g., GHG emissions). More attention should be paid to environmentally or ecologically optimum N rates from the perspective of ecosystem services (Millar *et al.*, 2010; Chen *et al.*, 2011a; Davis *et al.*, 2012).

Approximation and simulation in modeling

Agroecosystem models and crop models share expanding common interests, yet they also have their own specialties. Both groups facilitate the application of models in a system approach to quantifying crop ecosystem dynamics. Both provide a framework to integrate knowledge about soil, climate, plant, and management to transfer the understanding from one location to another, from site to region, supporting decision making with less time and resources required for analyzing complex systems (Raich *et al.*, 1991; Jones *et al.*, 2003; Loucks *et al.*, 2005). However, crop models are mostly used in the agriculture sector to help understand the impacts of environment factors and especially management practices on crop growth and therefore crop yield (grain based) or biomass (non-grain or not interested in grain), and to provide recommendations on agricultural management or hazard protection. Model simulations focus on finer resolutions,

for instance, at site- or field- scale for a specific crop type (e.g., CERES-Maize for maize, Hodges *et al.*, 1987) or for specific purposes (e.g., AquaCrop for water management, Steduto *et al.*, 2009). In contrast, agroecosystem models have usually been used to understand the impacts of natural (e.g., climate) or anthropogenic activities (e.g., cropping) on ecosystem dynamics (e.g., McGuire *et al.*, 2001; Felzer *et al.*, 2009). Crop yields or biomass production is part of the C cycle. The spatial scale can be region, nation and even globe (Bondeau *et al.*, 2007).

In our study, AgTEM models the C and N dynamics for agroecosystems with vegetation-specific parameters for each species or crop type. The model structure and algorithms used to describe the biogeochemical and physical processes (e.g., photosynthesis, biomass allocation) are similar, with only minor changes for specific crops. For example, maize has an extra C pool (grain) while switchgrass and *Miscanthus* do not have one. Vegetation-specific parameters calibrated with observational data were used to capture the magnitude of differences among crops. Some of these parameters can be found from either experiment-based models or crop models (e.g., Tables 3 and 4). Management practices such as irrigation and fertilization were considered in AgTEM, and grain and biomass harvest were estimated.

In the validation and sensitivity analyses, we used the annual total value at multiple sites instead of daily fluxes from a single site to evaluate the NPP and N₂O fluxes. We also combined estimates of three species, maize, switchgrass, and *Miscanthus*, instead of making separate calculations. In the agroecosystem model, biomass (e.g., grain) is estimated based on NPP, a large-scale and long-term average quantity considering both natural and anthropogenic effects. In comparison with crop models, crop yields are small-scale and short-term results of G × E × M (gene/species × environment × management) interactions. Therefore, using agroecosystem models to estimate small-scale C and N dynamics of crop ecosystems, by calibrating parameters to capture short-term (e.g., day-by-day) fluxes, might result in high uncertain ecosystem dynamics (Bell *et al.*, 2012). In addition, observational data might not be in agreement between experiments or repeated samples as a result of measurement uncertainty such as ground disturbance, investigator biases, method divergences and laboratory requirement differences (Müller & Höper, 2004; Kessel *et al.*, 2013). In this study, for example, the N₂O experiments collected gas samples at different time intervals during various time courses (e.g., McSwiney & Robertson, 2005; Omonode *et al.*, 2011) at weekly (Parkin & Hatfield, 2010), biweekly (Nikiéma *et al.*, 2011) or irregular (Hoben *et al.*, 2011) time steps. Frequency, timing and quantity of N fertilization may affect daily N₂O

fluxes significantly (Mosier, 1994), and the N₂O variations could be principally due to the degree of coincidence of fertilizer application and major rainfall events (Dobbie *et al.*, 1999). It is therefore useful to use seasonal or annual total N₂O emissions from several years' data from a certain ecosystem in a variable climate to obtain a robust estimate of mean N₂O fluxes (Dobbie *et al.*, 1999).

Estimation uncertainties and future needs

The discrepancies between modeled and observed NPP and N₂O come from several sources of uncertainties. Imperfect representation of processes (structural uncertainty) and limited knowledge of parameter value (parameter uncertainty) in a model constitute model uncertainty (Loucks *et al.*, 2005). In addition, AgTEM only considers irrigation and fertilization in terms of agricultural management. Tillage, crop rotation, crop straw management that affect the biomass and N₂O emissions (Halvorson *et al.*, 2008; Liu *et al.*, 2011), however, were not considered. This is partly because of the difficulty to quantify the spatial variability of human activities due to a lack of consistent evidence (Millar *et al.*, 2010), and no spatially explicit data concerning these management practices are available for regional simulations (Felzer *et al.*, 2004). Input data are another source of uncertainty. First, the observational data could be biased due to experimental uncertainty. Compared with maize, there are less data for switchgrass and *Miscanthus* for model validation. More observational data will help to parameterize and validate AgTEM at locations under different environmental conditions (e.g., Europe and China). The forcing data for model simulations were collected from various sources, thus may not represent local environmental conditions. For example, the temperature and precipitation data used in AgTEM were obtained from the ECMWF reanalysis database. The data may be suitable for regional estimation, but not accurate for site-level simulations (Dee *et al.*, 2011). Thus, local climate, soil and vegetation data at the site are desirable.

Uncertainty cannot be removed but can be narrowed, and the model can be improved. From the perspective of observation, better estimates can be achieved via dedication to cross-site experimental research that are of considerable long period with appropriate time intervals during sufficient time courses (e.g., N₂O), covering various climate and management (Dalal *et al.*, 2003). The ecosystem C budget quantification can be improved using eddy flux data (e.g., Chen *et al.*, 2011b). In this study, however, the NCE data of crop ecosystems are not available. Among the many Ameriflux sites (<http://ameriflux.ornl.gov/>), only a very limited number of

sites cover croplands (IGBP) with ecosystem C balance data (e.g., NEE, net ecosystem exchange). There are only two sites listed (Rosemount G21 Conventional Management Corn Soybean Rotation/US-Ro1, Minnesota; Mead Irrigated Rotation/US-Ne2, Nebraska) covering maize croplands that can be potentially used for AgTEM. However, the observed fluxes at these sites measure the maize-soybean rotation system, which did not well represent continuous maize ecosystems. Thus, Ameriflux data were not used in this study. Continuous efforts in the maize-, switchgrass-, and *Miscanthus*-based ecosystem flux measurements, together with agronomic observations (e.g., yield, management) (e.g., Suyker *et al.*, 2004) should be made to improve the model performance.

Our understanding about the underlying ecophysiological and biogeochemical processes shapes the way we interpret and model agroecosystems. Improved observational data will help calibrate and validate models. The AgTEM, as well as many other agroecosystem models can be improved using more data. These models can be appropriately extrapolated to regional scales when they are well calibrated and validated (e.g., McGuire *et al.*, 2001; Bondeau *et al.*, 2007). The developed AgTEM can be used to quantify C and N dynamics of maize, switchgrass and *Miscanthus* ecosystems at regional scales.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Simulation of nitrification responding to substrate concentration, climate, and soil environment.

Figure S2. Simulation of denitrification responding to substrate concentration and soil environment.

Figure S3. Sensitivity of NPP responding to model input ($\pm 20\%$ change) in different ecosystems.

Figure S4. Sensitivity of N₂O responding to model input ($\pm 20\%$ change) in different ecosystems.

Table S1. Variables and parameters used in AgTEM to simulate soil N dynamics and nitrogen oxide emissions.

Table S2. Values of parameters used to calibrate nitrogen oxide emissions in AgTEM.

Model S1. Nitrification and denitrification in AgTEM.