

Spatial and temporal patterns of CH₄ and N₂O fluxes in terrestrial ecosystems of North America during 1979–2008: application of a global biogeochemistry model

H. Tian^{1,2}, X. Xu^{1,2}, M. Liu^{1,2}, W. Ren^{1,2}, C. Zhang¹, G. Chen^{1,2}, and C. Lu^{1,2}

¹Ecosystem Dynamics and Global Ecology (EDGE) Laboratory, School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL, 36849, USA

²International Center for Climate and Global Change Research, Auburn University, Auburn, AL, 36849, USA

Received: 16 March 2010 – Published in Biogeosciences Discuss.: 21 April 2010

Revised: 30 August 2010 – Accepted: 1 September 2010 – Published: 10 September 2010

Abstract. Continental-scale estimations of terrestrial methane (CH₄) and nitrous oxide (N₂O) fluxes over a long time period are crucial to accurately assess the global balance of greenhouse gases and enhance our understanding and prediction of global climate change and terrestrial ecosystem feedbacks. Using a process-based global biogeochemical model, the Dynamic Land Ecosystem Model (DLEM), we quantified simultaneously CH₄ and N₂O fluxes in North America's terrestrial ecosystems from 1979 to 2008. During the past 30 years, approximately $14.69 \pm 1.64 \text{ T g C a}^{-1}$ ($1 \text{ T g} = 10^{12} \text{ g}$) of CH₄, and $1.94 \pm 0.1 \text{ T g N a}^{-1}$ of N₂O were released from terrestrial ecosystems in North America. At the country level, both the US and Canada acted as CH₄ sources to the atmosphere, but Mexico mainly oxidized and consumed CH₄ from the atmosphere. Wetlands in North America contributed predominantly to the regional CH₄ source, while all other ecosystems acted as sinks for atmospheric CH₄, of which forests accounted for 36.8%. Regarding N₂O emission in North America, the US, Canada, and Mexico contributed 56.19%, 18.23%, and 25.58%, respectively, to the continental source over the past 30 years. Forests and croplands were the two ecosystems that contributed most to continental N₂O emission. The inter-annual variations of CH₄ and N₂O fluxes in North America were mainly attributed to year-to-year climatic variability. While only annual precipitation was found to have a significant effect on annual CH₄ flux, both mean annual temperature and annual precipitation were significantly correlated to annual

N₂O flux. The regional estimates and spatiotemporal patterns of terrestrial ecosystem CH₄ and N₂O fluxes in North America generated in this study provide useful information for global change research and policy making.

1 Introduction

Methane (CH₄) and nitrous oxide (N₂O) are two potent greenhouse gases which in sum contribute to more than one fourth of global warming caused by anthropogenic activities (Forster et al., 2007). Although the concentrations of CH₄ and N₂O in the atmosphere are relatively low, their warming potentials are much higher than that of carbon dioxide (Denman et al., 2007). CH₄ and N₂O also play significant roles in ozone layer chemistry (Denman et al., 2007; Forster et al., 2007). Similar to the increase of atmospheric CO₂ concentration, the concentrations of these two gases dramatically increased since the Industrial Revolution (Forster et al., 2007; Tuet et al., 2007; Rigby et al., 2008). Although the importance of CH₄ and N₂O emissions in changing the Earth's climate has been recognized, scientific community has placed large emphasis on the CO₂ problem. Understanding and quantifying CH₄ and N₂O fluxes in terrestrial ecosystems at large spatial scales, therefore, becomes an urgent task for accurately predicting the future climate change (Rigby et al., 2008; Forster et al., 2007; Sheldon and Barnhart, 2009).

Terrestrial ecosystems could act as either sources or sinks for atmospheric CH₄ and N₂O, depending on the time and location (Liu, 1996; Potter, 1997; Ridgwell et al., 1999; Chapuis-Lardy et al., 2007; Xu et al., 2008). Globally, natural sources from terrestrial ecosystems contribute



Correspondence to: H. Tian
(tianhan@auburn.edu)

approximately 40% to the CH₄, and more than half to the N₂O releases to the atmosphere when removing oceanic contribution (Denman et al., 2007). North America, with its large land area and high proportion of natural wetland (approximately 30% of the global wetland) (Bridgham et al., 2006; Mitsch and Gosselink, 2007), plays a critical role in global carbon cycling (Schimel et al., 2000). However, only a few studies have investigated CH₄ and N₂O fluxes over terrestrial ecosystems in North America (Bridgham et al., 2006). For example, Zhuang et al. (2004) estimated that soils in Canada and Alaska emitted 7.1 and 3.8 Tg CH₄ a⁻¹, respectively, during the 1990s. Bridgham et al. (2006) estimated that CH₄ emission in North America's wetlands is 9 Tg CH₄ a⁻¹. Using a satellite-derived modeling approach, Potter et al. (2006) estimated that the CH₄ emission from the natural wetlands in the conterminous US is 5.5 Tg CH₄ a⁻¹. Several studies also reported the fluxes of N₂O in terrestrial ecosystems at global and regional scales using empirical approaches (Xu et al., 2008). While these studies improved our understanding of CH₄ and N₂O fluxes in North America, accurate estimations of terrestrial ecosystem CH₄ and N₂O fluxes in the entire continent over a long time period are still needed (Wofsy and Harriss, 2002).

Many factors can influence CH₄ and N₂O fluxes in terrestrial ecosystems at site and regional levels, such as elevated CO₂ (Hutchin et al., 1995; Schroppe et al., 1999; Phillips et al., 2001a, 2001b), tropospheric ozone pollution (Morsky et al., 2008), nitrogen input (Ding et al., 2004), climate change (Goldberg and Gebauer, 2009) and land cover change (Willison et al., 1995; Huang et al., 2010). However, most previous process-based modeling efforts did not take into account the concurrent effects of multiple global change factors (Potter, 1997; Cao et al., 1998; Walter et al., 2001; Zhuang et al., 2007, 2004). Large uncertainty still exists in the magnitudes, spatial and temporal patterns of CH₄ and N₂O fluxes at large scales (Kort et al., 2008; Christensen et al., 1996; Zhuang et al., 2004; Bridgham et al., 2006; Potter et al., 2006).

Recently, we developed a process-based biogeochemistry model, the Dynamic Land Ecosystem Model (DLEM), to simulate biogeochemical cycling of carbon, nitrogen and water in the land ecosystems. The DLEM considers multiple factors including climate, atmospheric compositions (CO₂, O₃), precipitation chemistry (nitrogen composition), natural disturbances (fire, insect/disease, hurricane, etc), land-use/land-cover change, and land management (harvest, rotation, fertilization, irrigation, etc.) (Tian et al., 2005, 2008, 2010; Ren et al., 2007a, 2007b, 2009; Zhang et al., 2007, 2008; Lu, 2009; Liu et al., 2008; Chen et al., 2006; Xu, 2010). This model has been successfully applied to simulate the effects of multiple environmental factors on carbon and water cycles in China (Ren et al., 2007a, 2007b; Lu, 2009; Liu et al., 2008; Chen et al., 2006; Xu, 2010) and USA (Tian et al., 2008, 2010; Zhang et al., 2007, 2008).

In this study, we enhanced the model's capability by addressing the biogeochemical processes of CH₄ and N₂O and

simulated CH₄ and N₂O fluxes over terrestrial ecosystems in North America from 1979 to 2008. The objectives of this study are: (1) to develop the CH₄ and N₂O modules in the framework of an extant process-based model, DLEM; (2) to compare modeled results with field observations and other regional estimates; (3) to estimate CH₄ and N₂O fluxes in North America's terrestrial ecosystems from 1979 to 2008; and (4) to quantify the contributions of individual countries and biomes to regional CH₄ and N₂O fluxes in North America.

2 Methodology

2.1 The DLEM model and its trace gas modules

The Dynamic Land Ecosystem Model (DLEM) couples major biogeochemical cycles, hydrological cycles, and vegetation dynamics to make daily, spatially-explicit estimates of carbon, nitrogen, and water fluxes and pool sizes (C and N) in terrestrial ecosystems. There are five core components in the DLEM: (1) biophysics, (2) plant physiology, (3) soil biogeochemistry, (4) dynamic vegetation, and (5) disturbance, land use and management. Briefly, the biophysics component simulates the instantaneous fluxes of energy, water, and momentum within land ecosystems and their exchanges with the surrounding environment. The plant physiology component simulates major physiological processes, such as plant phenology, C and N assimilation, respiration, allocation, and turnover. The soil biogeochemistry component simulates the dynamics of nutrient compositions and major microbial processes. The biogeochemical processes, including the nutrient mineralization/immobilization, nitrification/denitrification, decomposition, and methane production/oxidation are considered in this component. The dynamic vegetation component simulates the structural dynamics of vegetation caused by natural and human disturbances. Two processes are considered: the biogeography redistribution when climate change occurs, and the recovery and succession of vegetation after disturbances. Like most dynamic global vegetation models, the DLEM builds on the concept of plant functional types (PFT) to describe vegetation attributes. The disturbances, land use and management component simulates cropland conversion, reforestation after cropland abandonment, and forest management practices such as harvest, thinning, fertilization and prescribed fires.

The interactions and feedbacks of various processes among core components are simulated as controls or material flows (Fig. 1). The biophysics component yields influences on plant physiology component through the effects of water, temperature and radiation, and on soil biogeochemistry component through the effects of soil moisture and temperature; the plant physiology component yields influences on the biophysics component through changes in leaf area index (LAI), canopy conductance, and transpiration, on the soil

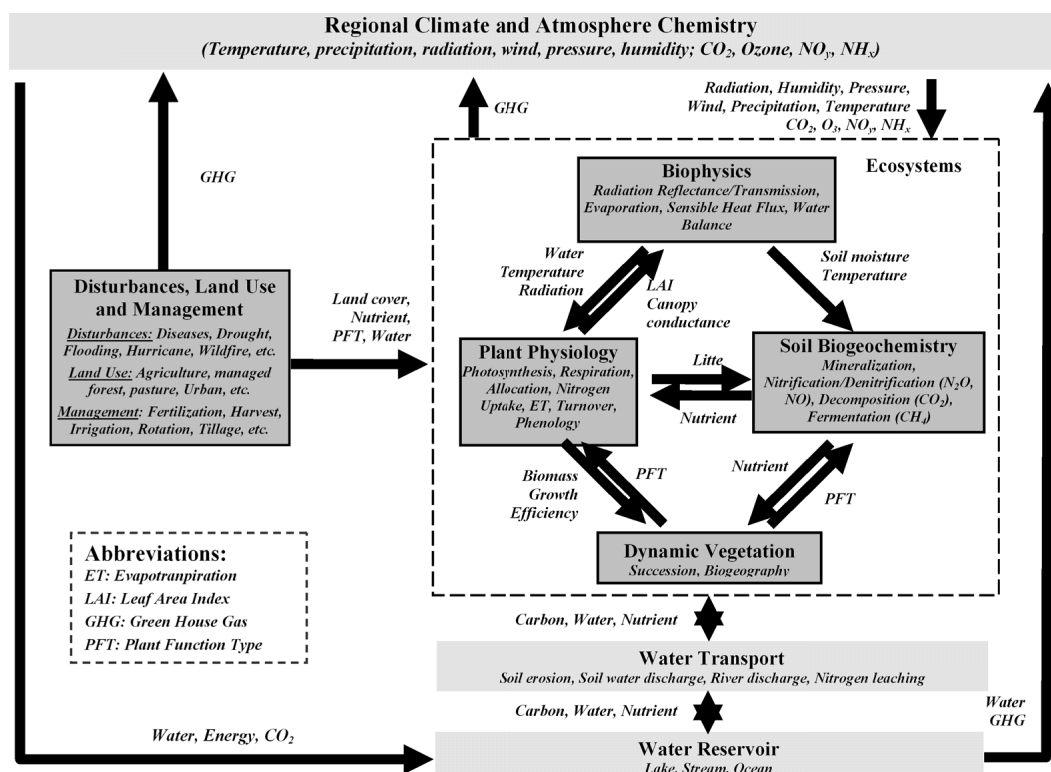


Fig. 1. Conceptual model of the Dynamic Land Ecosystem Model (DLEM) (Five core components are included in the DLEM).

biogeochemistry component through litter-fall, and on the dynamic vegetation component through biomass growth; the dynamic vegetation component yields influences on the plant physiology and soil biogeochemistry components through shifts of plant function type (PFT); the soil biogeochemistry component yields influences on the dynamics vegetation and plant physiology components through nutrient flow; disturbances, land use and management component yields influences on the other four components through changes in land cover type, PFT and nutrient and water flow (Fig. 1).

Meanwhile, the DLEM uses climate data from regional climate and atmosphere chemistry component which could be a climate model or input data. The DLEM outputs including ecosystem carbon and nitrogen pools and fluxes (e.g. greenhouse gases) will enter the atmosphere; and the water output and associated nutrients from the DLEM will enter water transport module and flow into lake, river and ocean. All the components are also linked together by water and energy fluxes (Fig. 1).

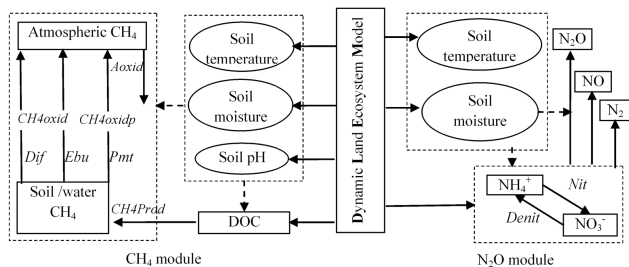
The DLEM emphasizes the modeling and simulation of managed ecosystems including agricultural ecosystems, plantation forests and pastures. The spatial data sets of land management, such as irrigation, fertilization, rotation, and harvest can be used as input information for simulating influences of land management on the structure and functioning of ecosystems. This model has been calibrated

against various field data from US Long-Term Ecological Research (LTER) network, AmeriFlux network, and the Chinese Ecological Research Network (CERN) which cover various ecosystems, including forests, grasslands, shrub, tundra, desert, wetland, and croplands. The major carbon, nitrogen and water variables have been validated with observational data. The simulated results have been compared with independent field data and satellite products. The DLEM operates at a daily time step and at varied spatial resolutions, from meters to kilometers, from regional to global. The additional information on the processes, interactions and feedbacks in the DLEM and associated input/output data (Fig. 1) can be found in our previous studies (Tian et al., 2005, 2008, 2010; Ren et al., 2007a, 2007b, 2009; Zhang et al., 2007, 2008; Lu, 2009; Liu et al., 2008; Chen et al., 2006).

In this paper, we provide a detailed description of the CH₄ and N₂O modules with an emphasis on major processes that control fluxes of CH₄ and N₂O in terrestrial ecosystems (Fig. 2).

2.1.1 The CH₄ module

The CH₄ exchanges between ecosystems and the atmosphere are a combination of CH₄ production, oxidation, and transportation from soil pore water to the atmosphere. The DLEM only considers CH₄ production from dissolved



Major processes: *Aoxid*: Atmospheric CH₄ oxidation; *CH4prod*: CH₄ production; *CH4oxid*: CH₄ Oxidation during diffusion and ebullition transport; *CH4oxidp*: CH₄ oxidation during plant-mediated transport (Occur in herbaceous wetland only); *Dif*: CH₄ diffusion transport; *Ebu*: CH₄ ebullition transport; *Pmt*: Plant-mediated transport of CH₄; (Occur in herbaceous wetland only); *Nit*: Nitrification; *Denit*: Denitrification;

DLEM provides the environment factors and substrate for CH₄ and N₂O modules; the environmental controls were shown as dash lines.

Fig. 2. Modules of CH₄ and N₂O in the Dynamic Land Ecosystem Model (DLEM) (CH₄ production, oxidation, and transport are considered in the CH₄ module; nitrification and denitrification are considered in the N₂O module).

organic carbon (DOC), which is indirectly controlled by environmental factors including soil pH, temperature and soil moisture content. The production of DOC mainly comes from two sources: allocation of gross primary production (GPP) and decomposition of litter-fall and soil organic matter. The accumulated DOC is either used as substrate for methane, leaves system as leachate, or enters the atmosphere as CO₂ via decomposition. CH₄ oxidation, including the oxidation during CH₄ transport to the atmosphere, CH₄ oxidation in the soil pore water, and atmospheric CH₄ oxidation on the soil surface, is determined by CH₄ concentrations in the air or soil pore water, as well as soil moisture, pH, and temperature. Most CH₄-related biogeochemical reactions in the DLEM are described by using the Michaelis-Menten equation with two coefficients: maximum reaction rate and half saturation coefficient. Three pathways for CH₄ transport from soil to the atmosphere include ebullition, diffusion, and plant-mediated transport. It is assumed that methane-related biogeochemical processes only occur in the top 50 cm of soil profile. The net CH₄ flux between the atmosphere and soil is determined by the following equation:

$$F_{\text{CH}_4} = F_P + F_D + F_E - F_{\text{air, oxid}} - F_{\text{trans, oxid}} \quad (1)$$

where F_{CH_4} is the flux of CH₄ between soil and the atmosphere ($\text{g C m}^{-2} \text{d}^{-1}$); F_P is plant-mediated transport from soil pore water to the atmosphere ($\text{g C m}^{-2} \text{d}^{-1}$); F_D is the diffusive flux of CH₄ from water surface to the atmosphere ($\text{g C m}^{-2} \text{d}^{-1}$); F_E is the ebullitive CH₄ emission to the atmosphere; $F_{\text{air, oxid}}$ is the rate of atmospheric methane oxidation ($\text{g C m}^{-2} \text{d}^{-1}$); $F_{\text{trans, oxid}}$ is the oxidized CH₄ during plant-mediated transport ($\text{g C m}^{-2} \text{d}^{-1}$).

The concentration of CH₄ in the soil pore water was governed by the following equations:

$$\begin{aligned} \frac{d[\text{CH}_4]}{dt} &= f([\text{CH}_4]) \\ &= \text{CH}_{4\text{prod}} - \frac{F_P}{H} - \frac{F_D}{H} - \frac{F_E}{H} - \text{CH}_{4\text{soil, oxid}} \end{aligned} \quad (2)$$

where [CH₄] is the concentration of CH₄ in water (g C m^{-3}); CH_{4prod} is the production of CH₄ in soil pore water ($\text{g C m}^{-3} \text{d}^{-1}$); CH_{4soil, oxid} is the oxidation rate of CH₄ in soil pore water ($\text{g C m}^{-3} \text{d}^{-1}$); H is the soil depth of the first layer for methane production and oxidation.

CH₄ production

The production of CH₄ in soil pore water is controlled by the concentration of DOC and environmental factors (Eq. 2),

$$\begin{aligned} \text{CH}_{4\text{prod}} &= V_{\text{prod, max}} \times \frac{[\text{DOC}]}{[\text{DOC}] + K_{m\text{prod}}} \\ &\times f(T_{\text{soil}}) \times f(\text{pH}) \times f_{\text{prod}}(\text{vwc}) \end{aligned} \quad (3)$$

where $V_{\text{prod, max}}$ is the maximum rate of CH₄ production ($\text{g C m}^{-3} \text{d}^{-1}$), [DOC] is the concentration of DOC (g C m^{-3}); $K_{m\text{prod}}$ is the half-saturation coefficient of CH₄ production (g C m^{-3}); $f(T_{\text{soil}})$ is a multiplier that describes the effect of soil temperature on CH₄ production and oxidation; $f(\text{pH})$ is a multiplier that describes the effect of soil pH on CH₄ production and oxidation; $f_{\text{prod}}(\text{vwc})$ is a multiplier that describes the effect of soil moisture on CH₄ production.

CH₄ oxidation

Three pathways are considered in the DLEM for CH₄ oxidation: (1) atmospheric CH₄ oxidation, also called the diffusion processes of CH₄ from the atmosphere to the soil pore water, mainly simulates the oxidation of atmospheric CH₄ in the soil pore water; (2) the process of CH₄ oxidation in the soil pore water mainly simulates the oxidation of CH₄ which is dissolved in water or accumulated in soil porosity; and (3) the process of CH₄ oxidation occurs during the plant-mediated transport of CH₄ from soil pore water to the atmosphere. The DLEM assumes that the process of CH₄ oxidation in soil pore water includes the CH₄ oxidation during ebullition and diffusion because these two processes only occur in water.

Atmospheric CH₄ oxidation

Oxidation of atmospheric CH₄ is estimated as:

$$\begin{aligned} F_{\text{air, oxid}} &= V_{\text{air, oxid, max}} \times \frac{[\text{Atm CH}_4]}{[\text{Atm CH}_4] + K_{m\text{air, oxid}}} \\ &\times f(T_{\text{soil}}) \times f(\text{pH}) \times f_{\text{oxid}}(\text{vwc}) \end{aligned} \quad (4)$$

where $V_{\text{air, oxid, max}}$ is the maximum oxidation rate of atmospheric CH₄ ($\text{g C m}^{-2} \text{d}^{-1}$); $k_{m\text{air, oxid}}$ is the half saturation coefficient of atmospheric CH₄ oxidation (g C m^{-3});

[Atm CH₄] is the atmospheric CH₄ concentration (g C m⁻³); $f_{\text{oxid}}(\text{vwc})$ is a multiplier that describes the effect of soil moisture on atmospheric CH₄ oxidation. Because the atmospheric CH₄ oxidation is mainly carried out by soil methanotrophy, and low soil organic matter means lower soil microbial biomass (Conrad, 1996), the DLEM assumes that there is no atmospheric CH₄ oxidation when soil organic matter is less than 10 g C m⁻².

CH₄ oxidation during plant-mediated transport

During the process of plant-mediated CH₄ transport from soil to the atmosphere, portions of CH₄ will be oxidized at the rate of:

$$F_{\text{trans, oxid}} = \min \left(V_{\text{trans, oxid, max}} \times \frac{F_{\text{P}}}{F_{\text{P}} + Km_{\text{trans, oxid}}} \times f(T_{\text{air}}), F_{\text{P}} \right) \quad (5)$$

where $F_{\text{trans, oxid}}$ is the oxidation rate of CH₄ during plant-mediated transport (g C m⁻² d⁻¹); $V_{\text{trans, oxid, max}}$ is the maximum rate of CH₄ oxidation (g C m⁻² d⁻¹); $Km_{\text{trans, oxid}}$ is the half saturation coefficient of soil CH₄ oxidation during transportation (g C m⁻²); T_{air} is the air temperature; $f(T_{\text{air}})$ is a multiplier that represents the effect of air temperature on the oxidation of CH₄ during plant-mediated transport.

Soil pore water CH₄ oxidation

The accumulated CH₄ in soil pore water is oxidized at the rate of:

$$\text{CH}_{4\text{soil, oxid}} = \min \left(V_{\text{soil, oxid, max}} \times \frac{[\text{CH}_4]}{[\text{CH}_4] + Km_{\text{soil, oxid}}} \times f(T_{\text{soil}}) \times f(\text{pH}) \times f_{\text{oxid}}(\text{vwc}), [\text{CH}_4] \right) \quad (6)$$

where $V_{\text{soil, oxid, max}}$ and $Km_{\text{soil, oxid}}$ are maximum soil pore water CH₄ oxidation rate (g C m⁻³ d⁻¹) and half saturation coefficient of CH₄ oxidation in soil pore water (g C m⁻³), respectively; $[\text{CH}_4]$ is the concentration of CH₄ in soil pore water (g C m⁻³).

CH₄ transport

In this model, ebullition, diffusion and plant-mediated transport, are considered the three pathways by which CH₄ can be transported from soil pore water to the atmosphere.

Ebullition

The ebullition transport of CH₄ from water to the atmosphere is estimated as:

$$F_{\text{E}} = \max ([\text{CH}_4] - 6, 0) \times H \quad (7)$$

where F_{E} is the flux of CH₄ from water to the atmosphere via ebullition (g C m⁻² d⁻¹); 6 is the threshold value above

which the dissolved CH₄ will form bubbles and leave water (g C m⁻³), and is equals to 0.5 mol CH₄ m⁻³ (Walter et al., 2001). Because this process occurs in very short time (Walter et al., 2001; Zhuang et al., 2004), the DLEM assumes that all the dissolved CH₄ above this threshold value will leave water via bubbles in one day.

Plant-mediated transport

The plant-mediated CH₄ emission from water to the atmosphere is estimated as:

$$F_{\text{P}} = V_{\text{plant, trans}} \times ([\text{CH}_4] - [\text{CH}_4]_{\text{max}}) \times \min \left(\frac{\text{GPP}}{\text{GPP}_{\text{max}}}, 1 \right) \quad (8)$$

$$[\text{CH}_4]_{\text{max}} = [\text{Atm CH}_4] \times \beta \quad (9)$$

where F_{P} is the CH₄ transport via vascular plant (g C m⁻² d⁻¹); $V_{\text{plant, trans}}$ is the transport coefficient of CH₄ transportation through plant (m d⁻¹), which is set as 0.68 (Kettunen, 2003); $[\text{CH}_4]_{\text{max}}$ is the maximum CH₄ concentration in soil solution (g C m⁻³); GPP is the gross primary productivity of current day (g C m⁻² d⁻¹); GPP_{max} is the maximum daily GPP (g C m⁻² d⁻¹), which is set as 5 in this study; β is the Bunsen solubility coefficient (0.035 ml ml⁻¹) (Yamamoto et al., 1976). Since there is no report on the plant-mediated transport of CH₄ by woody plant, the DLEM assumes that the plant-mediated transport only occurs in herbaceous biomes; F_{P} is set to zero for all woody ecosystems.

Diffusion

The DLEM treats the top 0.5 m of the soil profile as one layer, and the CH₄ generated under water's surface is assumed to have a fast diffusion rate to water's surface. The diffusion estimated here is the exchange of CH₄ between the water surface and the atmosphere.

$$F_{\text{D}} = V_{\text{exchange}} \times ([\text{CH}_4] - [\text{CH}_4]_{\text{max}}) \quad (10)$$

where V_{exchange} is the exchange coefficient of CH₄ through the interface of soil pore water and the atmosphere (m d⁻¹); it is set as 0.3 m d⁻¹ (Happell and Chanton, 1995).

Environmental factors affecting methane processes

To simulate the environmental effects on methane production, oxidation and transport, the DLEM considers three environmental factors: soil pH, soil moisture, and temperature. These three factors have been considered as the most important external factors on CH₄ production, consumption, and transport (Cao et al., 1995; Huang et al., 1998; Mer and Roger, 2001; Zhuang et al., 2004). The line graphs showing the environmental controls on CH₄ production and consumption could be found in the Fig. 3.

In the DLEM, the effect of soil pH on methane production and oxidation ($f(\text{pH})$) is calculated as a bell shape curve,

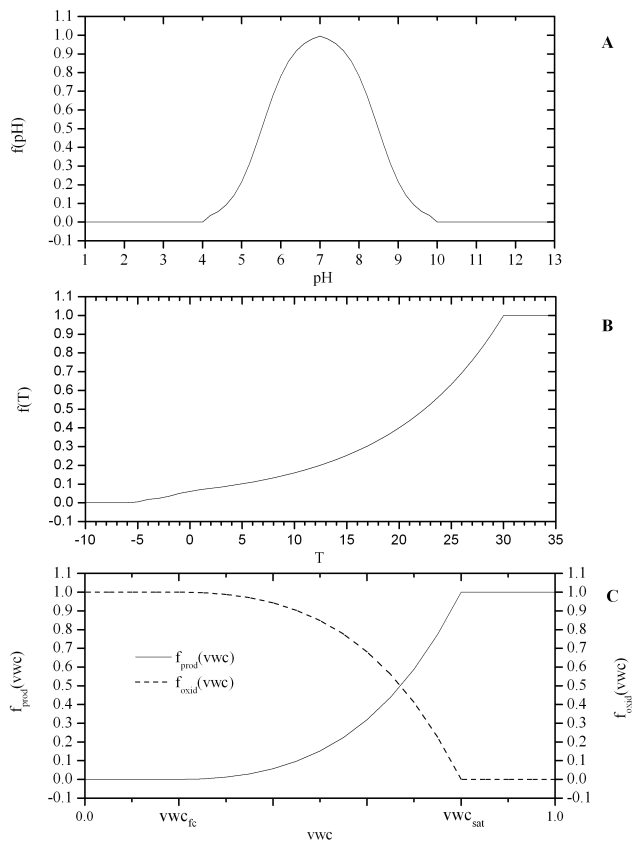


Fig. 3. Graphs showing environmental effects on methane production and oxidation – (A) pH effects; (B) Temperature effect; (C) Moisture effects on methane production and oxidation.

following Cao et al. (1995) and Zhuang et al. (2004). Given that a number of reports showing CH₄ production and consumption at the circumstances of pH < 5 or pH > 9 (Amaral et al., 1998; Mer and Roger, 2001; Sorokin et al., 2000), we set the effects of soil pH on CH₄ production and oxidation to zero when soil pH is smaller than 4 or larger than 10 (Eq. 11), which is different from Zhuang et al. (2004) and Cao et al. (1995).

$$f(\text{pH}) = \begin{cases} 0 & \text{pH} \leq 4.0 \text{ or } \text{pH} \geq 10.0 \\ \frac{1.02}{1 + 1\,000\,000 \times e^{(-2.5 \times \text{pH})}} & 4.0 < \text{pH} < 7.0 \\ \frac{1.02}{1 + 1\,000\,000 \times e^{(-2.5 \times (14.0 - \text{pH}))}} & 7.0 < \text{pH} < 10.0 \end{cases} \quad (11)$$

where pH is the pH value of the soil profile.

The effect of temperature on methane processes ($f(T)$) is estimated by Q_{10} response curve which has been used by Huang et al. (1998). The difference between our model and Huang et al.'s (1998) model is that we set the Q_{10} as 2.5 (Song et al., 2009), rather than 3.

$$f(T) = \begin{cases} 0.0 & T < -5 \\ Q_{10}^{\frac{T-30}{10}} & -5 < T < 30 \\ 1 & T \geq 30 \end{cases} \quad (12)$$

where Q_{10} is a scalar for the temperature sensitivity; T is temperature of soil or air.

The effect of soil moisture on methane processes is estimated based on the volumetric water content in the top soil layer (50 cm). Methane production and methane oxidation have reciprocal responsive curves to soil moisture.

$$f_{\text{prod}}(\text{vwc}) = \begin{cases} 0 & \text{vwc} \leq \text{vwc}_{\text{fc}} \\ \left(\frac{\text{vwc} - \text{vwc}_{\text{fc}}}{\text{vwc}_{\text{sat}} - \text{vwc}_{\text{fc}}} \right)^2 \times 0.368 \times e^{\left(\frac{\text{vwc} - \text{vwc}_{\text{fc}}}{\text{vwc}_{\text{sat}} - \text{vwc}_{\text{fc}}} \right)} & \text{vwc}_{\text{fc}} < \text{vwc} < \text{vwc}_{\text{sat}} \\ 1 & \text{vwc} \geq \text{vwc}_{\text{sat}} \end{cases} \quad (13)$$

$$f_{\text{oxid}}(\text{vwc}) = 1 - f_{\text{prod}}(\text{vwc}) \quad (14)$$

where vwc is the volumetric water content of the top soil layer; vwc_{fc} is the field capacity and vwc_{sat} is the saturated water content. It is assumed that when the soil water content of an upland ecosystem is greater than field capacity, the extra water will percolate or leave the system as base-flow so that soil moisture is always under saturation.

2.1.2 The N₂O module

In the DLEM, both denitrification and nitrification processes are simulated as one-step process because we do not consider the mid-products in each process.

Nitrification

Nitrification, a process converting ammonium into nitrate, is simulated as a function of soil temperature, moisture, and soil NH₄⁺ concentration (Lin et al., 2000).

$$N_{\text{nit}} = \min(N_{\text{pot, nit}}, N_{\text{NH}_4}) \quad (15)$$

$$N_{\text{pot, nit}} = V_{\text{nit, max}} \times \frac{N_{\text{NH}_4}}{N_{\text{NH}_4} + Km_{\text{nit}}} \times f_{\text{nit}}(T_{\text{soil}}) \times f_{\text{nit}}(\text{vwc}) \quad (16)$$

$$f_{\text{nit}}(T_{\text{soil}}) = Q_{10_{\text{nit}}}^{\left(\frac{T_{\text{soil}} - T_{\text{opt, nit}}}{10} \right)} \quad (17)$$

$$f_{\text{nit}}(\text{vwc}) = \begin{cases} 1.17 \times \frac{\text{vwc}}{\text{vwc}_{\text{fc}}} + 0.165 & \text{vwc} < \text{vwc}_{\text{fc}} \\ 1 - 0.1 \times \frac{\text{vwc}}{\text{vwc}_{\text{fc}}} & \text{vwc} \geq \text{vwc}_{\text{fc}} \end{cases} \quad (18)$$

where N_{nit} is the nitrification rate (g N m⁻³ d⁻¹); $N_{\text{pot, nit}}$ is the potential nitrification rate (g N m⁻³ d⁻¹); N_{NH_4} is the concentration of NH₄⁺ in the soil (g N m⁻³); $V_{\text{nit, max}}$ is a parameter describing potential nitrification rate without limitation (g N m⁻³ d⁻¹); Km_{nit} is the half-saturation concentration of soil NH₄⁺ for the maximum nitrification rate (g N m⁻³); $f_{\text{nit}}(T_{\text{soil}})$ is a multiplier that describes the effect of soil temperature on nitrification; T_{soil} is the soil temperature (°C); $f_{\text{nit}}(\text{vwc})$ is a multiplier that describes the effect of water content on nitrification (Lin et al., 2000; Riedo et al., 1998); $Q_{10, \text{nit}}$ is the temperature sensitivity of nitrification, which

is set as 2; $T_{\text{opt, nit}}$ is the optimum temperature for nitrification, which is set as 20 °C following Riedo et al. (1998) and Lin et al. (2000); vwc is the volumetric water content; and vwc_{fc} is the soil field capacity.

Denitrification

Denitrification, through which the nitrate is converted into nitrogen gas, is simulated in the DLEM as a function of soil temperature, moisture, and soil NO₃⁻ concentration (Lin et al., 2000).

$$N_{\text{denit}} = \min(N_{\text{pot, denit}}, N_{\text{NO}_3}) \quad (19)$$

$$N_{\text{pot, denit}} = V_{\text{denit, max}} \times \frac{N_{\text{NO}_3}}{N_{\text{NO}_3} + Km_{\text{denit}}} \times f_{\text{denit}}(T_{\text{soil}}) \times f_{\text{denit}}(\text{vwc}) \quad (20)$$

$$f_{\text{denit}}(T_{\text{soil}}) = Q_{10, \text{denit}}^{\frac{T_{\text{soil}} - T_{\text{opt, denit}}}{10}} \quad (21)$$

$$f_{\text{denit}}(\text{vwc}) = \begin{cases} 0.0 & \text{vwc} < \text{vwc}_{\text{fc}} \\ \frac{\text{vwc}}{\text{vwc}_{\text{fc}}} & \text{vwc} \geq \text{vwc}_{\text{fc}} \end{cases} \quad (22)$$

where N_{denit} is the denitrification rate ($\text{g N m}^{-3} \text{d}^{-1}$); $N_{\text{pot, denit}}$ is the potential nitrification rate ($\text{g N m}^{-3} \text{d}^{-1}$); N_{NO_3} is the concentration of NO₃⁻ in the soil (g N m^{-3}); $V_{\text{denit, max}}$ is a parameter describing potential denitrification rate without limitation ($\text{g N m}^{-3} \text{d}^{-1}$); Km_{denit} is the half-saturation concentration of soil NO₃⁻ for the maximum denitrification rate (g N m^{-3}); $f_{\text{denit}}(T_{\text{soil}})$ is a multiplier that describes the effect of soil temperature on denitrification; $f_{\text{denit}}(\text{vwc})$ is a multiplier that describes the effect of water content on denitrification (Lin et al., 2000; Riedo et al., 1998); $Q_{10, \text{denit}}$ is the temperature sensitivity of denitrification, which is set as 3; and $T_{\text{opt, denit}}$ is the optimum temperature for denitrification, which is set as 25 °C following Lin et al. (2000).

N₂O emission

All the products of nitrification and denitrification are nitrogen-containing gases. The empirical equation reported by Davidson et al. (2000) is used to separate N₂O from other gases (mainly NO and N₂).

$$F_{\text{NO}_2} = (0.001 \times N_{\text{nitrif}} + N_{\text{denitrif}}) \times \frac{10^{\text{vwc}/\emptyset \times 0.026 - 1.66}}{(1 + 10^{\text{vwc}/\emptyset \times 0.026 - 1.66})} \quad (23)$$

where $F_{\text{N}_2\text{O}}$ is the fluxes of N₂O from soil to the atmosphere ($\text{g N m}^{-3} \text{d}^{-1}$), 0.001 is the proportion of nitrification product released as gaseous nitrogen (Lin et al., 2000), and it is converted to fluxes in the unit area ($\text{g N m}^{-2} \text{d}^{-1}$) by multiplying the depth of the first soil layer (0.5 m); \emptyset is the soil porosity.

2.2 Input data preparation, model initialization and simulation

We developed gridded (32 km × 32 km), geo-referenced, time-series input data sets of climate (including daily temperature, precipitation, humidity, and solar radiation), annual nitrogen deposition rate, annual land-cover change and land management practices (including fertilization, irrigation) for the entire North America (including Canada, the US, and Mexico). The climate dataset was generated based on North American Regional Reanalysis (NARR) dataset (http://nomads.nccdc.noaa.gov/data.php?name=access#narr_datasets). The maximum, minimum and average temperatures were calculated based on the eight 3-h average in one day. Precipitation, solar radiation, and relative humidity were directly derived from the NARR dataset. Land-use and land-cover change data were extracted from a global data set developed by History Database of the Global Environment (HYDE 3). Ozone data was retrieved from the global dataset developed by Felzer et al. (2005) covering 1900–2050. Annual nitrogen deposition data were retrieved from a global data set that was extrapolated from a three yearly maps (Dentener et al., 2006). Soil properties data, including soil texture, soil pH, soil bulk density, were extracted from a global data set Global Soil Data Task posted online in the Oak Ridge National Laboratory (daac.ornl.gov). Fertilization data for North America was developed by combining several data sources, including Food and Agriculture Organization (FAO) country-level data (www.fao.org), US county-level data (www.usda.gov), and Canada provincial-level data source (www.cfi.ca). All the datasets were transformed and re-projected to a consistent projection system for driving the DLEM model. The annual atmospheric concentration of CO₂ before 1959 was estimated by VEMAP (The Vegetation/Ecosystem Modeling and Analysis Project), and the data after 1959 were provided by National Oceanic and Atmospheric Administration (NOAA) (www.esrl.noaa.gov). The distributional map of contemporary vegetation types (Fig. 4) was developed using different sources of data, including global land-cover derived from Landsat imagery (De Fries et al., 1998), National Land Cover Dataset 2000 (www.usgs.gov), and global database of lakes, reservoirs and wetland (Lehner and Döll, 2004). It is assumed that the ice-covered land is not capable of producing or taking up CH₄ and N₂O, and thus was not considered in present simulation.

The implementation of DLEM simulation includes the following runs: (1) equilibrium run, (2) spinning-up run and (3) transient run. In this study, we used potential vegetation, long-term mean climate during 1979–2008, the concentration levels of nitrogen deposition, ozone, atmospheric CO₂ in the year 1900 to drive the model run to an equilibrium state (i.e. the inter-annual variations are < 1 g m⁻² for carbon storage, < 0.1 g m⁻² for nitrogen storage). After the system reaches equilibrium state, the model was run with an addition of cropland and urban areas for another 3000 years for

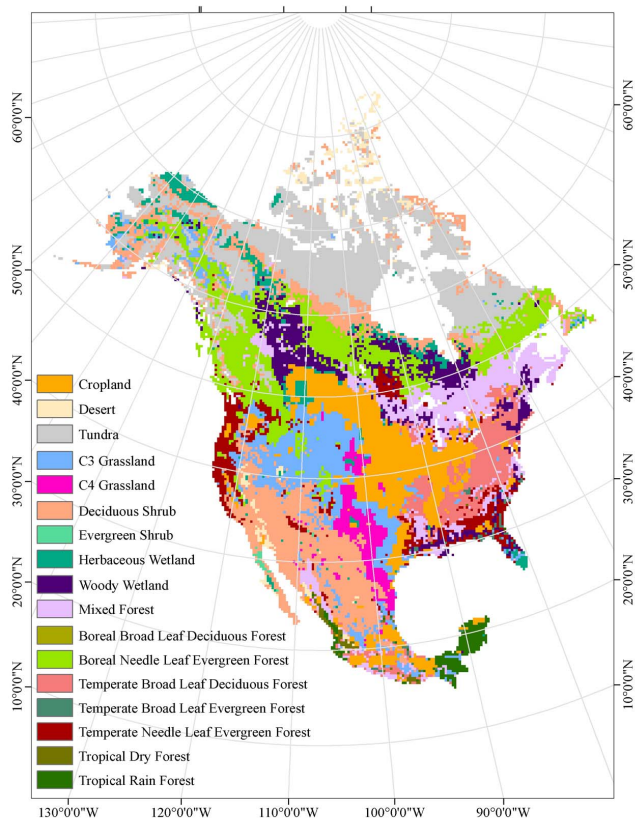


Fig. 4. Contemporary vegetation map used in this study (The year 2000 is shown).

spinning-up purposes. Finally, the model was run in transient mode with daily climate data, annual CO₂ concentration and nitrogen deposition inputs from 1901 to 2008 to simulate CH₄ and N₂O fluxes. The annual climate data between 1901 and 1978 were developed by randomly assigning a year between 1979 and 2008. Only the outputs between 1979 and 2008 were analyzed to show the spatial and temporal patterns of CH₄ and N₂O fluxes in North America's terrestrial ecosystems. Similar to other terrestrial biosphere models (McGuire et al., 2001), urban is treated as grassland.

2.3 Model parameterization

In this study, we used Bayesian calibration for model parameterization, which is to determine the optimal value for each parameter in the CH₄ and N₂O modules. A set of major parameters related to CH₄ and N₂O processes were listed with their prior values for simulation (Table 1). Based on these prior parameters and measured site-level fluxes of CH₄ (Table 2) and N₂O (Table 3), we used Monte Carlo method to find the optimal value for each parameter (Robert and Casella, 2005; Ricciuto et al., 2008). The parameters that give the best fit to the observational fluxes were considered as the optimal parameters and used for the regional simulation.

Because the site-level climatic data are not always available, we retrieved the site-level data from our regional dataset. We used measurement data of CH₄ and N₂O fluxes from field sites outside North America if the site-specific data of these fluxes for a specific ecosystem type are not available in North America. The sites chosen for model parameterization included 20 sites for CH₄ fluxes (Table 2), and 18 sites for N₂O fluxes (Table 3). Finally, a suite of parameters (eight for CH₄ module, and four for N₂O module) for each plant functional type were identified for regional model simulation (Tables 4 and 5).

2.4 Model verification

Two forest sites (Durham forest and Hubbard Brook forest) and two wetland sites (Alaska wetland and Sallie's fen) not used in model parameterization were selected for site-level model verification (Fig. 5). We obtained the observational flux data from various sources including The US Trace Gas Network (TRAGNET) online dataset (<http://www.nrel.colostate.edu/projects/tragnet/>), field observations in Hubbard Brook forest by Groffman et al. (2006, 2009) and Sallie's fen (P. Crill, personal communication, 2008). Four simulations for CH₄ and one for N₂O showed that model results are significantly correlated with observational data even though the DLEM model underestimated some fluxes (Fig. 5a–e). While the general seasonal patterns of CH₄ flux at these sites were consistent with the observations, the DLEM model did not capture a few CH₄ flux pulses during the peak growing season in the Sallie's fen (Fig. 5c), and underestimated CH₄ flux at Alaskan wetland site (Fig. 5b). For the N₂O flux, the DLEM model well captured the seasonal pattern and annual flux of N₂O in Hubbard Brook forest, but missed several spikes in observational data (Fig. 5e). This phenomenon of peak fluxes in CH₄ and N₂O has been observed in a number of field studies (Chapuis-Lardy et al., 2007; Song et al., 2009), but the underlying mechanisms still remain unknown.

The quantitatively point-to-point comparisons of the modeled and observed data also show that the DLEM captured the seasonal patterns of CH₄ and N₂O fluxes in terrestrial ecosystems at site level. The statistical results could be found in Fig. 5. Comparisons between CH₄ flux with soil temperature and precipitation indicate that the soil temperature is the major factor controlling CH₄ and N₂O fluxes at site-level. The soil temperature is negatively correlated with CH₄ uptake at Durham forest and Hubbard forest sites; while the precipitation events did cause some spikes in CH₄ emission (Fig. 5). For the Alaska wetland and Sallie's fen, temperature control on CH₄ emission was obvious, while the precipitation did not show apparent effects on CH₄ emission. For the N₂O emission, temperature effect was shown at seasonal scale, while the precipitation effect appeared at daily scale. This hierarchical control on N₂O emission was consistent with a field study (Brumme et al., 1999).

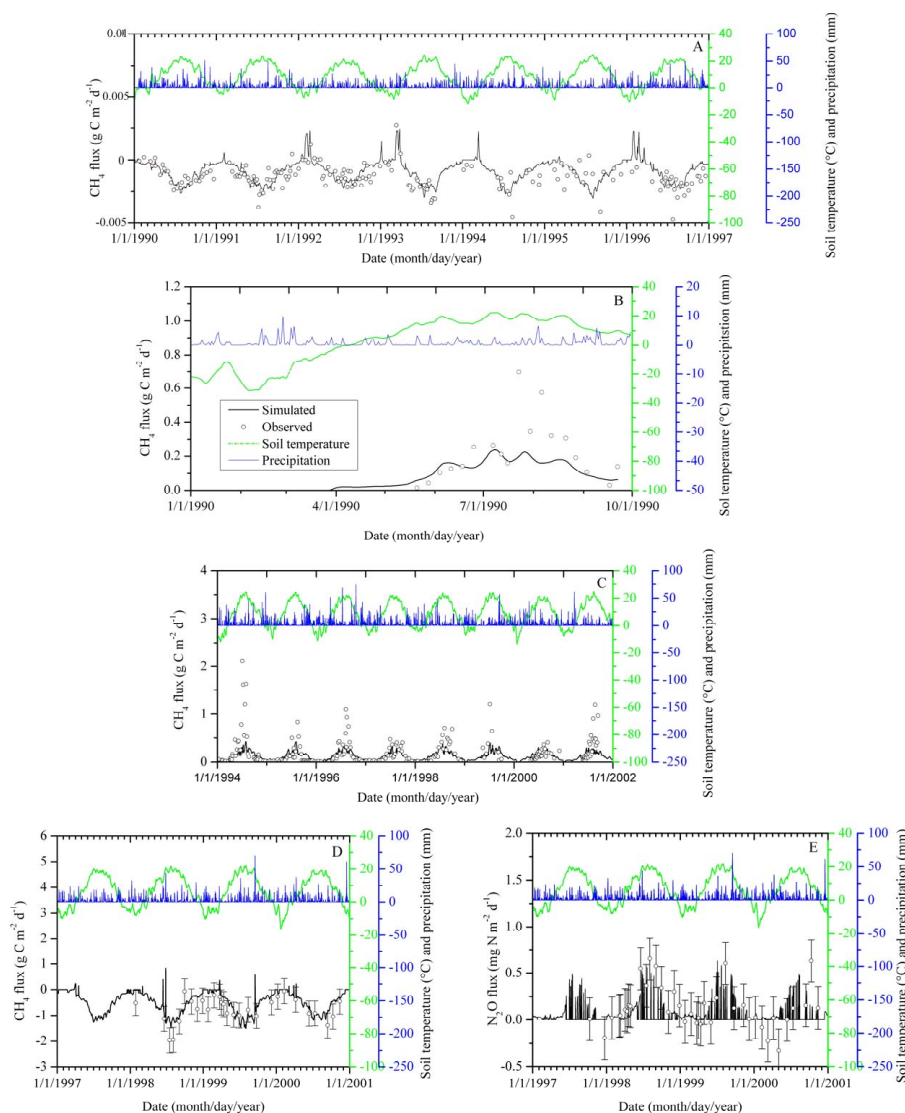


Fig. 5. Comparison of the DLEM-estimated CH₄ and N₂O fluxes with field observations – (A) CH₄ flux in Durham Forest (42° N, 73° W) (TRAGNET); (B) CH₄ flux in Alaska wetland (64.8° N, 147.7° W) (TRAGNET); (C) CH₄ flux in Sallie's fen (43.21° N, 71.05° W); (D) CH₄ flux in Hubbard Brook Forest (43.95° N, 71.74° W) (Groffman et al., 2006, 2009); (E) N₂O flux in Hubbard Brook Forest (43.95° N, 71.74° W) (Groffman et al., 2006, 2009). The error bars in Fig. 4d and e represent the standard deviations of four or five replicated observations; the regression models for these five site-level validations are: Modeled = 0.9389 × observed, $r = 0.562$, $P < 0.001$ for (A); Modeled = 0.5882 × observed, $r = 0.628$, $P < 0.001$ for (B); Modeled = 0.8795 × observed, $r = 0.502$, $P < 0.001$ for (C) when fluxes higher than 1000 mg C m⁻² day⁻¹ were removed; Modeled = 0.7937 × observed, $r = 0.595$, $P < 0.001$ for (D); Modeled = 0.7042 × observed, $r = 0.633$, $P < 0.001$ for (E)

Although the reliability of simulated CH₄ and N₂O fluxes was shown as the comparison with observational data (Fig. 5), inconsistencies exist, i.e. the underestimation of CH₄ emission in Sallie's fen and simulated peak in CH₄ flux that were rarely shown in observational data for Durham forest (Fig. 5). For the simulated CH₄ peak while rarely shown in observations, it might be due to the low sampling frequency of field work. The underestimation of CH₄ emission in Sallie's fen might be due to either the external environmental

trigger which are not included in the model (Tokida et al., 2007; Shoemaker and Schrag 2010), or the contribution to CH₄ from the microbial mat systems during summer season (Shoemaker and Schrag, 2010).

Table 1. Prior estimates of the major parameters for methane and nitrous oxide modules in the Dynamics Land Ecosystem Model (DLEM).

Parameter	Category	Value	Range	Literature
$V_{\text{CH}_4\text{ProMax}}$ (g C m ⁻³ day ⁻¹)	Aerobic	0.0207	0.0033–0.1306	Segers, 1998
	Intermediate	0.4	0.0394–3.9418	Segers, 1998
	Anaerobic	0.75	0.0313–4.9624	Segers, 1998
$V_{\text{CH}_4\text{OxidairMax}}$ (g C m ⁻³ day ⁻¹)		0.10	< 0.001–103.7	Sitaula et al., 1995; Segers, 1998; Saari et al., 2004
$V_{\text{CH}_4\text{OxidtransMax}}$ (g C m ⁻³ day ⁻¹)		0.5	0–>51.84	Segers, 1998
$V_{\text{CH}_4\text{Oxidsoilmax}}$ (g C m ⁻³ day ⁻¹)		0.5	0–>51.84	Segers, 1998
$Km_{\text{CH}_4\text{Prod}}$ (g C m ⁻³)		10	1.68–91.2	Lokshina et al., 2001
$Km_{\text{CH}_4\text{Oxidair}}$ (ppm)		10	5–18	Nedwell and Watson, 1995; Arah and Stephen, 1998; Saari et al., 2004
$Km_{\text{CH}_4\text{Oxidtrans}}$ (g C m ⁻³)		5	0.33–19.95	Harrison, 1973; Joergensen, 1985; Linton and Buckee, 1977; Lamb and Garver, 1980; Nagai et al., 1973; O'Neill and Wilktnson, 1977; Ferenci et al., 1975
$Km_{\text{CH}_4\text{Oxidsoil}}$ (g C m ⁻³)		10	0.33–19.95	Ferenci et al., 1975; Nagai et al., 1973; Linton and Buckee, 1977; Lamb and Garver, 1980; Joergensen, 1985; Harrison, 1973; O'Neill and Wilktnson, 1977
$V_{\text{max, denit}}$ (g N m ⁻³ day ⁻¹)	Natural ecosystems	0.01	0–0.109	Kim et al., 1997; Garcia-Ruiz et al., 1998; Starry et al., 2005
	Cropland	0.05	0–1.0*	
K_{denit} (g N m ⁻³)	Natural ecosystems	0.75	0.183–6.5	Garcia-Ruiz et al., 1998; Yu et al., 2006
	Cropland	1.5	1–10**	
$V_{\text{max, nit}}$ (g N m ⁻³ day ⁻¹)	Natural ecosystems	0.02	0–2.18	Kim et al., 1997; Sheibley et al., 2003
	Cropland	0.05	0–5*	
K_{nit} (g N m ⁻³)	Natural ecosystems	0.75	0.21–1.11	Sheibley et al., 2003
	Cropland	1.5	1–10**	

* Assume cropland has two time higher maximum rate for nitrification and denitrification, and higher half-saturation coefficient than natural ecosystems based on Wang et al.'s (2009) study. ** Assume cropland has higher half-saturation coefficient for nitrification and denitrification than natural ecosystems.

3 Results and analyses

3.1 Temporal patterns of CH₄ and N₂O fluxes in North America

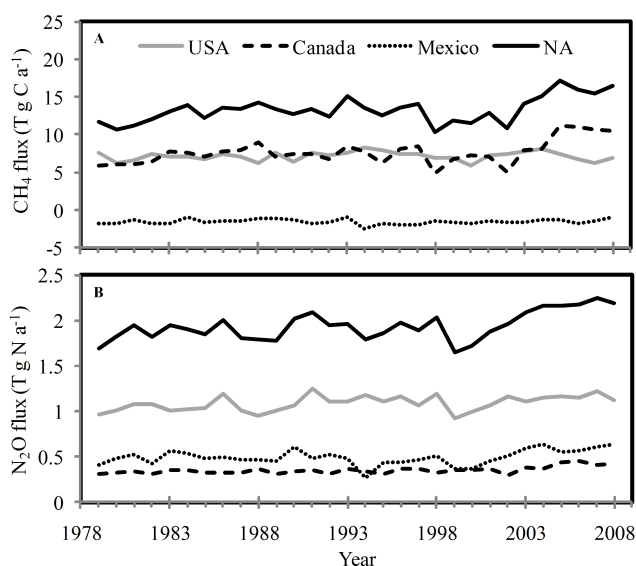
The annual fluxes of CH₄ and N₂O over the entire North America showed significant fluctuations during 1979–2008. The highest CH₄ emission was 18.42 Tg C a⁻¹ in 2005, and the lowest was 11.74 Tg C a⁻¹ in 1998. Before 2001,

the annual CH₄ flux was relatively constant with no obvious trend of change; however, since 2002 the CH₄ emission rate increased rapidly, reached the maximum in 2005, and decreased slightly since then (Fig. 6). The overall increasing rate of CH₄ flux was 0.10 Tg C a⁻¹ over the past 30 years. The highest N₂O emission was 2.25 Tg N a⁻¹ in 2007, and the lowest was 1.66 Tg N a⁻¹ in 1999 (Fig. 6). The overall increasing rate of N₂O was 0.01 Tg C a⁻¹ over

Table 2. Study sites from which CH₄ and auxiliary data were collected and used in the calibration of the Dynamics Land Ecosystem Model (DLEM).

Site	Vegetation type	Location	Reference
Glacier Lakes Ecosystem Experiment Site*	Subalpine meadow (tundra)	41.33° N, 106.22° W	Mosier et al., 1993
Bonanza Creek Experimental Forest	Boreal broad leaf deciduous forest	64.8° N, 148.0° W	Whalen et al., 1991
Bonanza Creek Experimental Forest	Boreal needle leaf evergreen forest	64.8° N, 148.0° W	Whalen et al., 1991
Saskatchewan boreal forest*	Boreal needle leaf evergreen forest	53.92° N, 104.69° W	Matson, 2008
Konstanz*,**	Temperate broad leaf deciduous forest	49,00° N, 8,00° E	Koschorreck and Conrad, 1993
Weiberbach*,**	Temperate broad leaf deciduous forest	49.17° N, 8.72° E	Dörr et al., 1993
Changbaishan**	Temperate broad leaf deciduous forest	46.6° N, 128.47° E	Xiao et al., 2004
Changbaishan**	Temperate broad leaf evergreen forest	46.6° N, 128.47° E	Xiao et al., 2004
Gongga Mountain**	Temperate needle leaf evergreen forest	29.0 ~ 30.33° N, 101.5 ~ 102.25° E	Dong et al., 2003
Pujo*,**	Tropical dry forest	1.39° S, 78.00° W	Dörr et al., 1993
Congo river basin*,**	Tropical rain forest	1.5° N, 18.0° E	Tathy et al., 1992
Konstanz*,**	Temperate mixed forest	49,00° N, 8,00° E	Koschorreck and Conrad, 1993
Sanjiang**	Deciduous shrub	47.69° N, 133.52° E	Song et al., 2009
“Castel Volturno” Nature Reserve*,**	Evergreen shrub	40.95° N, 1.55° E	Castaldi and Fierro, 2005
Central Plains Experimental Range	C3 grassland	40.8° N, 104.75° W	Mosier et al., 1996
Central Plains Experimental Range	C4 grassland	40.83° N, 104.7° W	Mosier et al., 2002
Sanjiang**	Herbaceous wetland	47.69° N, 133.52° E	Song et al., 2009
Marcell Experimental Forest*	Woody wetland	47.53° N, 93.47° W	Dise, 1991
High Plains Agricultural Research Laboratory*	Cropland	41.23° N, 103.00° W	Kessavalou et al., 1998
Mojave Desert*	Desert	37° N, 116° W	Strieg et al., 1992

* Indicates portions of model-driven forces from regional dataset; ** indicates site outside of the continental North America.

**Fig. 6.** CH₄ and N₂O fluxes in North America's terrestrial ecosystems by countries during 1979–2008.

the past 30 years. The mean annual fluxes over the past 30 years in North America's terrestrial ecosystems were $14.69 \pm 1.64 \text{ Tg C a}^{-1}$ for CH₄ and $1.94 \pm 0.16 \text{ Tg N a}^{-1}$ for N₂O, respectively.

3.2 Spatial distributions of CH₄ and N₂O fluxes in North America

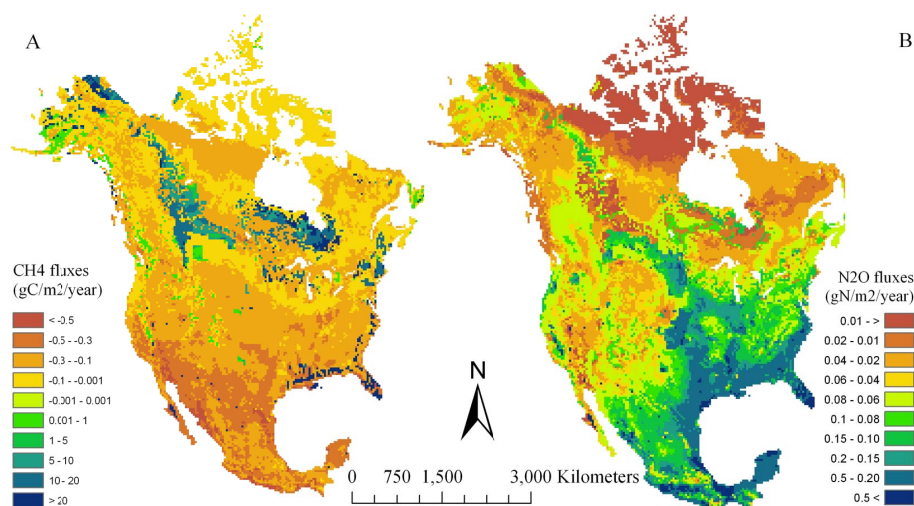
The CH₄ and N₂O fluxes over the entire continent of North America showed significant spatial variations (Fig. 7). The spatial pattern of CH₄ fluxes was mostly dependent on the biome distribution, with a major source located in northwestern part of North America, a region mainly featuring natural wetland. The southwestern part of North America acted as a sink for atmospheric CH₄. A weak sink of CH₄ was also shown in the northeastern part of North America.

All terrestrial ecosystems in North America acted as sources for atmospheric N₂O. The strong sources in southeastern part of North America included the southeastern US and entire Mexico, where N₂O emission reached as high as $0.8 \text{ g N m}^{-2} \text{ a}^{-1}$. The weak N₂O sources were observed in other areas, for example, the north part of North

Table 3. Study sites from which N₂O and auxiliary data were collected and used in the calibration of the Dynamics Land Ecosystem Model (DLEM).

Site	Vegetation type	Location	Reference
Glacier Lakes Ecosystem Experiment Site*	Tundra	41.33° N, 106.33° W	Sommerfeld et al., 1993
Saskatchewan boreal forest*	Boreal broad leaf deciduous forest	53.92° N, 104.69° W	Matson, 2008
Saskatchewan boreal forest*	Boreal needle leaf evergreen forest	53.92° N, 104.69° W	Matson, 2008
Changbaishan**	Temperate broad leaf deciduous forest	46.6° N, 128.47° E	Xiao et al., 2004
Changbaishan**	Temperate broad leaf evergreen forest	46.6° N, 128.47° E	Xiao et al., 2004
Gongga Mountain**	Temperate needle leaf evergreen forest	29.0 ~ 30.33° N, 101.5 ~ 102.25° E	Dong et al., 2003
Rondnia*,**	Tropical dry forest	10.5° S, 62.5° W	Garcia-Montiel et al., 2002
Rondnia*,**	Tropical rain forest	10.5° S, 62.5° W	Garcia-Montiel et al., 2002
Changbaishan**	Temperate mixed forest	46.6° N, 128.47° E	Xiao et al., 2004
Sanjiang**	Deciduous shrub	47.69° N, 133.52° E	Song et al., 2009
Arid Lands Ecology Reserve*,**	Evergreen shrub	46.37° ~ 46.56° N, 119.47° ~ 119.78° W	Mummey et al., 1997
Neimenggu**	C3 grassland	43.03° N, 119.15° E	Huang et al., 2003
Central Plains Experimental Range	C4 grassland	40.83° N, 104.7° W	Mosier et al., 2002
Sanjiang**	Herbaceous wetland	47.69° N, 133.52° E	Song et al., 2009
Saskatchewan boreal forest*	Woody wetland	53.63° N, 106.20° W	Matson, 2008
Arthur Post Farm in Bozeman*	Cropland	45.67° N, 111.15° W	Dusenbury et al., 2008
High Plains Agricultural Research Laboratory*	Cropland	41.23° N, 103.00° W	Kessavalou et al., 1998
Mojave Desert*	Desert	36.82° N, 115.92° W	Billings et al., 2002

* Indicates portions of model-driven forces from regional dataset; ** indicates site outside of the continental North America.

**Fig. 7.** Spatial distribution of (A) CH₄ and (B) N₂O fluxes in North America's terrestrial ecosystems during 1979–2008.

America where N₂O was released at a rate of approximately 0.01 g N m⁻² a⁻¹.

3.3 CH₄ and N₂O fluxes in different countries

The US, Canada, and Mexico are three diverse countries with different landscapes and anthropogenic activities,

resulting in various CH₄ and N₂O flux regimes. At the country level, CH₄ flux was 7.16 ± 0.58 Tg C a⁻¹ for the US, 7.68 ± 1.59 Tg C a⁻¹ for Canada, and -0.15 ± 0.03 Tg C a⁻¹ for Mexico. The US and Canada accounted for 48.76% and 52.29%, respectively, and Mexico captured 1.05% of the continental emission of CH₄ (Fig. 6). The country level N₂O flux was

Table 4. Values of the major parameters for different ecosystem types in methane module after the Bayesian calibration.

Major ecosystem type	$V_{\text{CH}_4\text{ProMax}}$ ($\text{g C m}^{-3} \text{ day}^{-1}$)	$V_{\text{CH}_4\text{OxidairMax}}$ ($\text{g C m}^{-3} \text{ day}^{-1}$)	$V_{\text{CH}_4\text{Oxidtrans}}$ ($\text{g C m}^{-3} \text{ day}^{-1}$)	$V_{\text{CH}_4\text{Oxidsoilmax}}$ ($\text{g C m}^{-3} \text{ day}^{-1}$)	$K_{\text{mCH}_4\text{Prod}}$ (g C m^{-3})	$K_{\text{mCH}_4\text{Oxidair}}$ (ppm)	$K_{\text{mCH}_4\text{Oxidtrans}}$ (g C m^{-3})	$K_{\text{mCH}_4\text{Oxidsoil}}$ (g C m^{-3})
Tundra	0.25	0.085	0.1	0.1	10	10	2.5	3
Boreal broad leaf deciduous forest	0.35	0.08	0.1	0.1	10	10	2.5	3
Boreal needle leaf evergreen forest	0.35	0.071	0.1	0.1	10	10	2.5	3
Temperate broad leaf deciduous forest	0.25	0.042	0.2	0.1	15	10	2.5	3
Temperate broad leaf evergreen forest	0.4	0.027	0.1	0.1	15	10	2.5	3
Temperate needle leaf evergreen forest	0.65	0.039	0.1	0.1	15	10	2.5	3
Tropical dry forest	0.5	0.02	0.1	0.1	15	10	2.5	3
Tropical rain forest	0.45	0.015	0.1	0.1	15	10	2.5	3
Temperate mixed forest	0.65	0.048	0.1	0.1	15	10	2.5	3
Deciduous shrub	0.5	0.031	0.25	0.1	15	10	2.5	3
Evergreen shrub	0.25	0.02	0.2	0.1	15	10	2.5	3
C3 grassland	0.5	0.03	0.2	0.1	15	10	2.5	3
C4 grassland	0.6	0.02	0.1	0.1	15	10	2.5	3
Herbaceous wetland	1.45	0.032	5	2.5	5	10	3.5	3.5
Woody wetland	0.55	0.032	5	2.5	5	10	3.5	3.5
Cropland (dry land)	0.4	0.02	0.3	0.35	15	10	10	12
Desert	0.25	0.05	0.25	0.1	15	10	2.5	3

Table 5. Values of the major parameters for different ecosystem types in nitrous oxide module after the Bayesian calibration.

Major ecosystem type	V_{denimax} ($\text{g Nm}^{-3} \text{ day}^{-1}$)	K_{deni} (g Nm^{-3})	V_{nitmax} ($\text{g Nm}^{-3} \text{ day}^{-1}$)	K_{nit} (g Nm^{-3})
Tundra	0.03	0.15	0.008	1
Boreal broad leaf deciduous forest	0.013	0.035	0.0025	1
Boreal needle leaf evergreen forest	0.05	0.05	0.003	1
Temperate broad leaf deciduous forest	0.012	0.15	0.0025	1
Temperate broad leaf evergreen forest	0.007	0.75	0.03	1
Temperate needle leaf evergreen forest	0.012	0.15	0.01	1
Tropical dry forest	0.008	0.25	0.004	1
Tropical rain forest	0.0065	0.15	0.006	1
Temperate mixed forest	0.012	0.15	0.01	1
Deciduous shrub	0.055	0.5	0.005	1
Evergreen shrub	0.16	0.75	0.0025	1
C3 grassland	0.055	0.75	0.005	1
C4 grassland	0.035	0.75	0.0035	1
Herbaceous wetland	0.007	0.5	0.005	1
Woody wetland	0.0013	0.35	0.005	1
Cropland (dry land)	0.052	4.5	0.25	5
Desert	0.01	0.05	0.005	1

$1.09 \pm 0.08 \text{ T g N a}^{-1}$ for the US, $0.35 \pm 0.04 \text{ T g N a}^{-1}$ for Canada, and $0.50 \pm 0.08 \text{ T g N a}^{-1}$ for Mexico. The US, Canada, and Mexico accounted for 56.19%, 18.23%, and 25.58%, respectively, of the continental emission of N₂O (Fig. 6).

The rate of changes in CH₄ and N₂O fluxes varied among countries. Based on the regression analysis, we estimated that over the past 30 years, CH₄ emission increased at rates of 5.7 G g C a^{-1} ($1 \text{ G g} = 10^9 \text{ g}$) in the US and $91.7 \text{ G g C a}^{-1}$ in Canada, while CH₄ consumption increased 0.2 G g C a^{-1}

Table 6. Biome contributions to the terrestrial fluxes of CH₄ and N₂O over continental North America (The fluxes are shown as mean plus and minus standard deviation).

		Tundra	Forest	Grassland	Shrub	Wetland	Cropland	Desert and others
CH ₄	Flux (T g C a ⁻¹)	-0.41 ± 0.03	-1.13 ± 0.07	-0.47 ± 0.03	-0.64 ± 0.02	17.75 ± 1.63	-0.32 ± 0.03	-0.10 ± 0.01
	Percentage	-2.79%	-7.67%	-3.19%	-4.34%	120.86%	-2.17%	-0.70%
N ₂ O	Flux (T g N a ⁻¹)	0.07 ± 0.01	0.63 ± 0.03	0.22 ± 0.04	0.25 ± 0.03	0.19 ± 0.01	0.56 ± 0.07	0.03 ± 0.004
	Percentage	3.68%	32.21%	11.24%	12.72%	9.78%	28.82%	1.55%

Biome-based estimates may not sum to totals because of the effects of rounding in reporting those estimates.

in Mexico. Our results also indicate that N₂O emission increased at rates of 4.2 G g N a⁻¹ in the US, 2.9 G g N a⁻¹ in Canada and 2.9 G g N a⁻¹ in Mexico, respectively, during the past 30 years.

3.4 CH₄ and N₂O fluxes in different biomes

CH₄ and N₂O fluxes varied remarkably among different ecosystems. Due to the perennial or ephemeral inundated condition, wetlands dominate CH₄ emissions in North America with a source of 17.75 ± 1.63 T g C a⁻¹ (Table 6). All the other ecosystems acted as sinks for atmospheric CH₄ with a total sink of 3.06 ± 0.14 g C a⁻¹, of which forest and shrub contributed 36.93% and 20.92%, respectively. All ecosystems functioned as sources of N₂O. Forest, grassland, shrub, and cropland contributed 32.21%, 11.24%, 12.72%, and 28.82%, respectively, for the N₂O emission in North America's terrestrial ecosystems (Table 6).

The fluxes of CH₄ and N₂O in each biome over the past 30 years varied significantly. From 1979 to 2008, the CH₄ emission increased at a rate of 103.9 G g C a⁻¹ in natural wetland, and the CH₄ oxidation increased at rates of 2.5 G g C a⁻¹ in forests, 0.8 G g C a⁻¹ in shrub, 0.8 G g C a⁻¹ in grassland, and 0.6 G g C a⁻¹ in desert and others, respectively. No significant changes were found for other ecosystem types. For the same time period, the N₂O emission increased at rates of 5.5 G g N a⁻¹ in cropland, 1.5 G g N a⁻¹ in grassland, 0.8 G g N a⁻¹ in tundra, and 0.3 G g N a⁻¹ in desert and others. We did not find significant changes for other ecosystem types.

4 Discussion

4.1 Regional comparison to other studies

We estimated annual fluxes of CH₄ and N₂O in terrestrial ecosystems of North America with a spatial resolution of 32 km × 32 km for the past 30 years. Wetlands predominately account for the continental CH₄ emission. Putting our estimate at the global context (Denman et al., 2007), it accounted for less than 20% of the global CH₄ emissions from natural wetlands at 100–231 T g CH₄ a⁻¹ (Denman et

al., 2007), which is lower than its areal portion of global natural wetland. This may be due to less tropical natural wetlands and rice paddies in this region, which are two strong emitters of CH₄ (Denman et al., 2007; Mitsch and Gosselink, 2007). While our regional estimations of CH₄ and N₂O in North America's terrestrial ecosystems were comparable to previous studies, we found that there were differences at some specific areas or ecosystems. For example, Zhuang et al. (2007) used a process-based model (Terrestrial Ecosystem Model) to estimate that the CH₄ emission in Alaska was 2.35 T g C a⁻¹ for the period of 1980–1996, which is 12% higher than our estimation of 2.10 T g C a⁻¹ for the same time period. However, their estimation of CH₄ emissions in Canada of 5.33 T g C a⁻¹ (Zhuang et al., 2004) is 26% lower than our estimation of 7.23 T g C a⁻¹ for the 1990s. Combining satellite imageries and a process-based ecosystem model, Potter et al. (2006) estimated that CH₄ emission from natural wetland in conterminous US during 1996–2005 was 4.13 T g C a⁻¹, which is 35% lower than our estimate of 6.34 T g C a⁻¹ for the same time period. In addition, a recent synthesis by Bridgman et al. (2006) indicated that CH₄ emission in North America's wetlands is 6.75 T g C a⁻¹, which is only 38% of our estimation (17.75 ± 1.63 T g C a⁻¹). Bridgman et al. (2006) used site specific estimates of CH₄ fluxes from literature to extrapolate to the wetlands of the entire North America. In Bridgman et al.'s study, they made the simplifying assumption that wetlands, soils and climate are uniform across the North America for the period of interest. In contrast, the DLEM estimates account for spatial variability of wetlands, soils and climate that give rise to place to place differences in CH₄ fluxes over a time period of 30 years. The difference in up-scaling methods used and the time periods examined in the two studies might explain this large discrepancy given the large range of CH₄ flux in different wetland types, soils and climate zones (Bridgman et al., 2006; Barlett and Harriss, 1993; Song et al., 2009). The differences between these estimates were caused largely by the data and models used for their estimations. Using an improved process-based ecosystem model and the most up-to-date and detailed input data, our modeling approach addressed various ecosystem processes and multiple

Table 7. Comparison of the DLEM-derived CH₄ and N₂O fluxes with other estimates at the regional scale (DLEM simulations were at a resolution of 32 km × 32 km).

Method	Period	Domain	CH ₄ (Tg C a ⁻¹)	N ₂ O (Tg N a ⁻¹)	Source
Satellite-based empirical method		Wetlands in the continental US	4.13		Potter et al., 2006
DLEM	1996–2005	Wetlands in the continental US	6.34 ± 0.43		This study
Process-based model	1990s	Canada	5.33		Zhuang et al., 2004
DLEM	1990s	Canada	7.23 ± 1.11		This study
Process-based model	1980–1996	Alaska	2.35		Zhuang et al., 2007
DLEM	1980–1996	Alaska	2.10 ± 0.27		This study
DNDC at State level	1990	Cropland in the continental US		0.50–0.74	Li et al., 1996
DLEM	1990	Cropland in the continental US		0.350	This study
Empirical method at half degree	1980–2000	North America		2.08 ± 0.048	Xu et al., 2008
DLEM	1980–2000	North America		1.85 ± 0.11	This study
DNDC	1970–1999	Agricultural soils in Canada		0.020–0.077 (0.0399)*	Smith et al., 2004
DLEM	1979–1999	Agricultural soils in Canada		0.031–0.055 (0.042)*	This study
DAYCENT at 63 minor regions at county level	1991–2000	Major crop in USA		~0.30**	Del Grosso et al., 2005
DLEM	1991–2000	All crops in USA		0.367 ± 0.048	This study

* Range is shown first and then the mean in bracket; **Data are read from a figure.

environmental factors that control CH₄ and N₂O fluxes in terrestrial ecosystems.

There are only a few studies of N₂O at large spatial and temporal scales (Smith et al., 2004; Liu, 1996; Li et al., 1996; Zhuang et al., 2004; Del Grosso et al., 2005; Xu et al., 2008). The DLEM simulated N₂O emission in North America's terrestrial ecosystems was consistent with a few other available studies. In the time period of 1980–2000, DLEM-modeled N₂O flux was 1.85 ± 0.11 Tg N a⁻¹, comparable to 2.08 ± 0.05 Tg N a⁻¹ estimated by Xu et al. (2008) (Fig. 8). Inter-annual variations of N₂O fluxes also showed a good agreement between these two studies ($R^2 = 0.39$; $P < 0.01$). The spatial correlation of N₂O fluxes between these two studies showed a correlation coefficient of 0.54 ($N = 7691$). The close agreement between these two studies indicated that DLEM reasonably captured the temporal and spatial patterns of N₂O emission in North America's terrestrial ecosystems. At the same spatial scale and over the same time period, the DLEM-simulated N₂O emission from cropland in US is higher than Del Grosso et al.'s estimate for major crops (2005), but is lower than Li et al.'s estimate for cropland in the continental US (1996) (Table 7). Putting our estimate at the global context, DLEM-estimated N₂O flux from North America accounted for 20% of the global N₂O source of 9.4 Tg N a⁻¹ from natural vegetation and agricultural land (Denman et al., 2007). This is proportional to the areal percentage of North America in the global land surface area.

There are also a few inverse estimates on CH₄ and N₂O (Hein et al., 1997; Hirsch et al., 2006; Kort et al., 2008; Chen and Prinn, 2006), and only one study reported the inverse results for natural fluxes from natural wetlands in North America at 9 ± 4.5 Tg C a⁻¹ (Chen and Prinn, 2006). However, their estimate did not consider the CH₄ flux from lower latitude, i.e. Mexico.

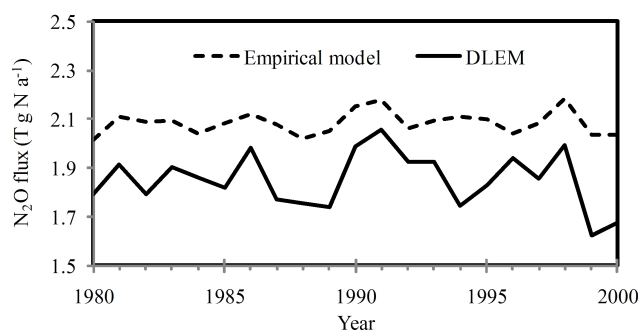


Fig. 8. Comparison of the DLEM-derived N₂O fluxes with the estimations by an empirical model (Xu et al., 2008). The regression model is: the DLEM-derived N₂O = 0.8887 × Empirically-modeled N₂O, $R^2 = 0.39$; $P < 0.01$.

4.2 Biome comparison to other studies

The model results showed that wetland ecosystems released CH₄ to the atmosphere while all other ecosystems acted as sinks for CH₄ (Table 8). Herbaceous wetland released CH₄ at a rate of 9.99 ± 0.93 g C m⁻² a⁻¹ and woody wetland at a rate of 7.87 ± 0.81 g C m⁻² a⁻¹. The strongest sink resided in subtropical/tropical dry forest, and rain forest, followed by grassland, shrub, and desert. The CH₄ emission and consumption in these ecosystems were comparable to other studies (Table 8). For example, the DLEM-estimated CH₄ uptake rate by boreal forest is 0.13 ± 0.01 g C m⁻² a⁻¹, which is close to Curry's (2007) estimate at 0.13 g C m⁻² a⁻¹, and Ridgwell et al.'s (1999) estimate at 0.14 g C m⁻² a⁻¹, yet is slightly lower than Dutaur and Verchot's (2007) estimate at 0.20 g C m⁻² a⁻¹; the DLEM-estimated CH₄ uptake rate by grassland is 0.18 ± 0.01 g C m⁻² a⁻¹, which is consistent with Curry et al.'s (2007) estimate at 0.17 g C m⁻² a⁻¹ and Dutaur and Verchot's (2007) estimate at 0.17 g C m⁻² a⁻¹, yet

Table 8. Comparison of the DLEM-estimated CH₄ emission rate (g C m⁻² a⁻¹) with other studies at biome level (Positive values represent CH₄ emission, and negative values represent CH₄ uptake).

Biome type	This study	Bridgham et al., 2006	Barlett and Harriss, 1993	Curry, 2007	Dutaur and Verchot, 2007	Ridgwell et al., 1999
Tundra	-0.101 ± 0.006		-0.055 ~ -0.575	-0.109	-0.112	-0.075
Boreal forest	-0.128 ± 0.010		-0.074 ~ -0.430	-0.125	-0.198	-0.140
Temperate forest	-0.178 ± 0.012		-0.068 ~ -1.15	-0.155	-0.428	-0.181
Tropical dry forest	-0.244 ± 0.013		-0.082 ~ -0.520	-0.199	-0.250	-0.354
Tropical rain forest	-0.221 ± 0.025			-0.202	-0.250	-0.260
Shrub	-0.178 ± 0.006				-0.169	-0.206
Grassland	-0.178 ± 0.010		-0.167		-0.174	-0.238
Desert	-0.185 ± 0.004			-0.129	-0.803	-0.172
Cropland	-0.125 ± 0.014					
Herbaceous wetland	9.985 ± 0.933	Arithmetic: 24.075 ± 5.925	26.28 for arctic wetlands; 23.82 for boreal wetlands; 36.96 for temperate bogs and fens; 20.52 for temperate swamps; 19.16 for temperate marshes; 13.14 for temperate floodplains			
Woody wetland	7.871 ± 0.807	Geometric: 6.075 ± 1.575				

Table 9. Comparison of the DLEM-estimated N₂O emission rate (g N m⁻² a⁻¹) with other studies at biome level (Positive values represent N₂O emission).

Biome type	This study	Potter et al., 1996	Recalculated from Xu et al., 2008
	Process-based model	Process-based model with remote sensing data	Empirical model
Tundra	0.018 ± 0.002	0.003–0.011	0.002–0.251
Boreal forest	0.047 ± 0.006	0.018	0.016–1.217
Temperate forest	0.107 ± 0.007	0.042–0.064	0.016–1.217
Tropical dry forest	0.110 ± 0.020	0.105	0.175–0.613
Tropical rain forest	0.246 ± 0.039	0.136	0.006–1.060
Shrub	0.061 ± 0.012	0.031	
Grassland	0.094 ± 0.010	0.016	0.004–0.107*
Desert	0.015 ± 0.003	0.004	
Cropland	0.220 ± 0.030	0.081**	0.010–0.725
Herbaceous wetland	0.169 ± 0.014		0.002–0.251
Woody wetland	0.053 ± 0.005		0.002–0.251

* Temperate grassland and tropical savanna and grassland; ** Without fertilization

is slightly lower than Ridgwell et al.'s (1999) estimate as 0.24 g C m⁻² a⁻¹; the DLEM-estimated CH₄ uptake rate by cropland is 0.12 ± 0.01 g C m⁻² a⁻¹, which is close to 0.11–0.15 g C m⁻² a⁻¹ (Dobbie et al., 1996; Mosier et al., 1998). The DLEM-estimated CH₄ sink strengths for tundra, temperate forest, shrub, cropland, herbaceous wetland and woody wetland fall in the range of others' estimates (Table 8).

The modeled biome-level fluxes of N₂O are comparable to other studies (Table 9). For almost all biome types, our modeled results are much higher than those estimated by Potter et al. (1996), yet in the lower end of the summarized ranges from Xu et al. (2008). For example, the average N₂O flux from tundra is estimated at 0.018 ± 0.002 g N m⁻² a⁻¹ in this study, which is more than 50% higher than Potter et al.'s (1996) estimation at 0.003–0.011 g N m⁻² a⁻¹; while it

is in the lower end of 0.002–0.251 g N m⁻² a⁻¹ summarized in Xu et al. (2008). It is same for boreal and temperate forest, shrub, grassland, and tropical rain forest. However, our estimate of N₂O flux from tropical rain forest is identical to Potter et al.'s (1996) estimate (Table 9). The DLEM-estimated N₂O flux from desert is 0.015 ± 0.003 g N m⁻² a⁻¹, which is almost three times of Potter et al.'s (1996) estimate; however, it is still reasonable comparing with the field observation of 0.04 g N m⁻² a⁻¹ at Sonoran Desert (Guilbault and Matthias, 1998). Our estimated N₂O fluxes from herbaceous and woody wetland are in the middle of summarized range from Xu et al. (2008). Given the reported high (Song et al., 2009) or low (Martikainen et al., 1993) N₂O emission from wetland, and current state of lacking regional estimation of N₂O from wetland, it is highly needed to have further

efforts on this issue. Emission of N₂O from croplands in the US in 1990 ($0.187 \pm 0.139 \text{ g N m}^{-2} \text{ a}^{-1}$) was also comparable to another estimates of $0.186\text{--}0.204 \text{ g N m}^{-2} \text{ a}^{-1}$ by Li et al. (1996).

4.3 Changes in CH₄ and N₂O fluxes among countries

The CH₄ and N₂O fluxes varied substantially among three countries. Canada had the highest flux and the highest increasing rate in CH₄ emission during 1979–2008, which might be due to its large area of wetland and the high increasing rate of CH₄ production in wetland (Sect. 3.4). The highest increasing rate of N₂O emission from the US was probably caused by large amount of cropland, which was an major source for atmospheric N₂O (Li et al., 1996) (Sect. 3.3.). Mexico showed relatively high N₂O emission, while acting as a sink for atmospheric CH₄. This decoupling was caused by the landscape composition; the relatively dense cropland made it a major source of N₂O, while small area of wetland emitted little CH₄ to the atmosphere, lower than atmospheric CH₄ consumption by cropland, grassland, and forest (Fig. 4).

4.4 Environmental controls on CH₄ and N₂O fluxes

Inter-annual fluctuation of CH₄ and N₂O fluxes in North America's terrestrial ecosystems was highly correlated with climate factors, especially the mean annual temperature and annual precipitation (Fig. 9). A recent study showed that a drought could reduce N₂O emission from a European spruce forest (Goldberg and Gebauer, 2009); this is consistent with our study, which shows that the droughts in 1994, 1999, and 2002 resulted in relative low N₂O emissions, due to the soil moisture control on denitrification process (see Eq. 15) (Conrad, 1996). Nitrogen input, including nitrogen deposition and nitrogen fertilizer application, might increase or decrease CH₄ and N₂O fluxes (Steudler et al., 1989; Ding et al., 2004; Liu and Greaver, 2009), while rising atmospheric CO₂ increased CH₄ emission (Hutchin et al., 1995) yet decreased N₂O emissions (Phillips et al., 2001a). Ozone pollution decreased CH₄ emission (Morsky et al., 2008) while increasing or decreasing N₂O emission (Kanerva et al., 2007). The effects of land-cover change are complicated, depending on the direction of the conversion (Willison et al., 1995; Huang et al., 2010). To accurately assess CH₄ and N₂O fluxes in terrestrial ecosystems, it is essential to better understand the underlying mechanisms and attribute the variations in terrestrial ecosystem CH₄ and N₂O fluxes to relative role of various environmental factors.

4.5 Uncertainties in this study and the way forward

We provided regional estimations of CH₄ and N₂O fluxes in North America's terrestrial ecosystems by using an improved process-based biogeochemical model driven by multiple-global change factors. Due to the complexity of the biogeochemical processes related to these two greenhouse gases

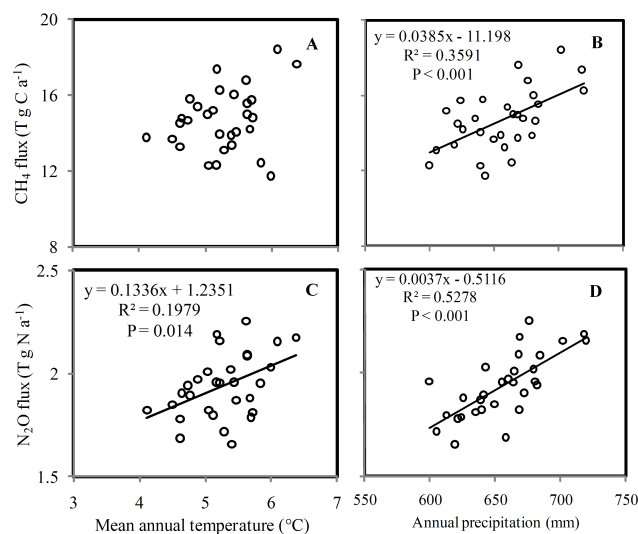


Fig. 9. Correlation between annual CH₄ and N₂O fluxes and mean annual temperature and annual precipitation – (A) Correlation between CH₄ flux and mean annual temperature; (B) Correlation between CH₄ flux and annual precipitation; (C) Correlation between N₂O flux and mean annual temperature; (D) Correlation between N₂O flux and annual precipitation)

(Conrad, 1996; Xu et al., 2008), some uncertainties need to be considered when interpreting the results. At the first place, only CH₄ production from DOC was considered in the current model. Other substrates may need to be included, for example, the CH₄ production from acetate could contribute nearly 20% to CH₄ production (Conrad, 1996; Mer and Roger, 2001). It might be better to include more components in CH₄ production, oxidation, and transport, if these substrates can be quantified. Similarly, improvement of our knowledge and inclusion of more processes in simulating N₂O production and oxidation may be needed. Secondly, current simulation of CH₄ and N₂O fluxes could be underestimated, as the DLEM runs at daily time step and might ignore some possible high pulses in CH₄ and N₂O fluxes at the time step of minute or hour. These high pulses may provide a substantial contribution to the annual fluxes (Brumme et al., 1999). In addition, the availability of soil moisture could turn CH₄ production on and off at the minute or hour time step (Moosavi et al., 1996). Third, the uncertainties in biogeochemical processes and model parameters need to be evaluated. For example, several studies have found the ebullition process might be different from the mechanism applied in the DLEM model (Baird et al., 2004; Kellner et al., 2005; Strack et al., 2005); although these studies pointed out the possible drawback of current representation for this process in process-based model, yet did not provide more reliable method as a replacement. This calls for additional field or experimental investigation before the process can be better addressed in the model.

Fourth, wetland area and classification could bring uncertainties to regional estimation of CH₄ and N₂O fluxes. The fluxes of CH₄ and N₂O have been reported at an order difference in magnitude among different wetland classes (Barlett and Harriss, 1993; Song et al., 2009), thus the small discrepancy in wetland area and wetland classification could lead to a substantial difference in regional estimation. Fifth, it is important to take into account different mechanisms that control methane production and oxidation in tropical and northern wetlands even though the mechanisms for the differences between tropical and northern wetlands are still not well documented (Blais et al., 2005). Lastly but not least, N₂O emission from pasture may contribute a great proportion to the continental flux of N₂O (Li et al., 1996; Ambus et al., 2006; Livesley et al., 2009). But N₂O emission from managed pasture was not simulated in current model, due to a lack of spatially-explicit information on pasture management.

5 Conclusions

Using the improved DLEM model, we estimated terrestrial ecosystem CH₄ and N₂O fluxes in North America over the past 30 years as a result of multiple global change factors including rising atmospheric CO₂ concentration, ozone pollution, climate change, nitrogen deposition, land-use change, and management. The continental-, country- and biome-level fluxes of CH₄ and N₂O during the past three decades were reported.

This study indicated that approximately $14.69 \pm 1.64 \text{ T g C a}^{-1}$ of CH₄, and $1.94 \pm 0.16 \text{ T g N a}^{-1}$ of N₂O were released from terrestrial ecosystems in North America during 1979–2008. Both the US and Canada acted as CH₄ sources to the atmosphere, but Mexico mainly oxidized and consumed CH₄ from the atmosphere; and all three countries released N₂O to the atmosphere. Forests and croplands were the two ecosystems that contributed most to continental N₂O emission.

This study provided, to the best of our knowledge, the first continental-level simultaneous quantification and maps at 32 km × 32 km resolution of annual CH₄ and N₂O fluxes in North America's terrestrial ecosystems over the past three decades. While there are some uncertainties related to the estimation of CH₄ and N₂O fluxes due to the simplification of the relevant biogeochemical processes in the model, we believe that this study might provide some useful information for policy making on greenhouse gas mitigation and management. To reduce uncertainties in regional estimation of CH₄ and N₂O fluxes, it is needed to further improve the representation of additional biogeochemical processes in the DLEM and the spatial data sets of wetland area and pasture management; the future incorporation of pasture into the DLEM simulation might be another way to reduce uncertainty of regional estimation of N₂O flux. We also face several key challenges that include attributing the mechanisms responsible

for CH₄ and N₂O fluxes and up-scaling from a modeled grid to continental scales.

Acknowledgements. This study has been supported by NASA Atmospheric Composition: Modeling and Analysis Program (NNH10CC80C), NASA terrestrial ecology program, and DOE National Institute of Climate Change Research (DUKE UN-07-SC-NICCR-1016). This study contributes to the NACP Non-CO₂ Greenhouse Gases Synthesis led by Steven Wofsy at Harvard University. We thank the TRAGNET program for making observational data available. We are also grateful for Peter Groffman at the Hubbard Brook Ecosystem Study to share his data with us for model validation. We thank Patrick Crill at Stockholm University for sharing his observational data for our model validation, Louis Verchot at the Center for International Forestry Research in Indonesia for sharing his collection of CH₄ flux around the globe, and Dennis Baldocchi, Dafeng Hui, Yao Huang, Steven Wofsy and two anonymous for constructive comments.

Edited by: M. Dai

References

- Amaral, J. A., Ren, T., and Knowles, R.: Atmospheric methane consumption by forest soils and extracted bacteria at different pH values, *Appl. Environ. Microbiol.*, 64, 2397–2402, 1998.
- Ambus, P., Zechmeister-Boltenstern, S., and Butterbach-Bahl, K.: Sources of nitrous oxide emitted from European forest soils, *Biogeosciences*, 3, 135–145, doi:10.5194/bg-3-135-2006, 2006.
- Arah, J. R. M. and Stephen, K. D.: A model of the processes leading to methane emission from peatland, *Atmos. Environ.*, 32, 3257–3264, 1998.
- Baird, A. J., Beckwith, C. W., Waldron, S., and Waddington, J. M.: Ebullition of methane-containing gas bubbles from near-surface Sphagnum peat, *Geophys. Res. Lett.*, 31, L21505, doi:10.1029/2004GL021157, 2004.
- Barlett, K. B. and Harriss, R. C.: Review and assessment of methane emissions from wetlands, *Chemosphere*, 26, 261–320, 1993.
- Billings, S. A., Schaeffer, S. M., and Evans, R. D.: Trace N gas losses and N mineralization in Mojave desert soils exposed to elevated CO₂, *Soil Biol. Biochem.*, 34, 1777–1784, 2002.
- Blais, A. M., Lorrain, S., and Tremblay, A.: Greenhouse gas fluxes (CO₂, CH₄ and N₂O) in forests and wetlands of boreal, temperate and tropical regions, in: *Greenhouse gas emissions-fluxes and processes: hydroelectric reservoirs and natural environments*, edited by: Bremlay, A., Varfalvy, L., Roehm, C., and Garneau, M., Springer Press, New York, 2005.
- Bridgman, S. D., Megonigal, J. P., Keller, J. K., Bliss, N. B., and Trettin, C.: The carbon balance of North American Wetlands, *Wetlands*, 26, 889–916, 2006.
- Brumme, R., Borken, W., and Finke, S.: Hierarchical control on nitrous oxide emission in forest ecosystems, *Global Biogeochem. Cy.*, 13, 1137–1148, 1999.
- Cao, M. K., Dent, J. B., and Heal, O. W.: Modeling methane emissions from rice paddies, *Global Biogeochem. Cy.*, 9, 183–195, 1995.

- Cao, M. K., Gregson, K., and Marshall, S.: Global methane emission from wetlands and its sensitivity to climate change, *Atmos. Environ.*, 32, 3293–3299, 1998.
- Castaldi, S. and Fierro, A.: Soil-atmosphere methane exchange in undisturbed and burned Mediterranean shrubland of Southern Italy, *Ecosystems*, 8, 182–190, 2005.
- Chapuis-Lardy, L., Wrage, N., Metay, A., Chotte, J. L., and Bernoux, M.: Soils, a sink for N₂O? A review, *Global Change Biol.*, 13, 1–17, doi:10.1111/j.1365-2486.2006.01280.x, 2007.
- Chen, G., Tian, H., Liu, M., Ren, W., Zhang, C., and Pan, S.: Climate impacts on China's terrestrial carbon cycle: an assessment with the dynamic land ecosystem model, in: *Environmental Modelling and Simulation*, edited by: Tian, H. Q., ACTA Press, Anaheim/Calgary/Zurich, 56–70, 2006.
- Chen, Y. H. and Prinn, R. G.: Estimation of atmospheric methane emissions between 1996 and 2001 using a three-dimensional global chemical transport model, *J. Geophys. Res.-Atmos.*, 111, D10307, doi:10.1029/2005JD006058, 2006.
- Christensen, T. R., Prentice, I. C., Kaplan, J. O., Haxeltine, A., and Sitch, S.: Methane flux from northern wetlands and tundra an ecosystem source modeling approach, *Tellus B*, 48, 652–661, 1996.
- Conrad, R.: Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O, and NO), *Microbiol. Rev.*, 60, 609–640, 1996.
- Curry, C. L.: Modeling the soil consumption of atmospheric methane at the global scale, *Global Biogeochem. Cy.*, 21, GB4012, doi:10.1029/2006GB002818, 2007.
- Davidson, E. A., Keller, M., Erickson, H. E., Verchot, L. V., and Veldkamp, E.: Testing a conceptual model of soil emissions of nitrous and nitric oxides, *Bioscience*, 50, 667–680, 2000.
- De Fries, R., Hansen, M., Townshend, J., and Sohlberg, R.: Global land cover classifications at 8 km spatial resolution: the use of training data derived from Landsat imagery in decision tree classifiers, *Int. J. Remote Sens.*, 19, 3141–3168, 1998.
- Del Grosso, S. J., Mosier, A. R., Parton, W. J., and Ojima, D. S.: DAYCENT model analysis of past and contemporary soil N₂O and net greenhouse gas flux for major crops in the USA, *Soil Till. Res.*, 83, 9–24, 2005.
- Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P. L., Wofsy, S. C., and Zhang, X.: Couplings between changes in the climate system and biogeochemistry, in: *Climate change 2007: The physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*, edited by: Solomon, S., Qin, D., Manning, M., and Chen, Z., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- Dentener, F., Drevet, J., Lamarque, J., Bey, I., Eickhout, B., Fiore, A., Hauglustaine, D., Horowitz, L., Krol, M., and Kulshrestha, U.: Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation, *Global Biogeochem. Cy.*, 20, GB4003, doi:10.1029/2005GB002672, 2006.
- Ding, W. X., Cai, Z. C., and Tsuruta, H.: Cultivation, nitrogen fertilization, and set-aside effects on methane uptake in a drained marsh soil in Northeast China, *Global Change Biol.*, 10, 1801–1809, 2004.
- Dise, N. B.: Methane emission from peatlands in Northern Minnesota, Ph.D., University of Minnesota, Minneapolis, 138 pp., 1991.
- Dobbie, K. E., Smith, K. A., Prieme, A., Christensen, S., Degorska, A., and Orlanski, P.: Effect of land use on the rate of methane uptake by surface soils in northern Europe, *Atmos. Environ.*, 30, 1005–1011, 1996.
- Dong, Y., Qi, Y., and Luo, J.: Experimental study on N₂O and CH₄ fluxes from the dark coniferous forest zone soil of Gongga Mountain, China, *Sci. China Ser. D*, 48, 285–295, 2003.
- Dörr, H., Katruff, L., and Levin, I.: Soil texture parameterization of the methane uptake in aerated soils, *Chemosphere*, 26, 697–713, 1993.
- Dusenbury, M. P., Engel, R. E., Miller, P. R., Lemke, R. L., and Wallander, R.: Nitrous Oxide Emissions from a Northern Great Plains Soil as Influenced by Nitrogen Management and Cropping Systems, *J. Environ. Qual.*, 37, 542–550, 2008.
- Dutaur, L. and Verchot, L. V.: A global inventory of the soil CH₄ sink, *Global Biogeochem. Cy.*, 21, GB4013, doi:10.1029/2006GB002734, 2007.
- Felzer, B., Reilly, J., Melillo, J., Kicklighter, D., Sarofim, M., Wang, C., Prinn, R., and Zhuang, Q.: Future effects of ozone on carbon sequestration and climate change policy using a global biogeochemical model, *Climatic Change*, 73, 345–373, doi:10.1007/s10584-005-6776-4, 2005.
- Ferenci, T., Strom, T., and Quayle, J. R.: Oxidation of carbon monoxide and methane by *Pseudomonas methanica*, *Microbiology*, 91, 79–91, 1975.
- Forster, P., Ramaswamy, V., Artaxo, P., Bernsten, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, N. R., Raga, G., Schulz, M., and Dorland, R. V.: Changes in atmospheric constituents and in radiative forcing, in: *Climate change 2007: The physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*, edited by: Solomon, S., Qin, D., Manning, M., and Chen, Z., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- Garcia-Montiel, D. C., Melillo, J. M., Steudler, P. A., Neill, C., Feigl, B. J., and Cerri, C. C.: Relationship between N₂O and CO₂ emissions from the Amazon Basin, *Geophys. Res. Lett.*, 29, 1090, doi:10.1029/2002GL013830, 2002.
- Garcia-Ruiz, R., Pattinson, S. N., and Whitton, B. A.: Kinetic parameters of denitrification in a river continuum, *Appl. Environ. Microbiol.*, 64, 2533–2538, 1998.
- Goldberg, S. D. and Gebauer, G.: Drought turns a Central European Norway spruce forest soil from an N₂O source to a transient N₂O sink, *Global Change Biol.*, 15, 850–860, doi:10.1111/j.1365-2486.2008.01752.x, 2009.
- Groffman, P. M., Hardy, J. P., Driscoll, C. T., and Fahey, T. J.: Snow depth, soil freezing and trace gas fluxes in a northern hardwood forest, *Global Change Biol.*, 15, 850–860, 2006.
- Groffman, P. M., Hardy, J. P., Fisk, M. C., Fahey, T. J., and Driscoll, C. T.: Climate variation and soil carbon and nitrogen cycling processes in a northern hardwood forest, *Ecosystems*, 12, 927–943, 2009.
- Guilbault, M. R. and Matthias, A. D.: Emissions of N₂O from Sonoran Desert and effluent-irrigated grass ecosystems, *J. Arid Environ.*, 38, 87–98, 1998.

- Happell, J. D. and Chanton, J. P.: Methane transfer across the water-air interface in stagnant wooded swamps of Florida: Evaluation of mass-transfer coefficients and isotopic fractionation, *Limnol. Oceanogr.*, 40, 290–298, 1995.
- Harrison, D. E. F.: Studies on the affinity of methanol- and methane-utilising bacteria for their carbon substrates, *J. Appl. Bacteriol.*, 36, 301–308, 1973.
- Hein, R., Crutzen, P., and Heimann, M.: An inverse modeling approach to investigate the global atmospheric methane cycle, *Global Biogeochem. Cy.*, 11, 43–76, 1997.
- Hirsch, A. I., Michalak, A. M., Bruhwiler, L. M., Peters, W., Dlugokencky, E. J., and Tans, P. P.: Inverse modeling estimates of the global nitrous oxide surface flux from 1998–2001, *Global Biogeochem. Cy.*, 20, GB1008, doi:10.1029/2004GB002443, 2006.
- Huang, B., Chen, G., Huang, G., and Hauro, T.: Nitrous oxide emission from temperate meadow grassland and emission estimation for temperate grassland of China, *Nutr. Cycl. Agroecosys.*, 67, 31–36, 2003.
- Huang, Y., Sass, R. L., and Fisher, F. M.: A semi-empirical model of methane emission from flooded rice paddy soils, *Global Change Biol.*, 4, 247–268, 1998.
- Huang, Y., Sun, W., Zhang, W., Yu, Y., Su, Y., and Song, C.: Marshland conversion to cropland in northeast China from 1950 to 2000 reduced the greenhouse effect, *Global Change Biol.*, 16, 680–695, doi:10.1111/j.1365-2486.2009.01976.x, 2010.
- Hutchins, P. R., Press, M. C., Lee, J. A., and Ashenden, T. W.: Elevated concentrations of CO₂ may double methane emissions from mires, *Global Change Biol.*, 1, 125–128, 1995.
- Joergensen, L.: The methane mono-oxygenase reaction system studied in vivo by membrane-inlet mass spectrometry, *Biochem. J.*, 225, 441–448, 1985.
- Kanerva, T., Regina, K., Rämö, K., Ojanperä, K., and Manninen, S.: Fluxes of N₂O, CH₄ and CO₂ in a meadow ecosystem exposed to elevated ozone and carbon dioxide for three years, *Environ. Pollut.*, 145, 818–828, 2007.
- Kellner, E., Waddington, J. M., and Price, J. S.: Dynamics of biogenic gas bubbles in peat: potential effects on water storage and peat deformation, *Water Resour. Res.*, 41, W08417, doi:10.1029/2004WR003732, 2005.
- Kessavalou, A., Mosier, A. R., Doran, J. W., Drijber, R. A., Lyon, D. J., and Heinemeyer, O.: Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat-fallow tillage management, *J. Environ. Qual.*, 27, 1094–1104, 1998.
- Kettunen, A.: Connecting methane fluxes to vegetation cover and water table fluctuations at microsite level: a modeling study, *Global Biogeochem. Cy.*, 17, 1051, doi:10.1029/2002GB001958, 2003.
- Kim, D.-H., Matsuda, O., and Yamamoto, T.: Nitrification, denitrification and nitrate reduction rates in the sediment of Hiroshima Bay, Japan, *J. Oceanogr.*, 53, 317–324, 1997.
- Kort, E. A., Eluszkiewica, J., Stephens, B. B., Miller, J. B., Gerbig, C., Nehrkorn, T., Daube, B. C., Kaplan, J. O., Houweling, S., and Wofsy, S. C.: Emissions of CH₄ and N₂O over the United States and Canada based on a receptor-oriented modeling framework and COBRA-NA atmospheric observations, *Geophys. Res. Lett.*, 35, L18808, doi:10.1029/2008GL034031, 2008.
- Koschorreck, M. and Conrad, R.: Oxidation of atmospheric methane in soil: measurements in the field, in soil cores and in soil samples, *Global Biogeochem. Cy.*, 7, 109–121, 1993.
- Lamb, S. C. and Garver, J. C.: Interspecific interactions in a methane-utilizing mixed culture, *Biotechnol. Bioeng.*, 22, 2119–2135, 1980.
- Lehner, B. and Döll, P.: Development and validation of a global database of lakes, reservoirs and wetlands, *J. Hydrol.*, 296, 1–22, 2004.
- Li, C. S., Narayanan, V., and Harriss, R. C.: Model estimates of nitrous oxide emissions from agricultural lands in the United States, *Global Biogeochem. Cy.*, 10, 297–306, 1996.
- Lin, B. H., Sakoda, A., Shibasaki, R., Goto, N., and Suzuki, M.: Modeling a global biogeochemical nitrogen cycle in terrestrial ecosystems, *Ecol. Modell.*, 135, 89–110, 2000.
- Linton, J. D. and Buckee, D. C.: Interaction in a methane-utilizing mixed bacterial culture in a chemostat, *J. Gen. Microbiol.*, 101, 219–225, 1977.
- Liu, L. and Greaver, T.: A review of nitrogen enrichment effects on three biogenic GHGs: the CO₂ sink may be largely offset by stimulated N₂O and CH₄ emission, *Ecol. Lett.*, 12, 1103–1117, 2009.
- Liu, M., Tian, H., Chen, G., Ren, W., Zhang, C., and Liu, J.: Effects of land-use and land-cover change on evapotranspiration and water yield in China during 1900–2000, *J. Am. Water Resour. Assoc.*, 44, 1193–1207, 2008.
- Liu, Y.: Modeling the emissions of nitrous oxide (N₂O) and methane (CH₄) from the terrestrial biosphere to the atmosphere, Doctor of Philosophy in Global Change Science, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Boston, 1996.
- Livesley, S. J., Kiese, R., Miehle, P., Weston, C. J., Butterbach-Bahl, K., and Arndt, S. K.: Soil-atmosphere exchange of greenhouse gases in a *Eucalyptus marginata* woodland, a clover-grass pasture, and *Pinus radiata* and *Eucalyptus globules* plantations, *Global Change Biol.*, 15, 425–440, 2009.
- Lokshina, L. Y., Vavilin, V. A., Kettunen, R. H., Rintala, J. A., Hølliger, C., and Nozhevnikova, A. N.: Evaluation of kinetic coefficients using integrated Monod and Haldane models for low-temperature acetoclastic methanogenesis, *Water Res.*, 35, 2913–2922, 2001.
- Lu, C.: Atmospheric nitrogen deposition and terrestrial ecosystem carbon cycle in China, Dissertation, Doctor of Philosophy, Chinese Academy of Sciences, Beijing, 2009.
- Martikainen, P. J., Nykänen, H., Crill, P., and Silvola, J.: Effect of a lowered water table on nitrous oxide fluxes from northern peatlands, *Nature*, 366, 51–53, 1993.
- Matson, A. L.: Greenhouse gas exchange and nitrogen cycling in Saskatchewan boreal forest soils, Master, Department of Soil Science, University of Saskatchewan, Saskatoon, 98 pp., 2008.
- McGuire, A., Sitch, S., Clein, J., Dargaville, R., Esser, G., Foley, J., Heimann, M., Joos, F., Kaplan, J., and Kicklighter, D.: Carbon balance of the terrestrial biosphere in the twentieth century: Analyses of CO₂, climate and land use effects with four process-based ecosystem models, *Global Biogeochem. Cy.*, 15, 183–206, 2001.
- Mer, J. L. and Roger, P.: Production, oxidation, emission and consumption of methane by soils: a review, *Eur. J. Soil Biol.*, 37, 25–50, 2001.
- Mitsch, W. J. and Gosselink, J. G.: *Wetlands*, 4th edition, John Wiley & Sons, Inc., New York, 2007.

- Moosavi, S. C., Crill, P. M., Pullman, E. R., Funk, D. W., and Peterson, K. M.: Controls on CH₄ flux from an Alaskan boreal wetland, *Global Biogeochem. Cy.*, 10, 287–296, 1996.
- Morsky, S., Haapala, J. K., Rinnan, R. A., Tiiva, P., Saarnio, S., Silvola, J., Holopainen, T., and Martikainen, P. J.: Long-term ozone effects on vegetation, microbial community and methane dynamics of boreal peatland microcosms in open-field conditions, *Global Change Biol.*, 14, 1891–1903, doi:10.1111/j.1365-2486.2008.01615.x, 2008.
- Mosier, A. R., Klemetsson, L. K., Sommerfeld, R. A., and Muselman, R. C.: Methane and nitrous oxide flux in a Wyoming subalpine meadow, *Global Biogeochem. Cy.*, 7, 771–784, 1993.
- Mosier, A. R., Parton, W. J., Valentine, D. W., Ojima, D. S., Schimel, D. S., and Delgado, J. A.: CH₄ and N₂O fluxes in the Colorado shortgrass steppe: 1. Impact of landscape and nitrogen addition, *Global Biogeochem. Cy.*, 10, 387–399, 1996.
- Mosier, A. R., Duxbury, J. M., Freney, J. R., Heinemeyer, O., Minami, K., and Johnson, D. E.: Mitigating agricultural emissions of methane, *Climatic Change*, 40, 39–80, 1998.
- Mosier, A. R., Morgan, J. A., King, J. Y., LeCain, D., and Milchunas, D. G.: Soil-atmosphere exchange of CH₄, CO₂, NO_x, and N₂O in the Colorado shortgrass steppe under elevated CO₂, *Plant Soil*, 240, 201–211, 2002.
- Mummey, D. L., Smith, J. L., and Bolton, H.: Small-scale spatial and temporal variability of N₂O flux from a shrub-steppe ecosystem, *Soil Biol. Biochem.*, 29, 1699–1706, 1997.
- Nagai, S., Mori, T., and Aiba, S.: Investigation of the energetics of methane-utilizing bacteria in methane- and oxygen-limited chemostat cultures, *J. Appl. Biotechnol.*, 27, 893–903, 1973.
- Nedwell, D. B. and Watson, A. J.: CH₄ production, oxidation and emission in a UK ombrotrophic peat bog: Influence of SO₄²⁻ from acid rain, *Soil Biol. Biochem.*, 23, 549–562, 1995.
- O'Neill, J. G. and Wilkenson, J. F.: Oxidation of ammonia by methane-oxidizing bacteria and the effects of ammonia on methane oxidation, *J. Gen. Microbiol.*, 100, 407–412, 1977.
- Phillips, R., Whalen, S., and Schlesinger, W.: Influence of atmospheric CO₂ enrichment on nitrous oxide flux in a temperate forest ecosystem, *Global Biogeochem. Cy.*, 15, 741–752, 2001a.
- Phillips, R. L., Whalen, S. C., and Schlesinger, W. H.: Influence of atmospheric CO₂ enrichment on methane consumption in a temperate forest soil, *Global Change Biol.*, 7, 557–563, 2001b.
- Potter, C. S., Matson, P. A., Vitousek, P. M., and Davidson, E. A.: Process modeling of controls on nitrogen trace gas emissions from soils worldwide, *J. Geophys. Res.*, 101, 1361–1377, 1996.
- Potter, C. S.: An ecosystem simulation model for methane production and emission from wetlands, *Global Biogeochem. Cy.*, 11, 495–506, 1997.
- Potter, C. S., Klooster, S., Hiatt, S., Fladeland, M., Genovese, V., and Cross, P.: Methane emissions from natural wetlands in the United States: satellite-derived estimation based on ecosystem carbon cycling, *Earth Interact.*, 10, Paper 10-022, 2006.
- Ren, W., Tian, H., Chen, G., Liu, M., Zhang, C., Chappelka, A. H., and Pan, S.: Influence of ozone pollution and climate variability on net primary productivity and carbon storage in China's grassland ecosystems from 1961 to 2000, *Environ. Pollut.*, 149, 327–335, doi:10.1016/j.envpol.2007.05.029, 2007a.
- Ren, W., Tian, H., Liu, M., Zhang, C., Chen, G., Pan, S., Felzer, B., and Xu, X.: Effects of tropospheric ozone pollution on net primary productivity and carbon storage in terrestrial ecosystems of China, *J. Geophys. Res.-Atmos.*, 112, D22S09, doi:10.1029/2007jd008521, 2007b.
- Ren, W.: Effects of Ozone Pollution and Climate Variability/Change on Spatial and Temporal Patterns of Terrestrial Primary Productivity and Carbon Storage in China, Dissertation, Doctor of Philosophy, School of Forestry and Wildlife Science, Auburn University, Auburn, 202 pp., 2009.
- Ricciuto, D. M., Davis, K. J., and Keller, K.: A Bayesian calibration of a simple carbon cycle model: the role of observations in estimating and reducing uncertainty, *Global Biogeochem. Cy.*, 22, GB2030, doi:10.1029/2006GB002908, 2008.
- Ridgwell, A. J., Marshall, S. J., and Gregson, K.: Consumption of atmospheric methane by soils: a process-based model, *Global Biogeochem. Cy.*, 13, 59–70, 1999.
- Riedo, M., Grub, A., Rosset, M., and Fuhrer, J.: A pasture simulation model for dry matter production, and fluxes of carbon, nitrogen, water and energy, *Ecol. Modell.*, 105, 141–183, 1998.
- Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L., Huang, J., Cunnold, D. M., Steele, L. P., Krummel, P. B., Weiss, R. F., O'Doherty, S., Salameh, P. K., Wang, H. J., Harth, C. M., Muhle, J., and Porter, L. W.: Renewed growth of atmospheric methane, *Geophys. Res. Lett.*, 35, L22805, doi:10.1029/2008GL036037, 2008.
- Robert, C. and Casella, G.: Monte Carlo statistical methods, Springer Verlag, 2005.
- Saari, A., Rinnan, R. A., and Martikainen, P. J.: Methane oxidation in boreal forest soils: kinetics and sensitivity to pH and ammonium, *Soil Biol. Biochem.*, 36, 1037–1046, 2004.
- Schimel, D., Melillo, J. M., Tian, H., McGuire, A. D., Kicklighter, D. W., Kittel, T., Rosenbloom, N., Running, S., Thornton, P., and Ojima, D.: Contribution of increasing CO₂ and climate to carbon storage by ecosystems in the United States, *Science*, 287, 2004–2006, 2000.
- Schrope, M. K., Chanton, J. P., Allen, L. H., and Baker, T. J.: Effect of CO₂ enrichment and elevated temperature on methane emissions from rice, *Oryza sativa*, *Global Change Biol.*, 5, 587–599, 1999.
- Segers, R.: Methane production and methane consumption: a review of processes underlying wetland methane fluxes, *Biogeochemistry*, 41, 23–51, 1998.
- Sheibley, R. W., Jackman, A. P., Duff, J. H., and Triska, F. J.: Numerical modeling of coupled nitrification – denitrification in sediment perfusion cores from the hyporheic zone of the Shingobee River, MN, *Adv. Water Resour.*, 26, 977–987, 2003.
- Sheldon, A. I. and Barnhart, E. P.: Nitrous oxide emissions research progress, Environmental science, engineering, and technology, Nova Science Publishers, Hauppauge, NY, 2009.
- Shoemaker, J. K. and Schrag, D. P.: Subsurface characterization of methane production and oxidation from a New Hampshire wetland, *Geobiology*, 8, 234–243, doi:10.1111/j.1472-4669.2010.00239.x, 2010.
- Sitaula, B. K., Bakken, L. R., and Abrahamsen, G.: CH₄ uptake by temperate forest soil: effect of N input and soil acidification, *Soil Biol. Biochem.*, 27, 871–880, 1995.
- Smith, W. N., Grant, B., Desjardins, R. L., Lemke, R., and Li, C.: Estimates of the interannual variations of N₂O emissions from agricultural soils in Canada, *Nutr. Cycl. Agroecosys.*, 68, 37–45, 2004.

- Sommerfeld, R. A., Mosier, A. R., and Musselman, R. C.: CO₂, CH₄ and N₂O flux through a Wyoming snowpack and implications for global budgets, *Nature*, 361, 140–142, 1993.
- Song, C., Xu, X., Tian, H., and Wang, Y.: Ecosystem-atmosphere exchange of CH₄ and N₂O and ecosystem respiration in wetlands in the Sanjiang Plain, Northeastern China, *Global Change Biol.*, 15, 692–705, 2009.
- Sorokin, D., Jones, B., and Gijs Kuenen, J.: An obligate methylo-trophic, methane-oxidizing Methylomicrobium species from a highly alkaline environment, *Extremophiles*, 4, 145–155, 2000.
- Starry, O. S., Valett, H. M., and Schreiber, M. E.: Nitrification rates in a headwater stream: influences of seasonal variation in C and N supply, *J. North Am. Benthol. Soc.*, 24, 753–768, 2005.
- Stuedler, P. A., Bowden, R. D., Melillo, J. M., and Aber, J. D.: Influence of nitrogen fertilization on methane uptake in temperate forest soils, *Nature*, 341, 314–316, 1989.
- Strack, M., Kellner, E., and Waddington, J. M.: Dynamics of biogenic gas bubbles in peat and their effects on peatland biogeochemistry, *Global Biogeochem. Cy.*, 19, GB1003, doi:10.1029/2004GB002330, 2005.
- Strieg, R. G., McConnaughey, T. A., Thorstenson, D. C., Weeks, E. P., and Woodward, J. C.: Consumption of atmospheric methane by desert soils, *Nature*, 357, 145–147, 1992.
- Tathy, J. P., Cros, B., Delmas, R. A., Marengo, A., Servant, J., and Labat, M.: Methane emission from flooded forest in Central Africa, *J. Geophys. Res.-Atmos.*, 97, 6159–6168, 1992.
- Tian, H., Liu, M., Zhang, C., Ren, W., Chen, G., Xu, X., and Lu, C.: DLEM-The Dynamic Land Ecosystem Model User Manual, Auburn, AL, USA, 2005.
- Tian, H., Xu, X., Zhang, C., Ren, W., Chen, G., Liu, M., Lu, D., and Pan, S.: Forecasting and assessing the large-scale and long-term impacts of global environmental change on terrestrial ecosystems in the United States and China, *Real world ecology: large-scale and long-term case studies and methods*, edited by: Miao, S., Carstenn, S., and Nungesser, M., Springer, New York, 2008.
- Tian, H., Chen, G., Liu, M., Zhang, C., Sun, G., Lu, C., Xu, X., Ren, W., Pan, S., and Chappelka, A.: Model estimates of net primary productivity, evapotranspiration, and water use efficiency in the terrestrial ecosystems of the southern United States during 1895–2007, *Forest Ecol. Manage.*, 259, 1311–1327, 2010.
- Tokida, T., Miyazaki, T., Mizoguchi, M., Nagata, O., Takakai, F., Kagemoto, A., and Hatano, R.: Falling atmospheric pressure as a trigger for methane ebullition from peatland, *Global Biogeochem. Cy.*, 21, GB2003, doi:10.1029/2006GB002790, 2007.
- Tueut, L., Somerville, H. R., Cubasch, U., Ding, Y., Mauritzen, C., Mokssit, A., Peterson, T., and Prather, M.: Historical overview of climate change science, in: *Climate change 2007: The physical science basis*, Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change, edited by: Solomon, S., Qin, D., Manning, M., and Chen, Z., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- Walter, B. P., Heimann, M., and Matthews, E.: Modeling modern methane emissions from natural wetlands 1. model description and results, *J. Geophys. Res.*, 106, 34189–34206, 2001.
- Wang, X., Yang, S., Mannaerts, C. M., Gao, Y., and Guo, J.: Spatially explicit estimation of soil denitrification rates and land use effects in the riparian buffer zone of the large Guanting reservoir, *Geoderma*, 150, 240–252, 2009.
- Whalen, S. C., Reeburgh, W. S., and Kizer, K. S.: Methane consumption and emission by taiga, *Global Biogeochem. Cy.*, 5, 261–273, 1991.
- Willison, T. W., Couilding, K. W. T., and Powlson, D. S.: Effect of land-use change and methane mixing ratio on methane uptake from United Kingdom soil, *Global Change Biol.*, 1, 209–212, 1995.
- Wofsy, S. C. and Harriss, R. C.: The North American Carbon Program (NACP). Report of the NACP Committee of the U.S. Interagency Carbon Cycle Science Program, US Global Change Research Program, Washington, DC, 2002.
- Xiao, D., Wang, M., Wang, Y., Ji, L., and Han, S.: Fluxes of soil carbon dioxide, nitrous oxide and firedamp in broadleaved/Korean pine forest, *J. Forest Res.*, 15, 107–112, 2004.
- Xu, X., Tian, H., and Hui, D.: Convergence in the relationship of CO₂ and N₂O exchanges between soil and atmosphere within terrestrial ecosystems, *Global Change Biol.*, 14, 1651–1660, doi:10.1111/j.1365-2486.2008.01595.x, 2008.
- Xu, X.: Modeling methane exchange between the atmosphere and marshland over China during 1949–2008: magnitude, spatiotemporal distribution and attribution, Dissertation, Doctor of Philosophy, Chinese Academy of Sciences, Beijing, 144 pp. 2010.
- Yamamoto, S., Alcauskas, J. B., and Crozier, T. E.: Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, 21, 78–80, 1976.
- Yu, K., DeLaune, R. D., and Boeckx, P.: Direct measurement of denitrification activity in a Gulf coast freshwater marsh receiving diverted Mississippi River water, *Chemosphere*, 65, 2449–2455, 2006.
- Zhang, C., Tian, H., Chappelka, A., Ren, W., Chen, H., Pan, S., Liu, M., Styers, D., Chen, G., and Wang, Y.: Impacts of climatic and atmospheric changes on carbon dynamics in the Great Smoky Mountains National Park, *Environ. Pollut.*, 149, 336–347, 2007.
- Zhang, C.: Terrestrial carbon dynamics of southern United States in response to changes in climate, atmosphere, and land-use/land cover from 1895 to 2005, Dissertation, Doctor of Philosophy, School of Forestry and Wildlife Sciences, Auburn University, Auburn, 248 pp., 2008.
- Zhuang, Q., Melillo, J. M., Kicklighter, D. W., Prinn, R. G., McGuire, A. D., Stuedler, P. A., Felzer, B. S., and Hu, S.: Methane fluxes between terrestrial ecosystems and the atmosphere at northern high latitudes during the past century: A retrospective analysis with a process-based biogeochemistry model, *Global Biogeochem. Cy.*, 18, GB3010, doi:10.1029/2004GB002239, 2004.
- Zhuang, Q., Melillo, J. M., McGuire, A. D., Kicklighter, D. W., Prinn, R. G., Stuedler, P. A., Felzer, B. S., and Hu, S.: Net emissions of CH₄ and CO₂ in Alaska: Implications for the region's greenhouse gas budget, *Ecol. Appl.*, 17, 203–212, 2007.