2015

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AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE
10.1002/2014JG002763

Special Section:
Carbon and Nitrogen Fluxes at the Land-Ocean Interface

Key Points:
- Nitrogen export from eastern North America increased from 1901 to 2008
- Climate determined the interannual variability of nitrogen export
- Enhanced nitrogen export was mainly contributed by increased nitrogen input

Supporting Information:
- Supporting Information S1

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Citation:
Yang, Q., H. Tian, M. A. M. Friedrichs, C. S. Hopkinson, C. Lu, and R. G. Najjar (2015), Increased nitrogen export from eastern North America to the Atlantic Ocean due to climatic and anthropogenic changes during 1901–2008, *J. Geophys. Res. Biogeosci.*, *120*, 1046–1068, doi:10.1002/2014JG002763.

Received 1 AUG 2014
Accepted 11 MAY 2015
Accepted article online 19 MAY 2015
Published online 10 JUN 2015

Increased nitrogen export from eastern North America to the Atlantic Ocean due to climatic and anthropogenic changes during 1901–2008

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Abstract We used a process-based land model, Dynamic Land Ecosystem Model 2.0, to examine how climatic and anthropogenic changes affected riverine fluxes of ammonium (NH_4^+), nitrate (NO_3^-), dissolved organic nitrogen (DON), and particulate organic nitrogen (PON) from eastern North America, especially the drainage areas of the Gulf of Maine (GOM), Mid-Atlantic Bight (MAB), and South Atlantic Bight (SAB) during 1901–2008. Model simulations indicated that annual fluxes of NH_4^+, NO_3^-, DON, and PON from the study area during 1980–2008 were 0.019 ± 0.003 (mean ± 1 standard deviation) Tg N yr^{-1}, 0.18 ± 0.035 Tg N yr^{-1}, 0.10 ± 0.016 Tg N yr^{-1}, and 0.043 ± 0.008 Tg N yr^{-1}, respectively. NH_4^+, NO_3^-, and DON exports increased while PON export decreased from 1901 to 2008. Nitrogen export demonstrated substantial spatial variability across the study area. Increased NH_4^+ export mainly occurred around major cities in the MAB. NO_3^- export increased in most parts of the MAB but decreased in parts of the GOM. Enhanced DON export was mainly distributed in the GOM and the SAB. PON export increased in coastal areas of the SAB and northern parts of the GOM but decreased in the Piedmont areas and the eastern parts of the MAB. Climate was the primary reason for interannual variability in nitrogen export; fertilizer use and nitrogen deposition tended to enhance the export of all nitrogen species; livestock farming and sewage discharge were also responsible for the increases in NH_4^+ and NO_3^- fluxes; and land cover change (especially reforestation of former agricultural land) reduced the export of the four nitrogen species.

1. Introduction

Enhanced nitrogen (N) export from land to rivers, estuaries, and other coastal waters has raised considerable environmental and human health concerns over recent decades [*Alvarez-Cobelas et al.*, 2008; *Jensen and Skop*, 1998; *Pinder et al.*, 2012; *Townsend et al.*, 2003]. In order to meet increasing food demands, nitrogen fertilizers have been widely used worldwide since the 1950s. Application of chemically synthesized nitrogen fertilizers together with other human activities such as urban sewage water discharge, livestock farming, and nitrogen deposition have substantially altered nitrogen cycling and caused eutrophication in aquatic ecosystems [*Galloway et al.*, 2008; *Li et al.*, 2012; *Maupin and Ivahnenko*, 2011].

In eastern North America, excessive nitrogen export is the major factor contributing to hypoxia in coastal waters [*Canton et al.*, 2010; *Jordan et al.*, 1997; *Kauffman et al.*, 2011]. However, the long-term trends and interannual variability of riverine fluxes for multiple nitrogen species, and the underlying mechanisms controlling nitrogen export across this region have not been fully investigated. An integrative understanding of how nitrogen export is regulated by climate and anthropogenic activity will provide valuable information for nutrient management and pollution mitigation in densely populated regions such as eastern North America.

Although significant efforts have been devoted to investigating nitrogen export from land to rivers and eventually to coastal waters, our understanding of the mechanisms controlling nitrogen transformation and transport at the terrestrial-aquatic interface are limited by scarce observational data and overly simplified model representations of the terrestrial nitrogen cycle [*Alvarez-Cobelas et al.*, 2008; *Goolsby et al.*, 2000]. Methodologies investigating nitrogen export can be generally categorized into three types: field observations, input-output analyses, and process-based modeling. Field observations have provided reliable nitrogen export estimates [*Howden et al.*, 2010; *Raymond et al.*, 2012]. For example, water quality data provided by the U.S. Geological Survey (USGS) gauge stations have made it possible to explore the spatial and temporal variability of riverine nitrogen fluxes in the U.S. [*Trench et al.*, 2011]. However, application of this method is directly limited by the availability and integrity of field data. Along eastern North America, there are still large, ungauged areas that make it difficult to conduct a comprehensive assessment of material export [*Stets and Striegl*, 2012]. Input-output analyses of nitrogen, which link nitrogen sources and export at watershed scales, have provided some insights into the factors controlling nitrogen export [*Hong et al.*, 2013]. One example of this type of export study is the Net Anthropogenic Nitrogen Input (NANI) methodology, which considers all nitrogen sources including nitrogen fixation through leguminous plants, wet and dry nitrogen deposition, nitrogen fertilizer use, and nitrogen input through food supply [*Boyer et al.*, 2006; *Howarth et al.*, 2006]. Significant correlations have been widely identified between NANI and nitrogen export over watersheds characterized by different climate conditions, geographical settings, and intensities of human activity, indicating that nitrogen input is a major factor controlling nitrogen export. However, the percentage of exported nitrogen to the total nitrogen input varied significantly over different river basins, suggesting that additional variables such as climate factors, hydrological conditions, and the underlying mechanisms regulating N export must be further explored to fully explain the variability of riverine nitrogen fluxes [*Alexander et al.*, 2002; *Hong et al.*, 2012; *Swaney et al.*, 2012]. Over recent decades, a variety of numerical models with different structures, representations of nitrogen cycling, and hydrological modules have been developed to simulate nitrogen export [*Drewry et al.*, 2006; *Dumont*, 2005; *Moore et al.*, 2011]. These models have provided useful information for identifying nitrogen sources and assessing the influence of anthropogenic activity on nitrogen export [*Alexander et al.*, 2008; *Sobota et al.*, 2009]. However, most current nitrogen export models have simple representations of the terrestrial nitrogen processes, such as nitrogen uptake, nitrogen mineralization, nitrification, and denitrification [*Canton et al.*, 2010; *Seitzinger et al.*, 2010]. Insufficient consideration of these critical processes may have hindered our understanding of mechanisms controlling nitrogen export [*Bernal et al.*, 2012].

Previous studies have tried to quantify nitrogen export from eastern North America to the Atlantic Ocean [*Alexander et al.*, 2002; *Canton et al.*, 2010; *Howarth et al.*, 2006; *Schaefer and Alber*, 2007]. However, the spatial and temporal variability of nitrogen export, as well as the impacts of multiple driving forces, have not yet been adequately addressed. An improved understanding of how human activities and climate factors have interactively affected nitrogen export from this area will contribute to water quality control and management of excessive nutrients in coastal regions. A comprehensive investigation of nitrogen export from this region will also be critical for exploring how biogeochemical processes in estuaries, such as the Chesapeake Bay and the Delaware Bay, have varied with time [*Castro et al.*, 2003; *Russell et al.*, 2008].

In this study, we applied a fully distributed land ecosystem model to investigate nitrogen export from eastern North America. Objectives of this study include (1) investigating temporal and spatial variability of nitrogen export to the East Coast of North America and (2) exploring the contributions of different driving forces on the variability of nitrogen export. The driving forces we considered in this study include climate, land cover, atmospheric CO_2 concentration, atmospheric nitrogen deposition, manure nutrient production, cropland management practices (irrigation and nitrogen fertilizer use), and human population growth.

2. Study Area

Our eastern North America study domain extends from Nova Scotia, Canada to southern Florida, U.S. (Figure 1), which has an area of 870,000 km^2 (about 9.9% of the U.S. land area) and a population over 84 million in 2010 (about 27.2% of the U.S. population). We partition the region into the watersheds of the three major coastal regions: the Gulf of Maine (GOM), Mid-Atlantic Bight (MAB), and South Atlantic Bight (SAB), which make up 22%, 42%, and 36% of eastern North America. As one of the most densely populated and urbanized areas in the U.S., land cover of this region has experienced great changes due to cropland abandonment since 1901 and intensifying urbanization over the past several decades. Climate factors (e.g., precipitation and temperature) have demonstrated divergent spatial patterns throughout the southern and northern areas of this region [*Yang et al.*, 2015]. Enhanced nitrogen input through nitrogen fertilizer use, atmospheric deposition, livestock farming, and urban sewage water discharge has

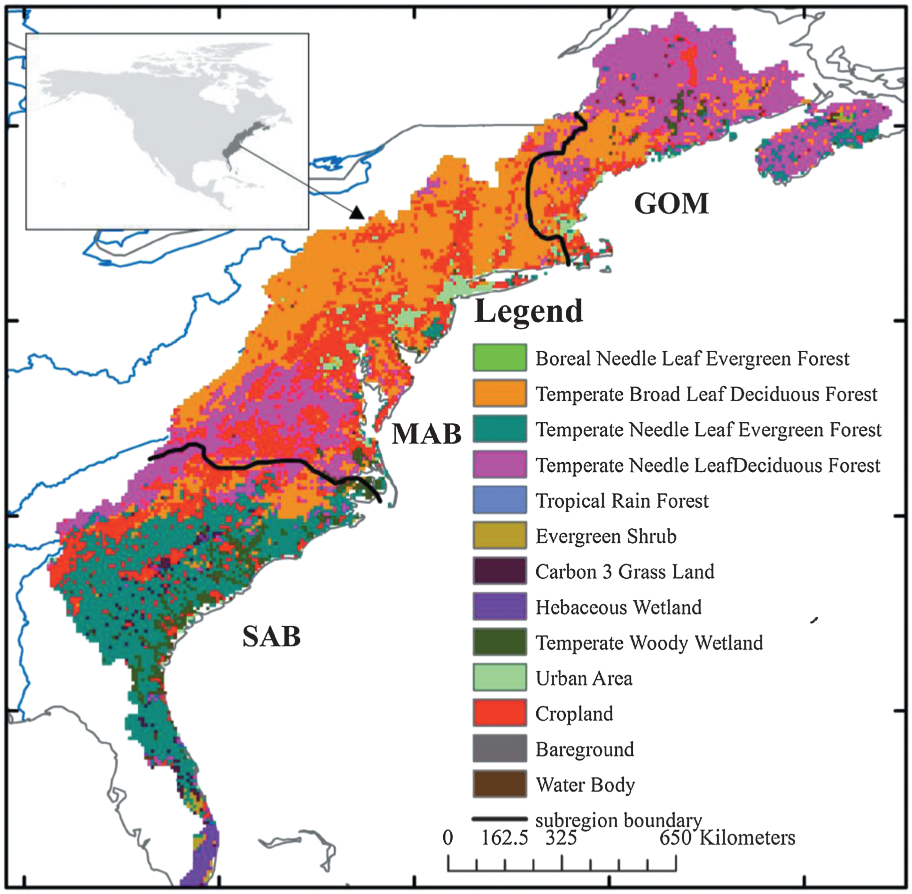


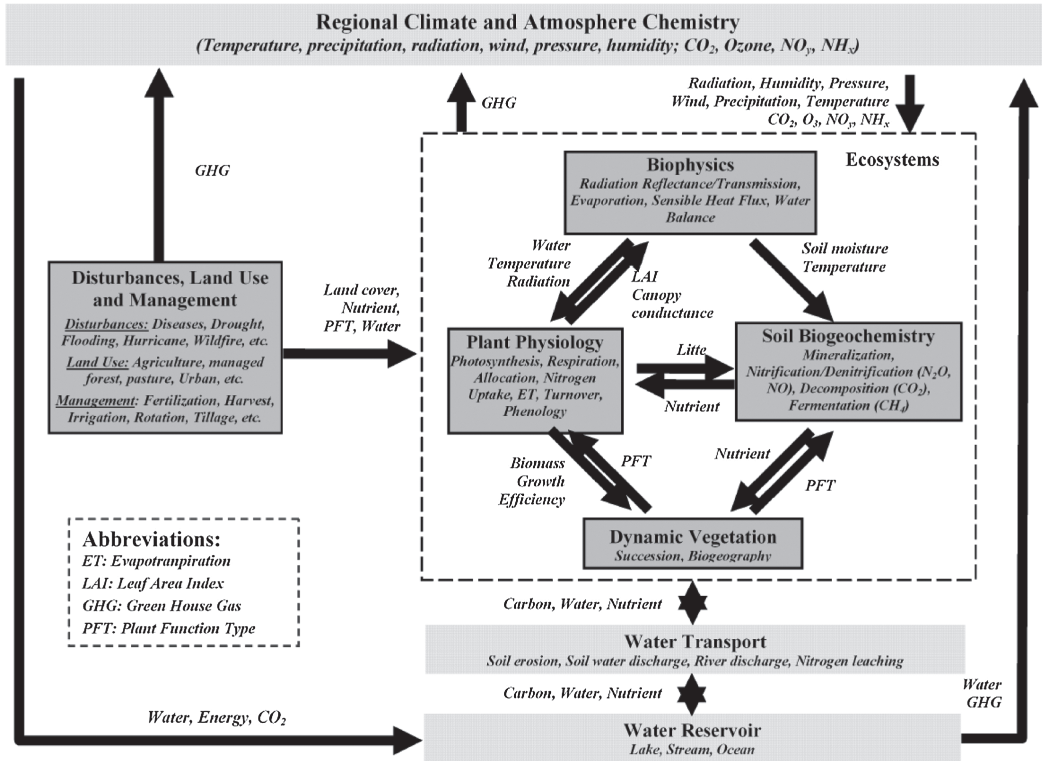
Figure 1. Location and land use types in eastern North America in 2005. Watersheds of the Gulf of Maine (GOM), Mid-Atlantic Bight (MAB), and South Atlantic Bight (SAB) are also delineated.

dramatically enhanced nitrogen delivery from land to coastal waters [*Boyer et al*., 2002]. Changes in natural and anthropogenic driving forces and responses in nitrogen export have made this area a good test bed for investigating riverine nitrogen fluxes in the context of multiple environmental changes.

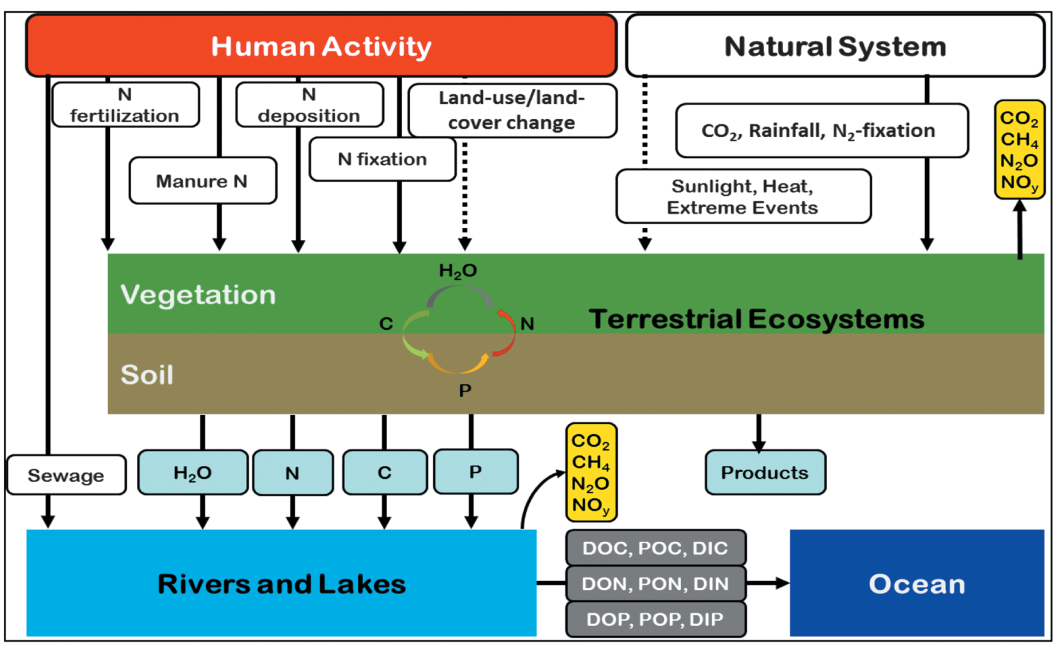
3. Model Introduction

This study uses version 2.0 of the Dynamic Land Ecosystem Model (DLEM 2.0). This is a grid cell based, fully distributed model that couples major water cycle [*Liu et al*., 2012; *Tian et al*., 2011a], carbon cycle [*Chen et al*., 2012; *Tian et al*., 2011b, 2012a, 2014; *Tao et al*., 2013], nitrogen cycle [*Lu and Tian*, 2012; *Tian et al*., 2012b], phosphorus cycle, and vegetation dynamics to estimate fluxes of water, greenhouse gases, and multiple elements in terrestrial ecosystems, and has recently been used extensively in eastern North America [*Yang et al*., 2014, 2015; *Tian et al*., 2015]. The basic calculation unit in this study is a grid cell with a spatial resolution of 5×5 arc min, and the time step is daily. To account for subgrid-scale processes, we developed a cohort structure, which divides each grid cell into seven land covers, including vegetation cover, impervious surface, glacier, lake, stream, sea, and bare ground. In this section, we primarily focused on introducing how the nitrogen cycle is simulated in DLEM 2.0 at the terrestrial-aquatic interface (Figure 2).

In DLEM 2.0, we improved hydrological components of the model to simulate riverine water [*Liu et al*., 2013; *Tao et al*., 2014; *Yang et al*., 2014, 2015], carbon [*Tian et al*., 2015; *Ren et al*., 2015], and nutrient fluxes from terrestrial ecosystems to rivers and eventually to coastal oceans (Figure 2). Water pools in each grid cell include lake, stream, surface runoff pool, subsurface drainage pool, snowpack, and water intercepted by the vegetation canopy.



(A)



(B)

Figure 2. Framework of DLEM 2.0. (a) Major components and processes, (b) major natural and human driving forces and key biogeochemical fluxes (C: Carbon; N: Nitrogen; and P: phosphorus) along the terrestrial-aquatic interfaces.

In DLEM 2.0, we assumed that decomposition of organic nitrogen in soil occurs with the soil organic carbon decomposition. Detailed descriptions of how DLEM defines different soil organic pools and how decomposition rates are calculated can be found in *Tian et al*. [2015]. The rate of organic nitrogen decomposition is determined by soil organic carbon decomposition and the carbon-to-nitrogen ratios in soil organic pools.

Nitrification and denitrification are the two most important processes regulating soil NH_4^+ and nitrate NO_3^- content. In DLEM 2.0, nitrification is simulated as a function of soil temperature, soil moisture, and soil ammonium [*Chatskikh et al.*, 2005; *Petersen et al.*, 2005]:

$$N_{\mathrm{nit}} = k_{\mathrm{nit}} \times f(T_{\mathrm{soil}}) \times f(\mathrm{wfp}) \times S_{\mathrm{NH4}} \tag{1}$$

$$f(T_{\mathrm{soil}}) = 7.24 \times e^{-3.432+0.168\times T_{\mathrm{soil}}\times(1-0.5\times T/36.9)} \tag{2}$$

$$f(\mathrm{wfp}) = -12.904\times\mathrm{wfp}^4 + 17.651\times\mathrm{wfp}^3 + 5.5368\times\mathrm{wfp}^2 + 0.9975\times\mathrm{wfp} - 0.0243 \tag{3}$$

$$\mathrm{wfp} = \frac{\theta}{\theta_{\mathrm{sat}}} \tag{4}$$

where N_{nit} is the rate of nitrification (g N m^{-2} d^{-1}); k_{nit} is maximum fraction of soil NH_4^+ that could be potentially nitrified on a daily basis (10% d^{-1}); S_{NH4} is the soil NH_4^+ content (g N m^{-2}); $f(T_{\mathrm{soil}})$ is the function of soil temperature impact on nitrification (unitless); *f*(*wf*) is the soil moisture impact on nitrification (unitless); T_{soil} is soil temperature (°C); wfp is the percentage of soil pore space that is filled by water; and θ is soil water content (mm); and θ_{sat} is soil water content at field capacity (mm).

In the denitrification process, nitrate is converted to multiple nitrogen gases. In DLEM 2.0, the rate of denitrification rate is calculated as follows [*Chatskikh et al.*, 2005]:

$$N_{\mathrm{den}} = N_{\mathrm{pot_{den}}} \times f(T_{\mathrm{soil}}) \times f(wf) \times f(C_{\mathrm{NO_3}}) \tag{5}$$

$$N_{\mathrm{pot_{den}}} = (0.151 + 0.015\times P_{\mathrm{clay}})\times \mathrm{Rh} \times K_{\mathrm{den}} \tag{6}$$

$$f(wf) = 0.0116 + 1.36/\left(1 + e^{-\frac{\mathrm{wfp}-0.815}{0.0896}}\right) \tag{7}$$

$$f(C_{\mathrm{NO_3}}) = 1.17\, C_{\mathrm{NO_3}}/(32.7 + C_{\mathrm{NO_3}}) \tag{8}$$

$$C_{\mathrm{NO_3}} = S_{\mathrm{NO_3}}/\mathrm{BD_{soil}} \tag{9}$$

where N_{den} is the rate of denitrification (g N m^{-2} d^{-1}); $N_{\mathrm{pot\_den}}$ represents the maximum denitrification rate (g N m^{-2} d^{-1}); P_{clay} is the percentage of clay content (%); *Rh* is the soil respiration rate (g C m^{-2} d^{-1}) that is introduced in *Tian et al*. [2015]; $f(T_{\mathrm{soil}})$ is the soil temperature impact on denitrification (unitless), which is the same as that in equation (1); K_{den} is the potential denitrification rate (g N m^{-2} d^{-1}); *f*(*wf*) represents the soil water impact on denitrification (unitless); $f(C_{\mathrm{NO_3}})$ represents the effect of nitrate concentration on denitrification (unitless); $C_{\mathrm{NO_3}}$ is the concentration of soil NO_3^- (g N g^{-1} soil); $S_{\mathrm{NO_3}}$ is the NO_3^- content in the soil per unit area (g N m^{-2}); and $\mathrm{BD_{soil}}$ is the soil bulk density (g soil m^{-3}).

Exports of dissolved organic nitrogen (DON), NO_3^-, and NH_4^+ are simulated with

$$R_{\mathrm{lchn}} = \mathrm{SN} \times \mathrm{fflow} \times \frac{\mathrm{SNC}}{\mathrm{SNC} + \mathrm{lchb}_n} \tag{10}$$

where R_{lchn} is the export rate of the NO_3^-, NH_4^+, or DON (g N m^{-2} d^{-1}); fflow is the runoff coefficient for export (unitless); SNC is the concentration of NH_4^+, NO_3^-, or DON (g N g soil^{-1}); *SN* is the total amount of NH_4^+, NO_3^-, or DON in the soil (g N m^{-2}); l_{chbn} is the adsorption coefficient for different DON (*lchbdon*), NH_4^+ (*lchbnh4*), or NO_3^- (*lchbno3*) (g N g soil^{-1}). The soil concentrations of DON, NH4$^+$, and NO3$^-$ are given by

$$\mathrm{SNC} = \frac{\mathrm{SN}}{W_{\mathrm{soil}}} \tag{11}$$

where W_{soil} is the mass of soil per unit area in the upper 0.5 m of soil (g soil m^{-2}). The total amount of DON in the soil is computed as the product of the total amount of decomposed organic nitrogen N_{dec} (g N m^{-2} d^{-1}) and the fraction of decomposed organic N that is dissolvable ($f_{\mathrm{don-dec}}$):

$$\mathrm{SN} = N_{\mathrm{dec}} \times f_{\mathrm{don-dec}} \tag{12}$$

For NO_3^- and NH_4^+, SN is the total amount of available NO_3^- or NH_4^+ in the soil, respectively.

Finally, the runoff coefficient, fflow, is a function of the surface runoff q_{srun} (mm d^{-1}), the drainage runoff q_{drain} (mm d^{-1}), and the soil water content of a given day (θ, mm):

$$\text{fflow} = \frac{q_{srun} + q_{drain}}{\theta + q_{srun} + q_{drain}} \tag{13}$$

In DLEM 2.0, surface runoff refers to water fluxes over the land surface, whereas drainage runoff refers to lateral water movement in soils toward streams.

We assumed that PON export occurs during soil erosion. The soil erosion rate is calculated using the Modified Universal Soil Loss Equation erosion equation [*Williams and Berndt*, 1977]:

$$R_{lchpon} = T_{onc} \times R_{erosion} \tag{14}$$

$$T_{onc} = \frac{T_{on}}{W_{soil}} \tag{15}$$

where R_{lchpon} is the export rate of PON (g N m^{-2} d^{-1}); T_{onc} is the concentration of total organic N in the soil column (g N g soil^{-1}); T_{on} is the total organic N in the soil (g N m^{-2}); and $R_{erosion}$ is the soil erosion rate (g soil m^{-2} d^{-1}).

Routing of nitrogen fluxes along river channels follows the same method used for river discharge in *Yang et al*. [2015]. We assumed that decomposed organic N species (DON and PON) are converted to NH_4^+, while degraded inorganic nitrogen species are converted to nitrogen gases [*Peterson et al*., 2001]. We used first-order models to simulate the instream transformation processes. For example, the respiration rate of dissolved organic nitrogen, R_{don} (g N d^{-1}), is modeled as

$$R_{don} = \text{DON}_{ls} \times k_{don} \times (Q10)^{\frac{T-T_s}{10}} \tag{16}$$

where DON_{ls} is the amount of DON in lakes or streams in each grid cell (g N); k_{don} is the calibrated value used to represent the long-term average DON decomposition rate in lakes and rivers (d^{-1}); $Q10$ is the temperature coefficient of DON decomposition (2.0); T_s is the reference temperature (20°C); and T is the water temperature (°C). The latter is modeled as a function of air temperature, T_{air} (°C) [*Donner et al*., 2002; *Mohseni et al*., 1998]

$$T = 0.8 + \frac{25.4}{1 + e^{0.18\times(13.3 - T_{air})}} \tag{17}$$

Similarly, the decomposition of PON, R_{pon} (g N d^{-1}), is simulated with a first-order model as

$$R_{pon} = \text{PON}_{ls} \times k_{pon} \times (Q10)^{\frac{T-T_s}{10}} \tag{18}$$

where PON_{ls} is the amount of PON in lakes or streams in each grid cell (g N) and k_{pon} is the calibrated value used to represent the long-term average decomposition rate of PON in lakes and rivers (d^{-1}).

Removal of inorganic nitrogen species (NH_4^+ or NO_3^-) in rivers and lakes through denitrification and burial is simulated as using the lentic nitrogen removal model provided by [*Harrison et al*., 2009]:

$$R_{DIN} = \text{DIN}_{ls} \times e^{\frac{-sv}{\Delta d}} \tag{19}$$

$$\text{sv} = \text{asv} \times (Q10)^{\frac{T-T_s}{10}} \tag{20}$$

$$\Delta d = \frac{Q}{A} \tag{21}$$

where R_{DIN} is the removal rate of inorganic N in water bodies (g N d^{-1}). DIN_{ls} is the NH_4^+ or NO_3^- in lake and rivers of each grid cell (g N); sv is the apparent settling velocity (m s^{-1}); asv is the average value of sv for NH_4^+ (*asv_nh4*) or NO_3^- (*asv_no3*); Δd is the depth of water that flows to the downstream grid cell (m); $Q10$ is the temperature coefficient of NH_4^+ or NO_3^- decomposition (2); Q is the water discharge from the current grid cell to the downstream grid cell (m^3 d^{-1}); and A is the surface water area in each grid cell (m^2).

Deposition of PON under low-flow conditions is another pathway for PON reduction in rivers and lakes [*Merritt et al*., 2003]. Here PON deposition, PON_{dep} (g N d^{-1}), is simulated as

$$PON_{dep} = W \times (PONC - PONC_{max}) \quad (22)$$

$$PONC_{max} = \frac{PON_{ls} \times POCC_{max}}{POC} \quad (23)$$

$$POCC_{max} = \frac{POC_{ls} \times (F_{max})^{1.5}}{SED} \quad (24)$$

$$F_{max} = R_{flow} \times \frac{W}{T_R} \quad (25)$$

where W is the total volume of water of rivers or lakes in each grid cell of a given day (m^3); PONC is the concentration of PON in rivers or lakes in each grid cell (g N m^{-3}); $PONC_{max}$ is the PON holding capacity of water bodies (g N m^{-3}); PON_{ls} is the total amount of PON in water bodies (g N); POC_{ls} is the total amount of particulate organic carbon in water bodies (g C); $POCC_{max}$ is the POC holding capacity of water bodies (g C m^{-3}); F_{max} is the maximum flow rate (m^3 s^{-1}); T_R is the residence time of water bodies in each grid cell (s); R_{flow} is the calibrated ratio of maximum flow rate to average flow rate; and SED is the total amount of suspended sediment of the same water body (g sediment).

The nitrogen flux from sewage water, S_{TN} (g N d^{-1}), is estimated as [*Van Drecht et al*., 2009]

$$S_{TN} = S_N \times Pop \quad (26)$$

where Pop is the population in each grid cell, and S_N (g N d^{-1} person^{-1}) is the average nitrogen emission to surface waters contributed by urban population; S_N is modeled as a function of the adjusted gross domestic production adjgdp (units and the removal fraction of nitrogen in wastewater treatment plants, *Tr* (unitless)):

$$S_N = \left(4 + 14 \times adjgdp^{0.3}\right) \times 0.365 \times (1. - Tr) \quad (27)$$

$$adjgdp = gdp/33000 \quad (28)$$

where gdp is the gross domestic production (dollar person^{-1} yr^{-1}). The total nitrogen flux from sewage water is divided between the ammonium flux ($S_{NH4} = 0.33\ S_{TN}$) and the nitrate flux ($S_{NO3} = 0.67\ S_{TN}$).

4. Input Data and Environmental Changes

4.1. Input Data Development

Data sets used to drive the DLEM 2.0 simulations include data on climate, land cover, the river network, atmospheric CO_2 concentration, and nitrogen deposition. All these data sets had the same georeference information, a spatial resolution of 5 × 5 arc min, and time coverage from 1901 to 2008. Detailed descriptions of how these input data sets were developed and used to force DLEM 2.0 are described in *Liu et al*. [2013] and *Yang et al*. [2015].

In addition to the above data sets, we developed another four data sets for nitrogen export simulation: nitrogen fertilizer use, nitrogen input from livestock farming, population, and gross domestic production. Nitrogen fertilizer use for different crop types from 1961 to 2008 was collected from the Food and Agriculture Organization of the United Nations' fertilizer use report [*Food and Agriculture Organization of the United Nations*, 2006]. A linear equation was used to generate annual nitrogen fertilizer use data from 1901 to 1961 by assuming that nitrogen fertilizer use increased linearly during this period and the nitrogen fertilizer use was zero in 1901. To account for nitrogen export that resulted from livestock farming, county-level manure nitrogen inputs were developed based on the United States Department of Agriculture census reports from 1930 to 2007. We assumed that manure nitrogen input was constant at the level of 1930 for the time period of 1901–1930 [*U.S. Department of Agriculture*, 2012]. To account for the sewage nitrogen flux, we also developed county-level annual population data and gross domestic production data from 1901 to 2008. U.S. population data were collected by combining county-level population data provided by *Waisanen and Bliss* [2002] and *The United States Census Bureau* [2012]. Gross domestic production data were derived from the World Bank data set [*World Bank*, 2012].

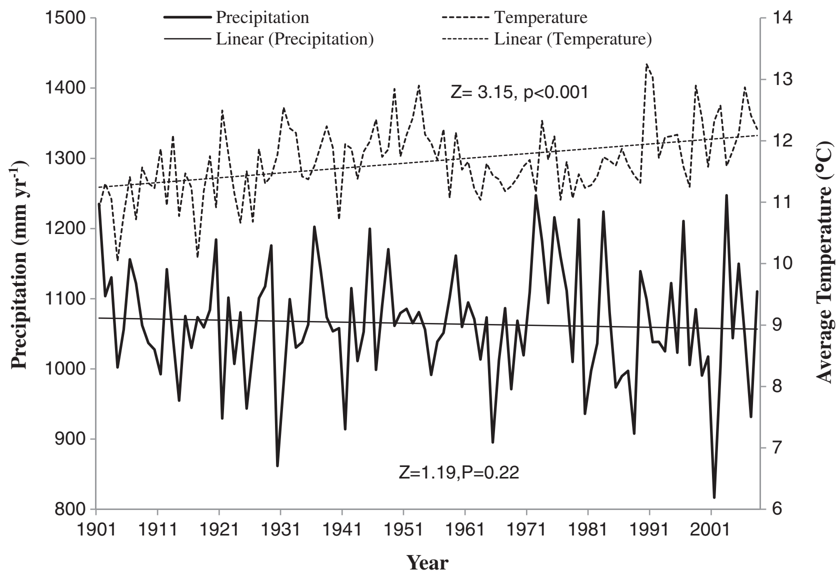


Figure 3. Precipitation and temperature changes in eastern North America from 1901 to 2008.

4.2. Environmental, Land Use Changes in Eastern North America

The study area has also experienced dramatic climate changes since 1901 (Figure 3). Annual precipitation during 1901–2008 in this region was 1064 ± 164 mm yr^{-1} (mean ± 1 standard deviation). The northern and southern parts of the study area were characterized by contrasting changes in precipitation: since 1901, precipitation has increased along the northern North America East Coast but decreased in the southern parts of this region [*Yang et al.*, 2015]. Annual mean temperature in this area over this time period was 11.7 ± 1.2°C (Figure 3). Temperature exhibited an increasing trend with a rate of 0.0079°C yr^{-1} ($P < 0.01$). Warming areas were mainly located in the northern and central parts of the study area, whereas decreasing temperatures were generally limited to the central parts of Georgia.

Land use in the study area has changed substantially since 1901 (Table 1), with land conversion from cropland to forest and other land covers being the primary land cover change. Cropland decreased by about 48% from 1901 to 2005. Forest area increased by about 12% from 1901 to 2000 but decreased slightly in the early 2000s. Cropland abandonment occurred in the central and southern parts of the study area, with reforestation generally occurring coincidentally with cropland abandonment.

Nitrogen input into the study area from atmospheric deposition (Figure 4) and fertilizer use (Figure 5) increased dramatically over the past century. Nitrogen fertilizer use has increased by more than 500%

Table 1. Land Cover in Eastern North America From 1901 to 2005 (km^2)

	Land Use			
Time	Crop Land	Forest	Impervious Surface	Others (Grassland, Wetlands, Etc.)
1901	191982	547600	7216	123202
1911	191289	548251	7936	122524
1921	180623	558936	8278	122163
1931	159723	579179	8661	122437
1941	155185	583642	8793	122380
1951	150684	586034	10241	123041
1961	127286	604041	12559	126114
1971	118137	609353	14835	127675
1981	115909	609880	16273	127938
1991	105610	615564	19074	129752
2001	101119	614578	22874	131429
2005	99851	612825	25214	132110

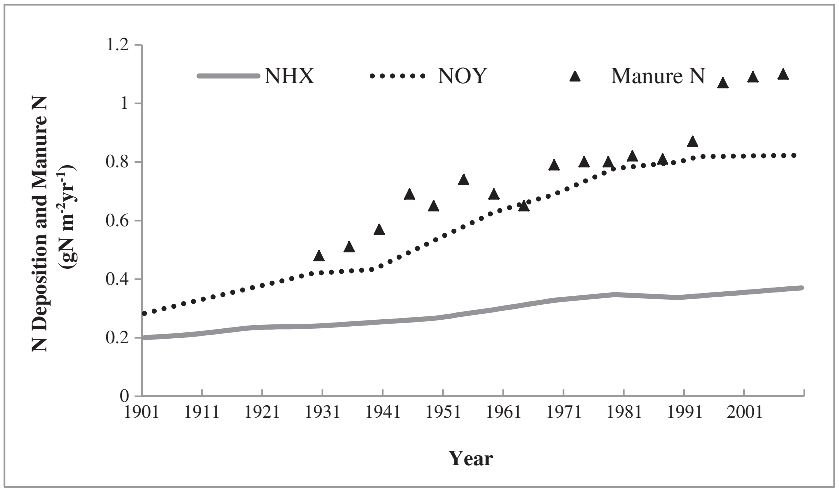


Figure 4. Nitrogen deposition (NH_x: reduced nitrogen and NO_y: nitrogen oxides) and manure nitrogen production in eastern North America from 1901 to 2008.

from the 1900s to the 2000s for all major crop plants. Total nitrogen deposition has increased by about 150% from the 1900s to 2000s. Manure nitrogen input increased by 129% from 1930 to 2007 (Figure 4).

Other changes (not shown) are a considerable population increase (245% from 1901 to 2008) and increases in atmospheric CO_2 concentration by 16 ppm from 1901 to 1950 and 74 ppm from 1951 to 2008.

5. Model Simulation Experiments, Statistical Analyses, and Data for Model Performance Evaluation

Nine simulations were conducted to investigate the relative contributions of the major environmental factors to the variability of nitrogen export (Table 2). Driving forces considered in this study include climate, land cover change, CO_2 increases, manure nutrient production, population increase, cropland management practices (irrigation and nitrogen fertilizer use), and atmospheric nitrogen deposition. In the “Control” experiment, the averaged climate data between 1901 and 1930 and other driving forces in 1901 were used as input data for the simulation (1901–2008). For the single factor simulations, only one factor was dynamic while the remaining input data were held unchanged for each simulation (Table 2). For the “All” experiment, all the above driving forces from 1901 to 2008 were used to simulate nitrogen export during 1901–2008. The relative contribution of each driving force to changes in nitrogen export was calculated by subtracting the results of the Control simulation from that of each single factor simulation (Table 2).

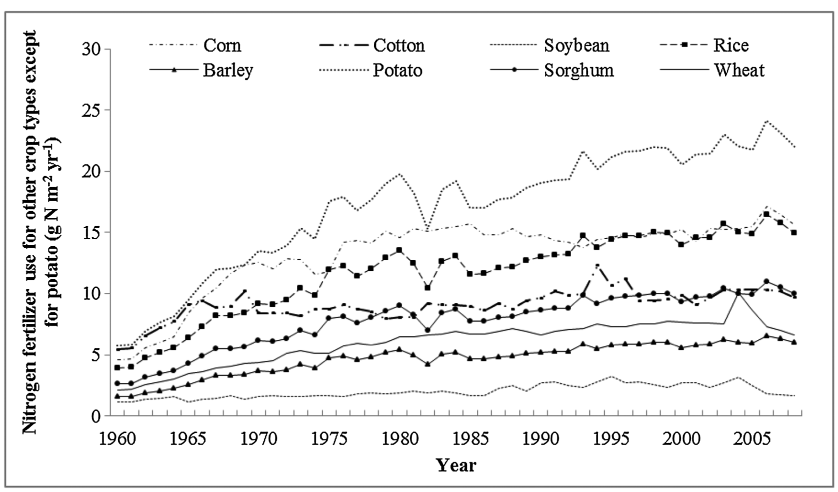


Figure 5. Nitrogen fertilizer use for major crop types in eastern North America.

Table 2. Design of Model Simulation Experiments

Simulations	Factors						
	Climate	Land Cover Change	CO_2	Livestock	Population	Management	Nitrogen Deposition
Control	1901–1930[a]	1901	1901	1901	1901	1901	1901
Climate change and variability only	1901–2008	1901	1901	1901	1901	1901	1901
Land cover change only	1901–1930	1901–2008	1901	1901	1901	1901	1901
CO_2 only	1901–1930	1901	1901–2008	1901	1901	1901	1901
Livestock only	1901–1930	1901	1901	1901-2008	1901	1901	1901
Population only	1901–1930	1901	1901	1901	1901-2008	1901	1901
Management only	1901–1930		1901	1901	1901	1901–2008	1901
Nitrogen deposition only	1901–1930	1901	1901	1901	1901	1901	1901–2008
All	1901–2008	1901–2008	1901–2008	1901–2008	1901–2008	1901–2008	1901–2008

[a]1901–1930 denotes we use average climate condition over the period 1901–1930 to represent long-term mean.

To demonstrate the temporal and spatial variability of environmental input factors and simulated nitrogen export fluxes, the Mann-Kendall test was used with a 95% confidence level to determine whether statistically significant trends exist. Trends of input climate factors (temperature and precipitation) and simulated nitrogen export for each grid cell were also calculated to demonstrate their spatial patterns. Time series trends were tested with the Sen's Slope test to calculate the magnitude of variability. We used the Nash-Sutcliffe model efficiency coefficient (NSE) to evaluate model performance in simulating riverine nitrogen fluxes [*Mccuen et al.*, 2006]. The closer the NSE is to 1, the better the model performs. Positive NSE values indicate reasonable simulation results that are an improvement over the observational average.

Annual nitrogen export estimates from major rivers simulated by DLEM 2.0 were compared with the LOAD ESTimator (LOADEST) estimates to evaluate our model performance. Depending on the availability of field data, the comparison was mainly conducted for the period during the 1970s–2000s. LOADEST is a statistical model that uses water quality data and streamflow data provided by USGS gauge stations to estimate riverine carbon and nutrient fluxes. In this study, riverine N fluxes ($Tg\,N\,yr^{-1}$) refer to the amount of N transported through river channels to the coastal oceans, whereas N loads indicate average N export ($g\,N\,m^{-2}\,yr^{-1}$) per unit land area. LOADEST is considered to be among the most reliable observationally based methods for estimating riverine fluxes. Based on data availability and integrity, we selected five major rivers for evaluation of NH_4^+ and six rivers for evaluation of NO_3^- export. Since the USGS water quality database provides limited observations of PON, total organic nitrogen (TON) was used to evaluate model performance in simulating organic nitrogen export. For the DLEM 2.0 simulation, DON and PON fluxes were added together to obtain the TON fluxes, whereas the TON flux in LOADEST was calculated using the USGS water quality parameter P00605. DON and TON simulations were evaluated for eight and six rivers, respectively. Nitrogen loads were calculated for each nitrogen species by dividing annual nitrogen fluxes with the corresponding drainage areas for the selected basins in order to make estimates of the two models comparable.

6. Results

6.1. Parameter Sensitivity Analysis

In this study, model parameters regulating terrestrial N cycling and N export were calibrated manually by adjusting parameter values to minimize the discrepancies between model simulation and observation. The optimized set of parameters that produced least bias in river N export estimates was used for this study. Values of key parameters regulating N export are listed in Table S1 in the supporting information. To demonstrate the sensitivity of the model simulations to key parameters, we conducted a local sensitivity analysis for seven parameters that control leaching and instream transformation of N species. We assumed that all parameters were normally distributed. The response of simulated nitrogen fluxes to a 20% increase and decrease of each parameter is shown in Table 3.

Results indicated that the export of $NH4^+$, $NO3^-$, and DON were negatively correlated with the adsorption coefficients for the three species (*lchbdon, lchbnh4, lchbno3*) and were moderately sensitive to them. Specifically, with 20% reduction of *lchbdon*, DON fluxes were enhanced by 9.2%, whereas 20% increase in

Table 3. Sensitivity Response of Riverine Nitrogen Fluxes to Key Parameters in DLEM 2.0

			Changes in Fluxes (%)			
Parameters	Definition	Parameter Change (%)	DON	PON	NH_4^+	NO_3^-
lchbdon	Soil adsorption coefficient for DON	−20	9.2	−0.8	−0.2	−0.4
		+20	−3.3	0.3	0.1	0.2
lchbnh4	Soil adsorption coefficient for NH_4^+	−20	−0.1	−0.1	17.1	−3.3
		+20	0.2	0.1	−12.4	4.1
lchbno3	Soil adsorption coefficient for NO_3^-	−20	2.3	−1.1	−3.6	14.3
		+20	−1.2	−0.1	1.4	−15.9
k_{don}	Decomposition rate of DON in surface waters	−20	3.5	0.1	−0.2	−0.4
		+20	−1.4	0.1	0.3	0.2
k_{pon}	Decomposition rate of PON in surface waters	−20	1.1	3.5	−0.6	−0.2
		+20	−0.9	−4.6	0.2	0.1
asv_no3	Apparent settling velocity for NO_3^-	−20	0.1	−0.1	−2.2	36.4
		+20	0.1	0.1	1.3	−29.5
asv_nh4	Apparent settling velocity for NH_4^+	−20	0.1	0.3	29.6	−2.6
		+20	−0.2	−0.1	−31.4	2.3

this parameter reduced DON export by 3.3%. Inorganic nitrogen species had stronger responses to the adsorption coefficients than DON did. With the changes in *lchbnh4,* export of $NH4^+$ varied from a reduction of 12.4% to an increase of 17.1%. NO_3 export was reduced by 15.9% with the 20% increase in *lchbno3,* but increased by 14.3% with the 20% decline in this parameter. Export was also negatively correlated with the parameters controlling instream degradation, with a weak sensitivity for the organic N species (parameters k_{don} and k_{pon}) and a very high sensitivity for the inorganic N species (parameters *asv_no3* and *asv_nh4*). Organic N species were less responsive to the parameters (k_{don} and k_{don}) controlling instream degradation than those (parameters *asv_no3* and *asv_nh4*) for the two inorganic species. A decreased DON decomposition rate (−20% of k_{don}) induced an increase of 3.5% for DON, whereas increase in this parameter by 20% reduced DON export by 1.4%. Decreased (−20% of k_{pon}) NO_3 export increased by 36.4% and decreased by 29.5% in response to the reduction and increase of the NO_3 settling velocity (*asv_no3*), respectively. $NH4^+$ export was enhanced by 29.6% by the reduction of *asv_no3* (20%) but declined by 31.4% in response to the 20% increase of this parameter. PON fluxes were negatively correlated with PON decomposition rates. PON decomposition rates increased PON fluxes by 3.5% but increased decomposition (20%) reduced this flux by 4.6%.

6.2. Model Performance Evaluation

Model performance evaluation indicated that DLEM 2.0-simulated nitrogen fluxes were in good agreement with LOADEST estimates in both magnitude and temporal variability for the selected river basins (Figure 6). The coefficients of determination (R^2) between DLEM 2.0 and LOADEST estimates for NH_4^+ export ranged from 0.62 to 0.73 and NSE ranged from −0.13 to 0.53, indicating that the NH_4^+ loads provided by the two models were comparable. The two models also agreed well with each other in terms of NO_3^- export, with R^2 values greater than 0.7 for all selected river basins, and NSE ranging from −1 to 0.61. The two models showed higher discrepancies in NO_3^- export simulation than in NH_4^+ export. For example, in the Housatonic River basin the NO_3^- loads simulated by DLEM 2.0 had higher interannual variability than the LOADEST estimates. DLEM 2.0 estimates of DON and TON fluxes were consistent with LOADEST results for the selected rivers (NSE $>$ −0.13 and NSE $>$ 0.51 for DON and TON estimates, respectively).

We also evaluated the simulated concentrations of NH_4^+, NO_3^-, DON, and PON with field data provided by the USGS (Table S2 in the supporting information). In total, we selected 22 major rivers in this region for the comparison (Figures S1 and S2 in the supporting information). Results indicated that DLEM 2.0 provided reasonable estimates of average $NH4^+$, $NO3^-$, DON, and TON concentrations for most rivers, and the standard deviations of model estimates and field data were comparable. This result further validated the model's capability in providing reasonable estimates of riverine nitrogen fluxes.

6.3. Contemporary Estimates of Riverine Nitrogen Export

Riverine nitrogen fluxes to the coastal region differed among the four nitrogen species. For the period 1980–2008, inorganic nitrogen fluxes accounted for roughly 60% of the total nitrogen export from the

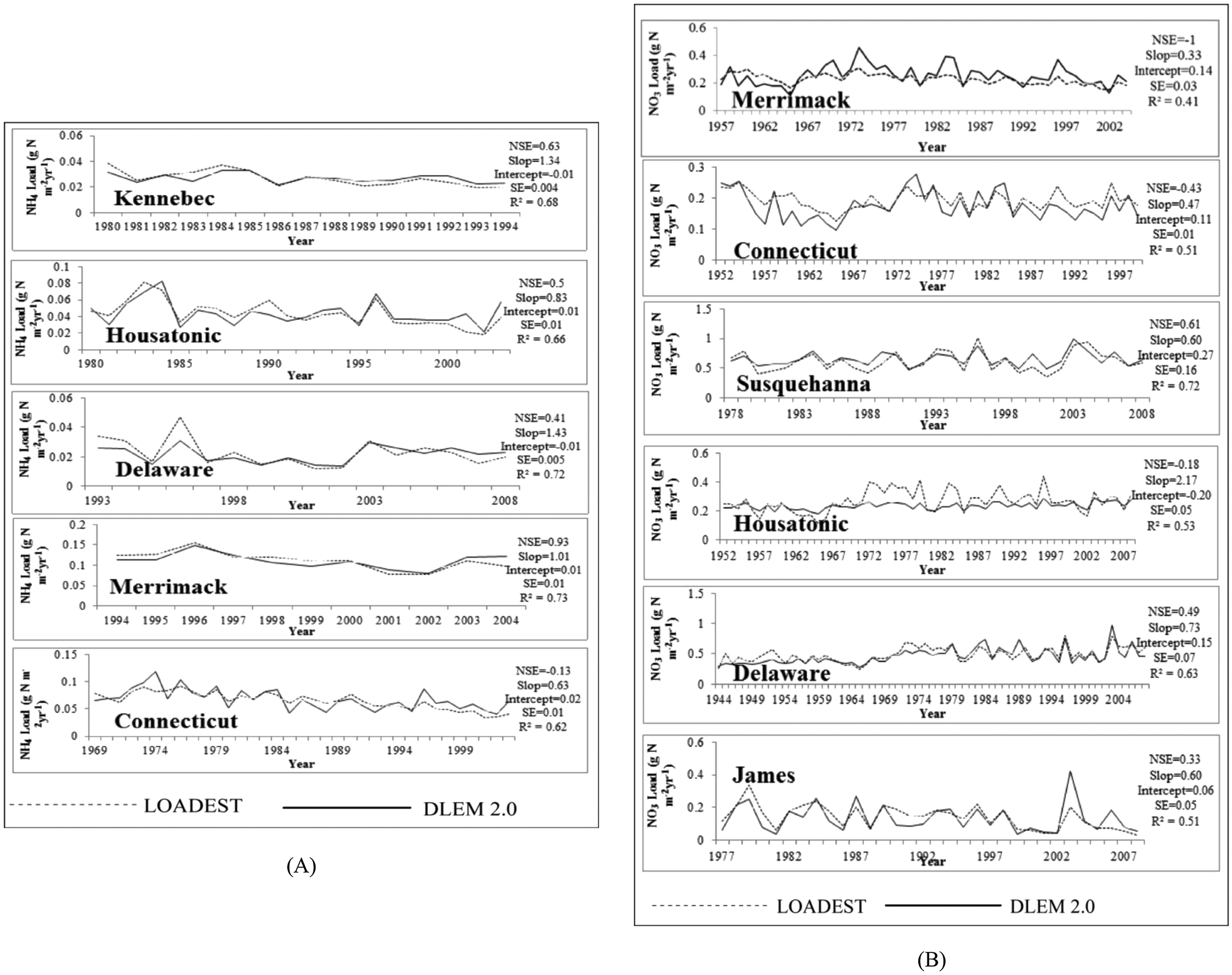
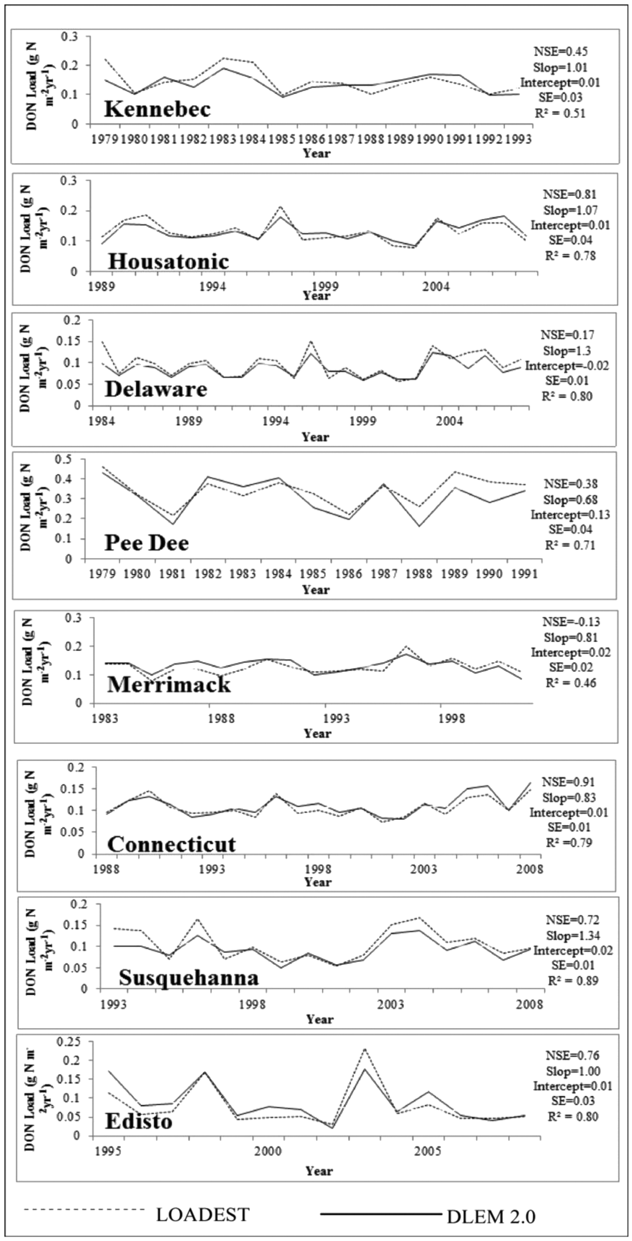


Figure 6. Comparison of nitrogen load estimated by Load Estimator (LOADEST) and DLEM 2.0 ((a) NH4, (b) NO3, (c) DON, and (d) TON). NSE is the Nash-Sutcliffe model efficiency coefficient; slops and intercept are for the linear regression between our simulations and LOADEST estimates; SE refers to standard error of the linear regression.

study area. Nitrate was the primary inorganic nitrogen species, contributing 90% of the total inorganic nitrogen fluxes. Average riverine fluxes of NH_4^+ and NO_3^- from 1980 to 2008 were 0.02 ± 0.003 Tg N yr^{-1} (mean ± standard deviation) and 0.18 ± 0.04 Tg N yr^{-1}, respectively. The primary organic nitrogen species was DON, which was responsible for 70% of the total organic nitrogen export from the study area. Average riverine fluxes of DON and PON from 1980 to 2008 were 0.10 ± 0.02 Tg N yr^{-1} and 0.04 ± 0.01 Tg N yr^{-1}, respectively.

Due to differences in drainage area, land use types, and population densities, riverine nitrogen fluxes among the three subregions varied significantly during 1980–2008 (Figure 7). The MAB watershed had the highest riverine nitrogen fluxes among the three subregions for all four nitrogen species. The SAB watershed also provided significant amounts of DON and PON. Nitrogen export from the GOM watershed was the lowest among the three subregions for all four nitrogen species. Specifically, for NH_4^+ export, the MAB watershed contributed 73% of the total NH_4^+ riverine fluxes, with smaller contributions from the SAB (16%) and the GOM (11%). Similarly, for NO_3^- riverine fluxes, the MAB watershed provided 78% of the total NO_3^- fluxes, again with smaller contributions from the SAB (15%) and the GOM (7%) watersheds. Riverine fluxes of DON (MAB: 51%; SAB: 37%; GOM: 22%) and PON (MAB: 45%; SAB: 34%; GOM: 21%) were somewhat more similar for the three subregions.



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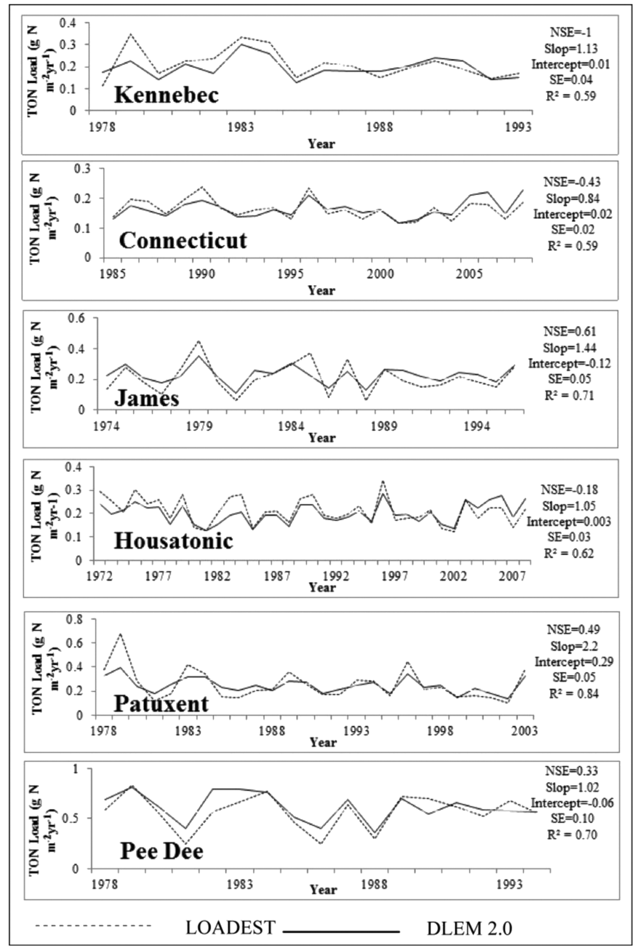

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Figure 6. (continued)

6.4. Interdecadal Variability of Riverine Nitrogen Export

Riverine nitrogen fluxes demonstrated considerable interdecadal variability over the past century (Figure 7). Maximum inorganic nitrogen export from eastern North America occurred in the 2000s, whereas maximum organic nitrogen export occurred in the 1970s, which coincided with the high precipitation (Figure 3) and river discharge [*Yang et al.*, 2015]. Riverine fluxes of all nitrogen species were particularly low in the 1960s, most likely as a result of the low precipitation (Figure 3) and river discharge in this decade [*Yang et al.*, 2015]. Nitrogen export demonstrated higher temporal variability in recent decades than in the earlier decades of this study, especially for the inorganic species. For example, standard deviations for NH_4^+ and NO_3^- from 1901 to 1928 were 0.0017 Tg N yr^{-1} and 0.012 Tg N yr^{-1}, respectively; for the recent years (1981–2008), the standard deviations increased to 0.003 Tg N yr^{-1} and 0.035 Tg N yr^{-1}, respectively.

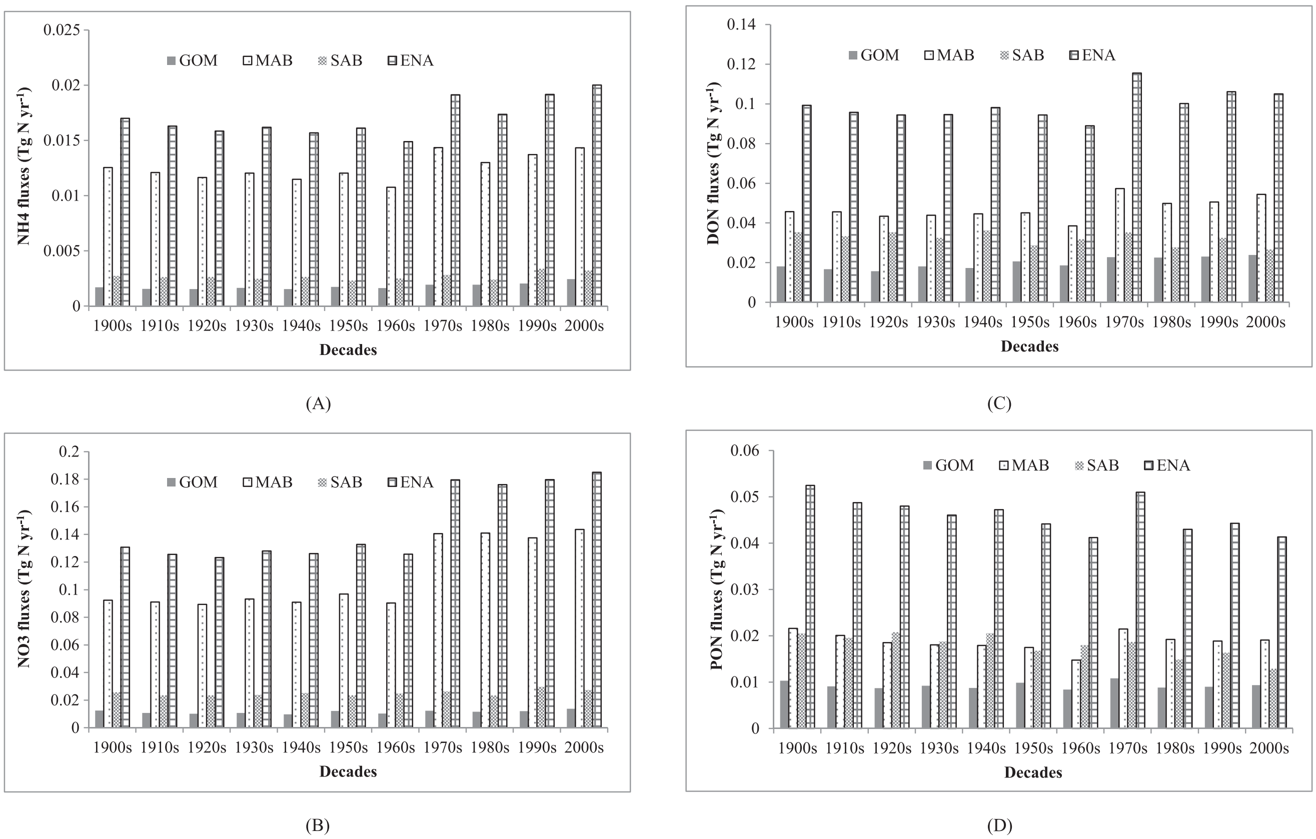


Figure 7. Riverine N fluxes from eastern North America (ENA) and the watersheds of the Gulf of Maine (GOM), Middle Atlantic Bight (MAB), and South Atlantic Bight (SAB) from the 1900s to the 2000s ((a) NH4, (b) NO3, (c) DON, and (d) PON).

For the three individual subregions, increasing trends were found for the riverine fluxes of NO_3^- and NH_4^+ to the GOM and the MAB, but not to the SAB. Total PON export from eastern North America demonstrated a decreasing trend ($P < 0.05$), with significant decreasing trends also found for the individual MAB and the SAB watershed, but not the GOM ($P < 0.05$ for MAB and SAB; $P = 0.44$ for GOM). Although riverine fluxes of DON showed a marginal increasing trend ($P = 0.07$) from eastern North America as a whole, DON fluxes into the SAB watershed actually exhibited a long-term decreasing trend. A significant upward trend was detected for DON fluxes to the GOM ($P < 0.01$), but DON export only demonstrated a marginal upward trend in the MAB watershed.

6.5. Spatial Variability of Nitrogen Export Changes

Spatial distribution of the changes in nitrogen export over the past century demonstrated dramatic heterogeneity for the four nitrogen species. Changes in NH_4^+ export varied significantly among the three subregions (Figure 8a). In the GOM watershed, enhanced NH_4^+ export mainly occurred in northern Maine, Nova Scotia, and eastern Massachusetts. For most parts of this subregion, changes in NH_4^+ export were not significant (±0.3 mg m^{-2} yr^{-1} yr^{-1}). Decreased NH_4^+ in this subregion occurred in parts of southern Maine. For the MAB watershed, NH_4^+ export increased around large metropolitan areas such as Washington D.C., New York City, and Baltimore, as well as in Delmarva Peninsula. In addition, enhanced NH_4^+ export was found in the upstream regions of the Delaware basin and the Hudson River basin. Decreased NH_4^+ export in this subregion was mainly located in eastern New York, central Pennsylvania, and Virginia. In the SAB watershed, increased NH_4^+ export mainly occurred in North Carolina. Most parts of the Piedmont regions had decreased NH_4^+ export. Areas with increased NH_4^+ export above 0.0003 g N m^{-2} yr^{-1} were mainly located in the MAB watershed (Figure 8a).

As the case for changes in NO_3^- export also differed significantly among the three subregions (Figure 8b). Small regions of decreased NO_3^- export were scattered in the SAB and the GOM watersheds, but in most

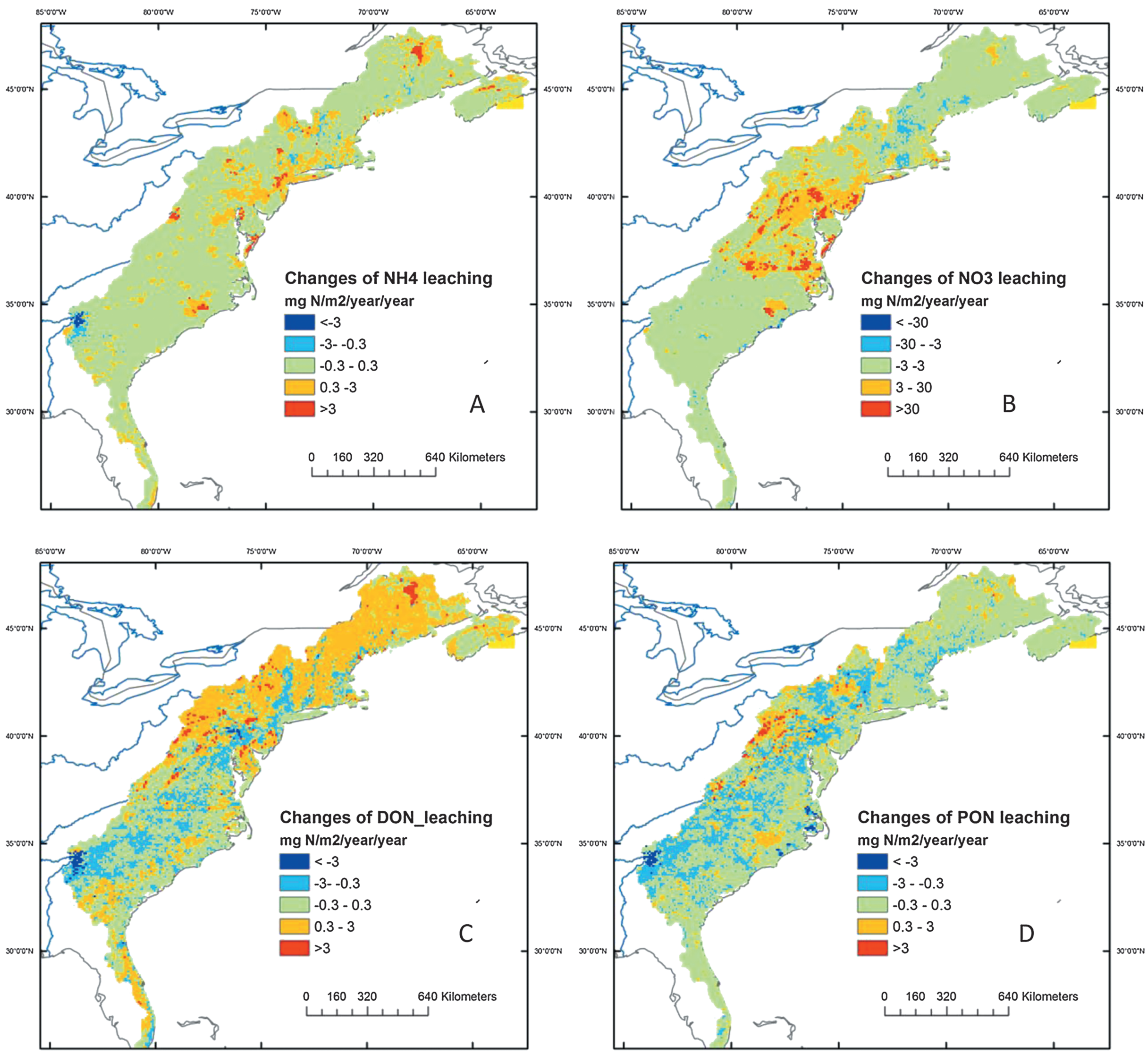


Figure 8. Spatial variability of the trend in annual mean nitrogen export across eastern North America during 1901–2008 ((a) NH4, (b) NO3, (c) DON, and (d) PON).

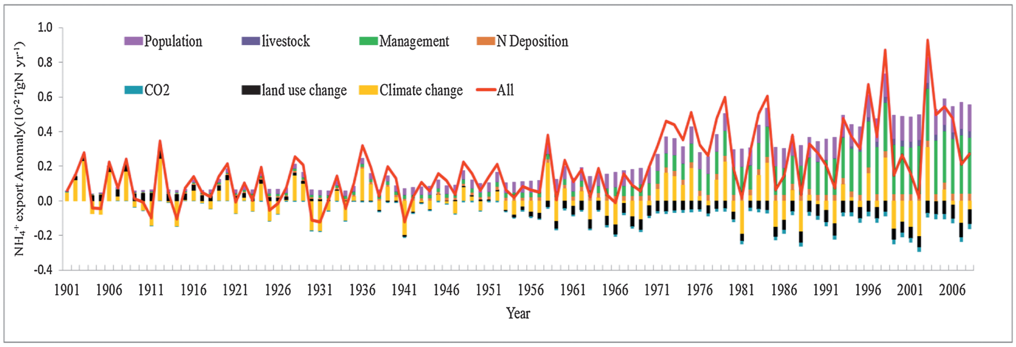
parts of the two subregions, changes in NO_3^- export were not significant (from −3 to 3 mg N m^{-2} yr^{-1}). In contrast, throughout most of the MAB drainage area, NO_3^- export has increased by over 3 mg N m^{-2} yr^{-1}.

DON export demonstrated opposite patterns in the northern and southern parts of the study area (Figure 8c). Throughout most of the GOM and the MAB watersheds, DON export increased over the past century, whereas in most parts of the SAB drainage area, DON export decreased or did not change significantly.

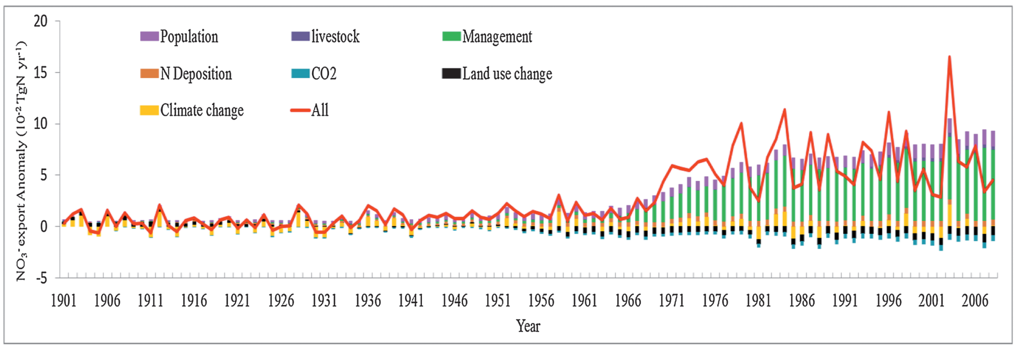
Changes in PON export varied among the three subregions (Figure 8d). Both decreased and increased PON export was found in the MAB watershed. Specifically, increased PON export in this subregion was mainly distributed in central Pennsylvania, New Jersey, Delaware, and Maryland, whereas decreased PON export mainly occurred in eastern Virginia, eastern Pennsylvania, and eastern New York. In the SAB watershed, decreased PON export occurred in the Piedmont region. In the coastal areas across North Carolina, South Carolina, Georgia, and Florida, PON export increased from 1901 to 2008. In the upstream regions of the Susquehanna River basin and coastal areas of North Carolina, changes in PON export were over 0.3 mg N m^{-2} yr^{-1}.

6.6. Relative Contributions of Multiple Environmental Factors to Changes in Riverine Nitrogen Fluxes

Contributions of different environmental forces to changes in nitrogen export were analyzed through the factorial model simulations outlined in Table 2. Results (Figure 9) show that climate change and variability



(A)



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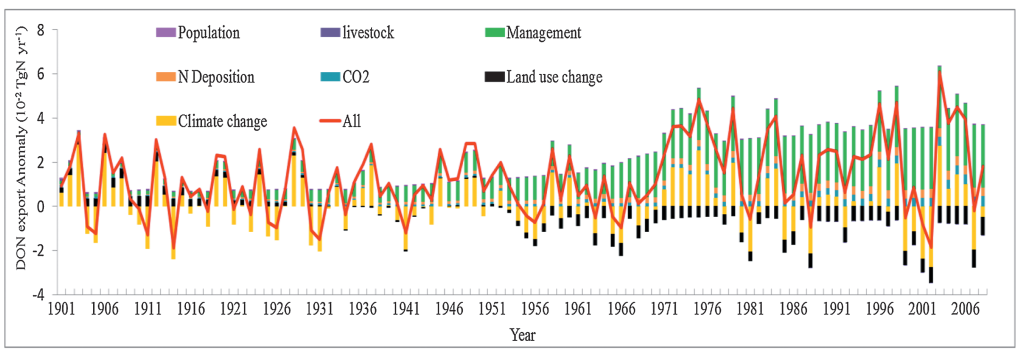

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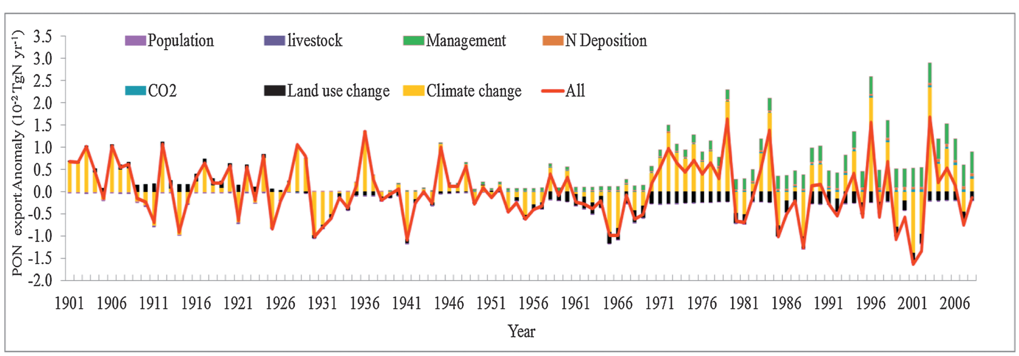

(D)

Figure 9. Relative contributions of individual environmental factors to changes in riverine nitrogen fluxes from eastern North America ((a) NH4 fluxes, (b) NO3 fluxes; (c) DON fluxes, and (d) PON flux).

was the most important factor for explaining the interannual variability of nitrogen export. For all four nitrogen species, the “climate change and variability only” simulated riverine fluxes were highly correlated with those from the “all” simulation. Specifically, the correlation coefficients between the two simulations were 0.90, 0.96, 0.68, and 0.94 for the NH_4^+, NO_3^-, DON, and PON fluxes, respectively. However, nitrogen export did not show a long-term trend in the climate change and variability only simulation for the four nitrogen species. The effect of climate change and variability increased or decreased riverine nitrogen fluxes depending on the specific hydrological conditions in different years.

Our simulation experiments reveal that the increasing trends for riverine NH_4^+ and NO_3^-fluxes are due to a number of factors (Figure 9). Increased fertilizer use has enhanced riverine export of NH_4^+ and NO_3^- by 86% and 198%, respectively, during the 1980s–2000s, compared with the average values from 1901 to 1930. Elevated NO_3^- and NH_4^+ fluxes are also attributable to increased atmospheric nitrogen deposition: ammonium and nitrate export were enhanced by 9% and 20% in the “N-deposition only” simulation during the 1980s–2000s, compared to that of 1901–1930. In such a densely populated area, urban sewage water is another important source of riverine NO_3^- fluxes. It was estimated that the growing population has increased NH_4^+ and NO_3^- export by 51% and 29% in recent decades (1980s–2000s), compared with that from 1901 to 1930. Livestock farming was responsible for a small increase in inorganic nitrogen riverine fluxes over this time period, whereas land cover change and atmospheric CO_2 elevation had small negative impacts on these exports.

As was the case for inorganic riverine export, the riverine fluxes of DON demonstrated a positive response to increased nitrogen input due to increased fertilizer use and atmospheric nitrogen deposition. However, whereas atmospheric CO_2 elevation reduced riverine fluxes of inorganic nitrogen, it increased export fluxes of DON. Input from livestock farming and sewage water discharge did not lead to a significant change in DON export, and land cover change impacts were negative for most years.

Unlike the fluxes of the other three nitrogen species, PON export demonstrated a decreasing trend. Our factorial experiments suggested that land cover change has been the primary reason for this decline. Although increased nitrogen input through fertilizer use, nitrogen deposition, and animal manure production all had positive impacts on PON fluxes, they did not reverse the long-term decreasing trend contributed by land cover changes which significantly reduced soil erosion and associated PON export.

7. Discussion

7.1. Nitrogen Export From Eastern North America

Increased nitrogen export has been widely reported in different regions of the world [*Donner et al*., 2002; *Howden et al*., 2010]. Due to increases in nitrogen input to terrestrial ecosystems through chemical fertilizer use, nitrogen deposition, and nitrogen fixation, stream nitrogen concentration has increased in most U.S. rivers [*Davidson et al*., 2012]. Dominance of $NO3^-$ and DON over the other two species can be explained by the fact that $NH4^+$ content is lower than $NO3^-$ in most soils [*Di and Cameron*, 2002]. In addition to the divergent mechanisms regulating DON and PON leaching, instream degradation and deposition of PON are also responsible for the different magnitudes of DON and PON fluxes. Nitrogen export in the study area as simulated by DLEM 2.0 is in line with previous estimates, which suggest that human activity have greatly increased nitrogen export to coastal waters [*Sprague and Lorenz*, 2009; *Trench et al*., 2011]. In particular, the increasing nitrogen export since the 1970s estimated by DLEM 2.0 agrees well with the analysis of *Jaworski et al*. [1997], which demonstrated elevated nitrogen export in major watersheds throughout the northeastern U.S.

Nitrogen export simulated by DLEM 2.0 is also comparable with previous estimates of riverine nitrogen fluxes from eastern North America. Of all the methods used to estimate riverine nutrient fluxes, the SPAtially Referenced Regressions On Watershed (SPARROW) model has perhaps been most widely applied to the U.S. SPARROW is a statistical model that combines stream concentration measurements (in this case, of total nitrogen), streamflow, and watershed characteristics to estimate long-term mean riverine fluxes. Comparison of DLEM 2.0 estimates with the SPARROW results of *Alexander et al*. [2008] indicated that DLEM 2.0 has a reasonable representation of nitrogen fluxes from eastern North America (Table 4). Simulations from the two models demonstrated similar spatial patterns of total nitrogen flux, showing

Table 4. Comparison of DLEM 2.0 Simulation (Average From 1980 to 2008) With Other Regional Total Nitrogen (TN) Export Estimates[a]

Data Source	TN Export (Tg N yr^{-1}) GOM	MAB	SAB	ENA	Time Period
Howarth et al. [1996] (USGS data)	___	___	0.24	0.75	1980s
Fennel et al. [2006] (USGS data)	___	0.252	___	___	1980s–2000s
Townsend [1998] (Observed discharge and N concentration)	0.0008	___	___	___	1990s
Alexander et al. [2008] (SPARROW)	0.058	0.335	0.145	0.538	1975–2000
This paper (DLEM 2.0)	0.055	0.271	0.112	0.438	1980–2008

[a]GOM, MAB, and SAB refer to the drainage areas of the Gulf of Maine, Mid-Atlantic Bight, and South Atlantic Bight, respectively, and ENA is eastern North America.

higher nitrogen export in the MAB watershed as compared to the other two subregions. DLEM 2.0-based estimates are in good agreement with regional studies based on stream nitrogen concentrations and river discharge data [*Fennel et al.*, 2006; *Howarth et al.*, 1996; *Townsend*, 1998]. Specifically, total nitrogen export from the GOM and the MAB watersheds estimated by DLEM 2.0 fell in the ranges formed by previous studies (Table 4). For the SAB and the whole study area, estimates by DLEM 2.0 were lower than that by *Howarth et al.* [1996] and *Alexander et al.* [2008]. Possible explanations for these differences include different drainage areas used for the nitrogen export calculations, as well as uncertainties in river discharge and river nitrogen concentration estimates.

Besides comparing our estimates of total nitrogen fluxes to the coastal region, we also compared our simulation results with studies that focused on nitrogen loads in watersheds along eastern North America [*Boyer et al.*, 2002; *Kane et al.*, 2008; *Schaefer and Alber*, 2007; *Seitzinger et al.*, 2002]. The comparison suggested that nitrogen loads varied dramatically among watersheds with different climate conditions, population sizes, and agricultural intensities [*Schaefer and Alber*, 2007]. Among the three subregions, rivers in the MAB watershed had the highest nitrogen loads (Table 5). DLEM 2.0 estimates were in line with the multiple estimates derived from either field observations or model simulations in all three subregions. Specifically, for the GOM watershed, our estimates were comparable with *Seitzinger et al.* [2002] and *Boyer et al.* [2002] but much lower than the estimates from the Nutrient Export from WaterSheds (NEWS) model, which estimated that average N load in the eastern U.S. (including the GOM and MAB watersheds) was about 0.84 g N m^{-2} $year^{-1}$. For the MAB watershed, DLEM 2.0 estimated total N load fell within the range of other studies. For the SAB watershed, our total N load was at the low end of the range from previous studies, whereas the NEWS model had the highest estimate.

This study has improved nitrogen export estimates in eastern North America by addressing two issues that are critical for the scientific community. First, instead of only providing the long-term average of nitrogen export, our DLEM 2.0 simulation also provided annual riverine nitrogen fluxes over the past century and identified the dramatic interannual variability associated with these fluxes. Because riverine nitrogen flux is the primary cause of hypoxia in coastal waters, the interannual variability presented by this study will contribute to explaining mechanisms that control the expansion and shrinkage of hypoxic zones in coastal

Table 5. Comparison of DLEM 2.0 Total Nitrogen Load Estimates With Estimates From Previous Studies[a]

Data Source	TN Load (g N m^{-2} $year^{-1}$) GOM	MAB	SAB	ENA	Time Period
Seitzinger *et al.* [2002]	0.32–0.50	0.31–1.7	___	___	1990
Schaefer and Alber [2007]	___	___	0.16–0.45	___	1980s–1990s
Kane et al. [2008]	0.02–0.05	0.72–3.04	___	___	1980s–2000s
Boyer et al. [2002]	0.32–0.50	0.31–1.76	___	___	1980s–1990s
McCrackin et al. [2013]	0.77–0.84		0.637	___	2000
Alexander et al. [2008]	0.48	0.96	0.41	0.65	1975–2000
DLEM 2.0	0.30	0.76	0.28	0.48	1980–2000

[a]GOM, MAB, and SAB refer to the drainage areas of the Gulf of Maine, Mid-Atlantic Bight, and South Atlantic Bight, respectively, and ENA is eastern North America.

waters between dry and wet years [*Hagy et al*., 2004]. Second, our DLEM 2.0 simulations have provided specific estimates of multiple nitrogen species instead of only estimating total nitrogen export. Due to differences in chemical activity and bioavailability, organic and inorganic nitrogen species are involved in different reactions during export in the soil and instream transformation in waters [*Alvarez-Cobelas et al*., 2008]. Aggregating all nitrogen species into one term oversimplifies the underlying processes controlling nitrogen export. In addition, the four nitrogen species have different roles in contributing to hypoxia in coastal waters [*Rabalais*, 2002; *Bever et al*., 2013]. Our simulated results provide valuable information for oceanographers wishing to assess the roles of different nitrogen species on nutrient and carbon cycling in coastal waters [*Hofmann et al*., 2008, 2011; (Y. Feng et al., Chesapeake Bay nitrogen fluxes derived from a land-estuarine-ocean biogeochemical modeling system: Model description, evaluation and nitrogen budgets, submitted to *Journal of Geophysical Research Biogeosciences*, 2015)].

7.2. Underlying Controls on the Spatial and Temporal Patterns of Nitrogen Export

Human-induced nitrogen inputs are receiving increasing attention as they continue to elevate riverine nitrogen fluxes [*Palmer-Felgate et al*., 2010; *Smith et al*., 2007]. Agreeing with previous NANI studies that highlighted the impacts of N inputs on N export [*Hong et al*., 2013], our simulations indicated that multiple sources of nitrogen inputs were the primary reason for the spatial variability of nitrogen export in the three subregions. Higher nitrogen loads in the MAB watershed mainly resulted from a combination of high nitrogen fertilizer use, high nitrogen deposition, dense population, and intensive livestock farming [*Boyer et al*., 2002]. Similarly, lower nitrogen input through fertilizer use and nitrogen deposition in the GOM watershed was responsible for the lower nitrogen export in this subregion. In addition, higher denitrification rates (88% higher on average) in the warmer climate of the SAB watershed compared with that of the MAB subregion with cooler climate suggested that temperature may also be responsible for the differences in riverine fluxes along the latitudinal gradient [*Schaefer and Alber*, 2007].

Unlike the NANI studies that primarily focused on the inputs and outputs of N fluxes in terrestrial ecosystems, DLEM 2.0 simulated key processes of N cycling and associated carbon and water cycling. Process-based simulations in this study enable us to identify key mechanisms controlling N export. Significant temporal variability of riverine nitrogen fluxes is attributable to changes in multiple factors. These factors can be categorized into three groups based on their roles in controlling hydrological processes, nitrogen input, and nitrogen cycling in terrestrial ecosystems [*Alexander et al*., 2002; *Kaushal et al*., 2008; *Schilling and Zhang*, 2004]. The first category includes driving forces that have significant impacts on water cycling. Significant positive correlations between river discharge and nitrogen export have been widely reported and thus demonstrate the significant impacts of hydrological processes on nitrogen export [*Alvarez-Cobelas et al*., 2008; *Howarth et al*., 2006]. Similarly, our factorial analyses indicated that climate factors (i.e., changes in temperature and precipitation) were the primary reason for the interannual variability associated with the nitrogen fluxes for all four nitrogen species. Nitrogen export increased in wet years but decreased in dry years, indicating that water availability is a limiting factor for nitrogen export and that precipitation largely controls water fluxes for delivering nitrogen from land to rivers [*Goolsby et al*., 2000]. Land cover change is another factor that influenced long-term trends in nitrogen export by affecting hydrological processes. Due to agricultural land abandonment and reforestation, forest area was 12% higher in 2008 compared with that in 1901. Increases in evapotranspiration associated with this reforestation have led to decreases in runoff over the past century [*Yang et al*., 2014]. In isolation, this reduction in runoff due to these changes in land cover would cause reductions in nitrogen export for all four nitrogen species (Figure 9); however, other environmental factors discussed below are simultaneously counteracting these reductions. In addition, land cover change from cropland to forest also contributed to decreased PON export, as forest has a lower soil erosion rate than cropland [*Seitzinger et al*., 2002].

The second category of environmental factors includes those that affect nitrogen input into the study area. Increased nitrogen input through atmospheric deposition, cropland management, livestock farming, and sewage nitrogen fluxes has enhanced the export of NH_4^+, NO_3^-, and DON [*Zhu and Reed*, 2014]. Results of the DLEM 2.0 simulation agreed with previous studies that have reported close correlations between nitrogen input and nitrogen export [*Hong et al*., 2012]. Our contribution analyses specifically indicated that organic nitrogen species were less sensitive to increased nitrogen input than inorganic species, since DON and PON exports are closely related to less labile nitrogen pools in litter and soil organic matter [*Goodale et al*., 2000].

Elevated atmospheric CO_2 is another mechanism that affects the nitrogen cycle in terrestrial ecosystems and ultimately controls nitrogen export by stimulating carbon sequestration [*Beedlow et al*., 2004]. Specifically, increased carbon accumulation stimulates nitrogen immobilization into plant biomass and soil organic pools [*Luo et al*., 2006]. As a result, in our simulations, atmospheric CO_2 elevation demonstrated negative impacts on NH_4^+ and NO_3^- exports, as plant uptake of inorganic nitrogen species was enhanced. Due to the increased organic N in litter and soil organic pools, DON and PON exports increased in response to elevated atmospheric CO_2. This result is consistent with studies that report elevated CO_2 could increase organic matter inputs to soils [*Schlesinger and Lichter*, 2001].

Results of our contribution analyses provide insights for managing excessive nitrogen export in eastern North America. According to this study, over the past century increased chemical fertilizer use was the primary factor contributing to enhanced inorganic nitrogen and DON export. Reduction of nonpoint nitrogen export from agricultural areas could effectively control nitrogen export [*Howarth et al*., 2002]. Contributions from atmospheric nitrogen deposition, sewage discharge, and livestock nitrogen production should be considered in nutrient management for specific watersheds that receive high nitrogen inputs through these pathways. However, throughout most of eastern North America, these inputs have generally produced smaller increases in riverine nitrogen fluxes than those resulting from the increased use of fertilizers.

7.3. Uncertainty Sources

Although our DLEM 2.0 simulations demonstrated reasonable estimates of riverine nitrogen export that are in agreement with results from previous studies, there are a number of factors that cause a certain degree of uncertainty in the model simulations, which should be noted to better interpret results of this study. For example, the quality of the input data used in our analyses could largely influence our simulation. In future studies, addressing the uncertainties from input data by improving data quality or using multiple input data sets will be helpful to further test model performance. Although nitrogen transformation processes were explicitly simulated on land, they were not yet specifically included within streams. In addition, nitrogen degradation in rivers and lakes was simplified such that the model could not simulate changes in nitrogen retention over different river orders [*Alexander et al*., 2000]. Flood plains and riparian zones are actively involved in the transformation of different nitrogen species, but these processes were also not considered in the current simulation and this may be a reason for the discrepancy between our simulation and LOADEST estimates [*Gergel et al*., 2005]. Dam construction can change the residence time of water and thus affect degradation of nitrogen in reservoirs [*Gergel et al*., 2005]. However, damming impacts were not addressed in this study. In addition, point-source inputs of nitrogen sewage from factories were not included in the current simulation; and thus, our simulation may be underestimating nitrogen export for watersheds that receive significant amounts of point-source pollutants. Many of these issues are currently being investigated and will be included in future versions of DLEM.

8. Conclusions

Here we investigated N export from eastern North America to the Atlantic Ocean using a process-based terrestrial ecosystem model. We analyzed the spatiotemporal patterns of N export and how changes in multiple factors have affected riverine N fluxes during 1901–2008. Results of this study indicated that inorganic nitrogen fluxes (ammonia and nitrate) accounted for roughly 60% of the total nitrogen export in the study area. Generally, the MAB subregion provided the largest amount of riverine nitrogen fluxes among the three subregions for the four nitrogen species riverine N fluxes demonstrated significant temporal variability, with inorganic nitrogen demonstrating an increasing trend, reaching a maximum export in the 2000s. The 1970s were characterized by particularly high organic nitrogen export, primarily resulting from the high precipitation and discharge in this decade, as compared with that occurring in the 1960s. Overall, DON export flux showed an increasing trend primarily due to significant increases in the GOM, whereas PON export flux showed a decreasing trend primarily due to a decrease in the SAB. Attribution analysis showed that variability associated with climate change determined the interannual variability in nitrogen export. Land cover change tended to reduce river N fluxes by affecting river discharge. Increasing chemical fertilizer use, nitrogen deposition, livestock farming, and sewage discharge greatly enhanced N export in the study area.

This study has improved previous investigations of N export by providing temporally and spatially explicit estimates of the export of four N species. Estimates of nitrogen export from this region will be critical for exploring biogeochemical processes in estuaries and coastal waters that are under the threats of nutrient enrichment (Y. Feng et al., submitted manuscript, 2015). Results of this study will also provide valuable information for quality control and management of excessive nutrient loading to coastal regions. Our work highlighted the importance of reducing N loads from agricultural lands to improve or maintain surface water quality in this region. In addition, we also identified several key uncertainty sources such as input data, model structure, and point-source nitrogen pollution for improving our knowledge of nitrogen fluxes at the land-ocean interface in the future.

Acknowledgments
This study was supported by the NASA Interdisciplinary Science Program (NNX11AD47G and NNX14AF93G). CSH was supported by NSF (1238212). We thank other members in the EDGE Laboratory at Auburn University for their contribution to DLEM 2.0 development. We also thank USGS scientists for their efforts in data collection and management. Supporting data are included in the supporting information; any additional data may be obtained from Hanqin Tian (email: tianhan@auburn.edu).

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