Global Biogeochemical Cycles

RESEARCH ARTICLE
10.1029/2019GB006475

Special Section:
Quantifying Nutrient Budgets for sustainable nutrient management

Key Points:
- Over the period 1901-2014, DIN and TON export from the Mississippi River basin increased by 85% and 60%, respectively. The Ohio River basin was largest contributor to the increase among seven subbasins
- Synthetic N fertilizer application was the dominant contributor to increases in the export of DIN (70%) and TON (40%) since the 1970s
- The highest DIN and TON export occurred in the spring, accounting for 39% and 36% of the total export from the MRB during 1990-2014

Supporting Information:
- Supporting Information S1

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Citation:
Tian, H., Xu, R., Pan, S., Yao, Y., Bian, Z., Cai, W.-J., et al. (2020). Long-term trajectory of nitrogen loading and delivery from Mississippi River basin to the Gulf of Mexico. *Global Biogeochemical Cycles*, *34*, e2019GB006475. https://doi.org/10.1029/2019GB006475

Received 15 NOV 2019
Accepted 24 MAR 2020
Accepted article online 15 APR 2020

Long-Term Trajectory of Nitrogen Loading and Delivery From Mississippi River Basin to the Gulf of Mexico

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Abstract The large areal extent of hypoxia in the northern Gulf of Mexico has been partially attributed to substantial nitrogen (N) loading from the Mississippi River basin, which is driven by multiple natural and human factors. The available water quality monitoring data and most of the current models are insufficient to fully quantify N load magnitude and the underlying controls. Here we use a process-based Dynamic Land Ecosystem Model to examine how multiple factors (synthetic N fertilizer, atmospheric N deposition, land use changes, climate variability, and increasing atmospheric CO_2) have affected the loading and delivery of total nitrogen (TN) consisting of ammonium and nitrate (dissolved inorganic N) and total organic nitrogen from the Mississippi River basin during 1901–2014. The model results indicate that TN export during 2000–2014 was twofold larger than that in the first decade of twentieth century: Dissolved inorganic N export increased by 140% dominated by nitrate; total organic nitrogen export increased by 53%. The substantial enrichment of TN export since the 1960s was strongly associated with increased anthropogenic N inputs (synthetic N fertilizer and atmospheric N deposition). The greatest export of TN was in the spring. Although the implementation of N reduction has been carried out over the past three decades, total N loads to the northern Gulf of Mexico have not decreased significantly. Due to the legacy effect from historical N accumulation in soils and riverbeds, a larger reduction in synthetic N fertilizer inputs as well as improved N management practices are needed to alleviate ocean hypoxia in the northern Gulf of Mexico.

1. Introduction

The Mississippi River basin is the world's third largest river basin, extends over 41% of the area of the conterminous United States (Battaglin et al., 2010), and is the largest contributor of freshwater and nutrients to the Gulf of Mexico (Dale et al., 2010). Over time, the Mississippi River has experienced major engineering modifications in response to urbanization and millions of hectares of land have been exploited for agricultural use (Figure 1). Intensive agricultural activities, especially in the Corn Belt where corn and soybean have been produced, are a major reason for the degradation of water quality in the northern Gulf of Mexico and contribute to the occurrence of seasonal hypoxia a.k.a. the “dead zone” each summer since at least 1980s. Long-term studies have found that the “dead zone” has expanded over time and has had negative impacts on ecological, economic, and commercial fisheries (Rabalais et al., 2007; Sinha et al., 2017). The summertime hypoxic area in the Gulf has averaged between 7,040 and 22,720 km^2 over the last 5 years (www.gulfhypoxia.net), and it is presently the world's second largest coastal hypoxic zone (Dale et al., 2010).

Previous studies indicated that nutrient fluxes, phosphorus (P) and especially nitrogen (N), from the Mississippi River basin are the primary cause of hypoxia in the northern Gulf (Bennett et al., 2001; Boesch et al., 2009; Howarth et al., 1996; Scavia & Donnelly, 2007; Turner & Rabalais, 2003). Nitrogen inputs to the river basin include synthetic N fertilizer, cultivation of N-fixing crops (e.g., soybean), livestock excreta, human sewage, and atmospheric deposition (Goolsby et al., 2000). Booth and Campbell (2007) found that

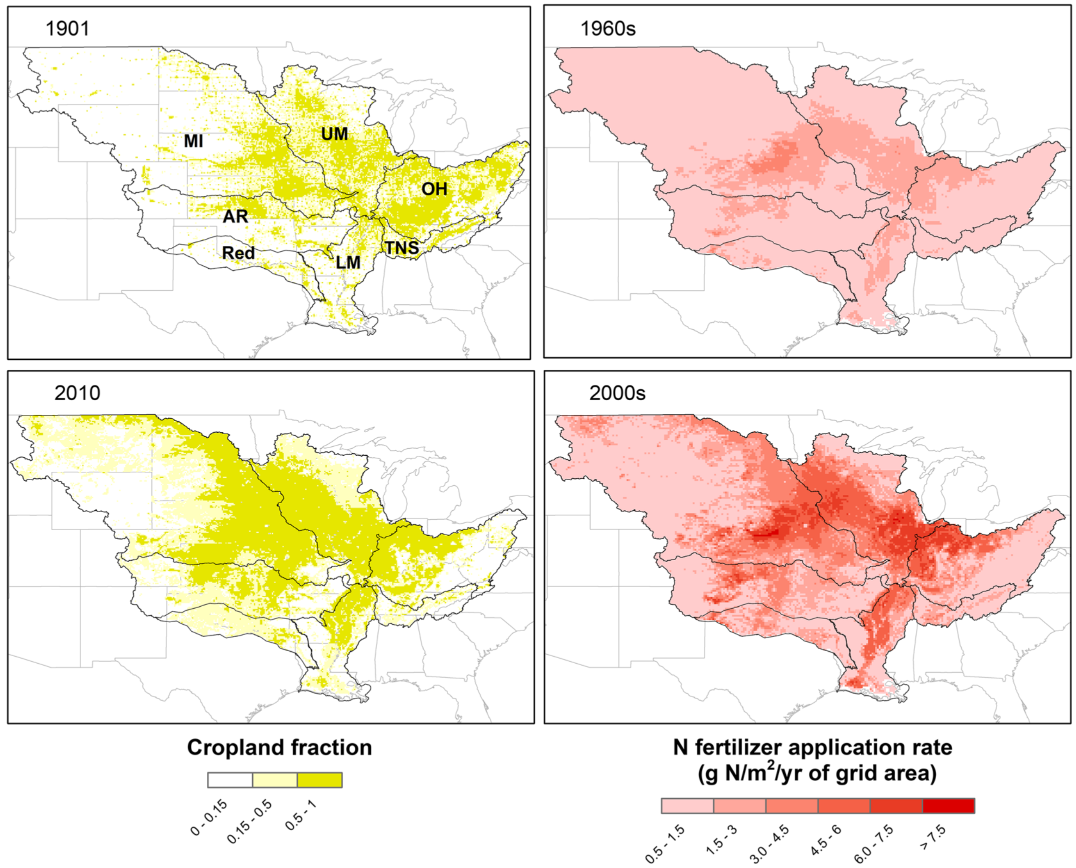

Figure 1. Cropland distribution in 1901 and 2010 (left two panels) and synthetic N fertilizer application rate in the 1960s and 2000s (right two panels). Note that MI represents Missouri River basin, UM represents Upper Mississippi River basin, OH represents Ohio River basin, AR represents Arkansas River basin, Red represents Red River basin, TNS represents Tennessee River basin, and LM represents Lower Mississippi River basin.

synthetic N fertilizer runoff accounted for 59% of nitrate (NO_3^-) loading, followed by atmospheric NO_3^- deposition and animal waste. *An integrated assessment of hypoxia in the northern Gulf of Mexico* (2000) reported that the upper Mississippi and Ohio River basins are two primary sources contributing to NO_3^- loading. Since 1980, the Mississippi River basin has exported an average of 1,600 Gg N year^{-1} to the northern Gulf of Mexico, of which the NO_3^- load was 950 Gg N year^{-1} [*An integrated assessment of hypoxia in the northern Gulf of Mexico*, 2000].

The United States Geological Survey (USGS) water monitoring stations provide real-time continuous water discharge and discrete water quality data that can be used to calibrate and validate statistical or process-based models for accurately simulating N loadings from the Mississippi River basin (Alexander et al., 2007; Goolsby et al., 2000; He et al., 2011; McCrackin et al., 2014). Data provided by the USGS mainly represent dissolved inorganic N (DIN) or total organic N (TON) remaining in the rivers without distinguishing the contributions by different sources. Early efforts to differentiate the sources have primarily focused on estimating N loads due to net anthropogenic N inputs in the Mississippi River basin; however, these estimates have not considered the effects of climate variability, increasing atmospheric CO_2 and land use changes (LUCs) (Billen et al., 2013; Caraco & Cole, 1999; David et al., 2010; Goolsby et al., 1999; Hong et al., 2013; McIsaac et al., 2001). Recently, the impacts of climate variability and extremes on N loads have been addressed (Sinha et al., 2016; Sinha et al., 2017; Lee et al., 2016). It is evident that climate variability, typically precipitation, has a controlling influence on interannual and seasonal variations in riverine N export from the Mississippi River basin (Scavia & Donnelly, 2007; Sinha et al., 2016; Sinha et al., 2017). Watersheds with higher freshwater discharge typically export a greater percentage of N loads to the Mississippi river (Howarth et al., 2012). Additionally, Yang et al. (2015) found that land cover change is another significant factor affecting the annual N export from eastern North America to the Atlantic Ocean. Thus, it is necessary to not only consider watershed N inputs but also include the effects of multiple environmental drivers (i.e., climate change and LUC) when estimating long-term changes in N export from the Mississippi River basin.

Estimating N delivery from the Mississippi River basin to the Gulf has been a topic of interest since the mid-1970s due to the expanding hypoxic zone. Previous estimates mainly focused on watershed N loads associated with N inputs using empirical/semimechanistic approaches. Nutrient Export from WaterSheds (Mayorga et al., 2010) and SPAtially Referenced Regressions On Watersheds (SPARROWs; http://water.usgs.gov/nawqa/sparrow) are two such models that have been applied to the continental United States. The mass-balance mechanism used in SPARROW modeling can estimate the overall delivery of nutrient sources and match them with water quality at monitoring stations. However, this model cannot represent the effect of individual land-to-water delivery factors and their interactions within the actual ecosystem (Robertson & Saad, 2013). To overcome limitations of empirical modeling approaches, here we used a coupled hydrological-biogeochemical land model, Dynamic Land Ecosystem Model version 2.0 (DLEM 2.0) to simulate all key biogeochemical processes and multiple environmental stresses occurring in the watershed. DLEM 2.0 has been used to simulate and predict water discharge and carbon exports in the Mississippi River basin and N exports in the eastern North America (Ren et al., 2015; Ren et al., 2016; Tao et al., 2014; Tian, Ren, et al., 2015; Tian, Yang, et al., 2015; Yang et al., 2015).

In this study, we partitioned the Mississippi River basin into seven subbasins (Upper Mississippi [UM], Ohio [OH], Missouri [MI], Arkansas [AR], Red, Tennessee [TNS], and Lower Mississippi [LM] River basin) and collected the observed DIN and TON loads from the USGS water monitoring stations during the last three decades for model performance evaluation. By implementing DLEM simulations for the period 1901–2014, we intend to (1) quantify century long dynamics of N export from the entire basin to the norther Gulf of Mexico, (2) examine seasonal and interannual and spatial variability of N export to the Gulf, and (3) attribute the effects of multiple driving factors on the variability of N export. The multiple driving factors for DLEM simulations included climate variability, LUC, atmospheric CO_2 concentration, atmospheric N deposition, and synthetic N fertilizer use.

2. Materials and Methods

2.1. Model Description

DLEM 2.0 is an integrated process-based model that is capable of quantifying daily, spatially explicit water, carbon, and nutrient dynamics in terrestrial ecosystems and their interactions with atmospheric and aquatic systems driven by multiple environmental forces at site specific, regional, and global scales (Tian et al., 2010). There are three major processes involved in simulating the export of water, carbon, and nutrients from land surface to coastal areas: (1) the generation of runoff and leachates, (2) the leaching of water, carbon, and nutrients from land to river networks in the form of overland flow and base flow, and (3) transport of riverine materials along river channels from upstream areas to coastal regions. The key processes and parameterization in DLEM 2.0 have been described in our previous publications regarding the water discharge (Liu et al., 2013; Tao et al., 2014), riverine carbon fluxes (Ren et al., 2015; Ren et al., 2016; Tian, Ren, et al., 2015), and riverine N fluxes (Yang et al., 2015) from the terrestrial ecosystem to coastal oceans. An illustration of the key processes influencing DIN and TON production, loss and transport in DLEM 2.0, and the mechanistic controls exerted by changes in natural and anthropogenic factors are represented in Figure 2. In detail, N can enter terrestrial/aquatic ecosystems through both inorganic (i.e., synthetic N fertilizer, biological N fixation, atmospheric N deposition, and human sewage) and organic forms (i.e., animal manure, crop residue, and litterfall). Subsequently, N can be transported from land to rivers/oceans through leaching and runoff. Here we show major processes associated with soil ammonium (NH_4^+) and NO_3^- dynamics and NH_4^+, NO_3^- and TON exports in supporting information. A more detailed description of the key processes of N dynamics in the model was documented in *Q* Yang et al. (2015).

2.2. Input Data

Data sets used to drive DLEM simulations include climate, atmospheric CO_2 concentration, atmospheric N deposition, synthetic N fertilizer application, and land use/cover change (Figure 1). The daily time-step

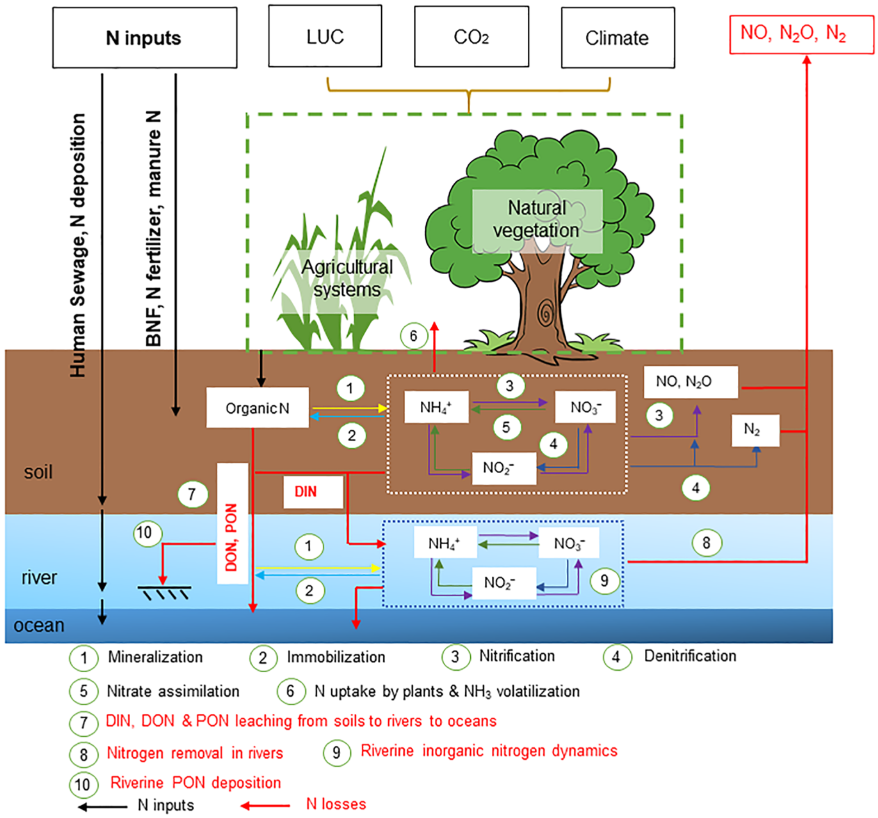

Figure 2. The conceptual framework of key processes involved in N dynamics simulated in the Dynamic Land Ecosystem Model (DLEM 2.0).

climate data sets (including daily temperature, precipitation, and solar radiation) in the continental United States at the spatial resolution of 0.125° from 1901 to 2014 were used. Climate conditions from 1979 to 2014 in the North American Land Data Assimilation System data set and climate conditions from 1901 to 1978 in the Climate Research Unit-National Centers for Environmental Prediction data set were merged by using the method by Liu et al. (2013). Monthly atmospheric CO_2 concentrations from 1860 to 2015 were obtained from the National Oceanic and Atmospheric Administration (NOAA) GLOBALVIEW-CO_2 data set derived from atmospheric and ice core measurements (https://www.esrl.noaa.gov). Atmospheric N deposition data were downscaled and interpolated from global data sets (Wei et al., 2014). The crop-specific N application rate was derived from the National Agricultural Statistics Service (https://quickstats.nass.usda.gov/). This study focuses on nine major crops, including wheat, corn, rice, soybean, cotton, sorghum, barley, oats, and peanut. Taking into account the total harvest area for each crop (Portmann et al., 2010) and cropland area data from the History Database of the Global Environment (HYDE 3.2; Klein Goldewijk et al., 2017), the annual total synthetic N fertilizer application was calculated and adjusted according to Food and Agriculture Organization (FAO) and United States Department of Agriculture (USDA) data. The potential vegetation map was taken from Ramankutty and Foley (1999) and historical cropland area during 1901–2014 was adopted from HYDE 3.2. River network related data sets, including flow direction and accumulation area, were derived from global river network data at 0.125° spatial resolution (Wu et al., 2012). Soil physical properties were taken from ISRIC-WISE Harmonized Global Soil Profile Data Set (version 3.1) (Batjes, 2008).

Substantial changes in the driving factors (i.e., atmospheric CO_2, climate, atmospheric N deposition, synthetic N fertilizer, and LUC) have occurred in the Mississippi River basin during the past 114 years. Atmospheric CO_2 concentration increased ~35%, from 300 parts per million in 1901 to 403 parts per million in 2014. Before the 1970s, temperature exhibited large annual variations but with no significant trend. Afterward through 2014, we found an increasing trend at a rate of 0.026 °C/year in the study region.

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Table 1
Experimental Design of DLEM Simulations

Experiments	Climate	CO_2	Atmospheric N deposition	Synthetic N fertilizer	LUC
S0	1900	1900	1900	1900	1900
S1	1901–2014	1901–2014	1901–2014	1901–2014	1901–2014
S2	1900	1901–2014	1901–2014	1901–2014	1901–2014
S3	1901–2014	1900	1901–2014	1901–2014	1901–2014
S4	1901–2014	1901–2014	1900	1901–2014	1901–2014
S5	1901–2014	1901–2014	1901–2014	1900	1901–2014
S6	1901–2014	1901–2014	1901–2014	1901–2014	1900

Annual precipitation showed large interannual variations without any specific trend (Figure S1a). Three subbasins (i.e., UM, MI, and AR) experienced a larger increase in temperature, and two subbasins (i.e., OH and LM) experienced precipitation increases. During the study period, the average temperature was 11.2 ± 0.7 °C and the mean precipitation was 753.7 ± 76.6 mm. Extreme events including severe droughts and wet periods have been previously described in Ren et al. (2016), which had a major impact on DOC and DIC exports (Tian, Ren, et al. 2015). We included N inputs from atmospheric deposition and synthetic N fertilizer application (Figure S1b). Atmospheric N deposition including oxidized (NO_y) and reduced N (NH_x) increased from 1.5 to 3.4 Tg N/year at a rate of 0.019 Tg N/year^2. Similarly, N fertilizer application increased by 437% from 1.5 to 8.1 Tg N/year during 1960–2014, showing a rapidly increasing trend from 1960 to 2000 and then becoming relatively stable thereafter. Nitrogen fertilizer use in the Mississippi River basin accounted for ~65% of the total fertilizer application in the continental United States. Presently, intensive agricultural activities associated with higher synthetic N fertilizer use have been implemented in the Midwestern United States, which encompasses most of the entire Mississippi River basin. Lands for agricultural use shifted from the Eastern to the Midwestern United States, covering most of the Mississippi river basin in the contemporary period (Figure 1) (Chen et al., 2006; Ren et al., 2016).

2.3. Simulation Experimental Design

DLEM simulations include three steps: (1) an equilibrium run that uses 30-year (1901–1930) mean climate to develop the simulation baselines for carbon, N, and water pools, (2) a spin-up simulation of 90 years before 1901 that was performed to eliminate noise caused by the simulation shift from the equilibrium to the transient mode, and (3) a transient mode using 114 years of input data sets to generate simulation results. We designed six numerical experiments to study the spatial and temporal patterns of N loading in the river basin and associated responses to multiple environmental changes (Table 1). A reference run (S0) was performed by holding all factors at the 1900 level during 1901–2014, including climate, CO_2 concentration, LUC, and atmospheric N deposition. This allowed for an examination of model fluctuations resulting from internal system dynamics. Then, we considered all time-series data sets as input drivers to simulate water discharge and N loading from the river basin (S1).

To quantify the individual contributions of environmental factors to annual variations of N loading, we then performed a series of factorial experiments: S2: holding climate constant; S3: holding CO_2 constant; S4: holding atmospheric N deposition constant; S5: holding N fertilizer constant; and S6: holding land use change constant. For instance, to determine the specific impact of climate, we ran the model using the gridded data of all other factors during 1901–2014 while keeping climate at the 1900 level. Then, we used results from S1 to subtract S2 to obtain the contribution of climate to annual N loading. The overall change induced by all environmental factors was the difference between S1 and S0 simulation, as defined as ΔDIN_{all} or ΔTON_{all}. The change associated with each factor is defined as $\Delta DIN_{factori}$ or $\Delta TON_{factori.}$ The relative contribution (%) of each factor to the overall change in DIN or TON fluxes is described as $\Delta DIN_{factori}/\Delta DIN_{all}$ or $\Delta TON_{factori}/\Delta TON_{all}$, respectively, and the interactive effect is calculated as $(\Delta DIN_{all}\text{-}\Sigma\Delta DIN_{factori})/\Delta DIN_{all}$ or $(\Delta TON_{all}\text{-}\Sigma\Delta TON_{factori})/\Delta TON_{all}$.

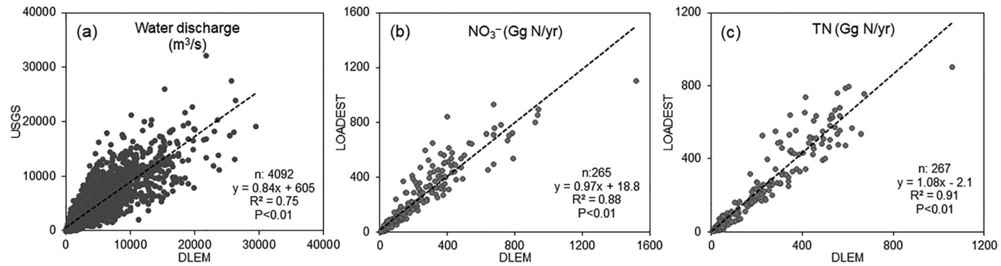

Figure 3. Comparisons of (a) monthly water discharges (m^3/s) between DLEM simulations and station observations from USGS water monitoring stations, (b) annual NO_3^- export and (c) annual TN (total nitrogen) export between DLEM simulations and LOADEST model from 1980 to 2014. Annual comparisons of water discharge, NO_3^- export, and TN export at each site are shown in Figures S2–S5. Note that USGS monitoring stations and their covering time periods for DLEM evaluations of water discharge, NO_3^- export, and TN export are not all the same (Table S1).

3. Results

3.1. Model Performance Evaluation

Ten USGS gauge stations with daily/monthly discharge and NH_4^+/NO_3^-/TON measurements were selected to evaluate the model performance in simulating riverine N fluxes (Table S1). We used the data sets from USGS and the LOAD ESTimator (LOADEST) model to generate N loading from subbasin rivers. The Nash-Sutcliffe model Efficiency (NSE) coefficient was calculated to represent the match of modeled discharge/NH_4^+/NO_3^-/TON to the observed data. A comparison between DLEM estimates and those from selected sites obtained from USGS water monitoring stations is given in Figure 3. The comparison of annual time series of all modeled/LOADEST N export values for available sites is described in supporting information (Figures S2–S5). These comparisons show general agreement and strong correlation, although some scatter in the relationship depending on location.

Seasonal water discharges from DLEM simulations and USGS water monitoring stations were consistent for the 10 selected locations (Figure S2). The coefficients of determination (R^2) ranged from 0.46 to 0.69, and NSE ranged from −0.14 to 0.68. Two stations (USGS Station IDs 03609750 and 07337000) in the TNS and Red river subbasins showed less consistency, with R^2 values of 0.31 and 0.27, respectively. The seasonal comparison demonstrates that DLEM is capable of simulating water discharge in the entire Mississippi River basin including a realistic representation of monthly peaks and troughs.

This analysis gives us the confidence that DLEM is capable of simulating DIN and TON loadings in the Mississippi River basin over a long-term period. For N loading comparisons, we included annual changes of NH_4^+, NO_3^-, and TON in the reference water quality data for the selected sites. Although water discharge provided by USGS water stations are available on a daily basis, data of water quality (NH_4^+, NO_3^-, and TON) are discrete, such as once a month. Here we used the LOADEST model to generate continuous N loading data for comparison with DLEM simulations on monthly and annual scales. There are only five sites available for NH_4^+ export comparisons. Although DLEM did capture the seasonal variations of NH_4^+ loading, the magnitudes of modeled and LOADEST estimates had large discrepancies (Figure S3). The Sutcliffe model efficiency coefficient ranged from −1.42 to 0.3 and R^2 ranged from 0.02 to 0.64. Nitrate loading comparisons agreed well for the two models with R^2 values greater than 0.5 at five sites, and NSE is ranging from 0.17 to 0.69 (Figure S4). Modeled and LOADEST estimates at three sites (USGS Station IDs 03612500, 07250550, and 07355500) in the OH, AR, and Red River subbasins were less consistent with R^2 values between 0.31 and 0.42 and NSE between −0.35 and 0.17. Similarly, DLEM simulations of TON export was in reasonable agreement with the LOADEST estimates for the selected sites of seven subbasins, but there were some exceptions with NSE ranging from 0.06 to 0.69 (Figure S5). Even though the interannual variations are comparable for two sets of estimates, R^2 values were less than 0.3 at two sites (USGS Station IDs 03612500 and 07355500) in the OH and Red River subbasins.

3.2. Long-Term Trend and Interannual Variations in N Loading

Over the past 114 year from 1901 to 2014, total DIN fluxes nearly doubled, from 387 to 715 Gg N/year, among which NO_3^- export showed a more substantial increase compared to NH_4^+ (Figure 4). Nitrate export

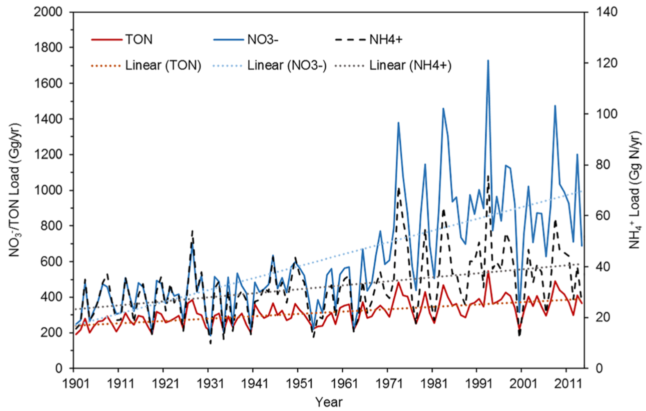

Figure 4. The trends and interannual variations in simulated NH_4^+, NO_3^-, and TON fluxes from the Mississippi River basin during 1901–2014.

accounted for an average of 95% of the total DIN export in the river basin. Compared with the first decade of the twentieth century, NO_3^- export during 2000–2014 increased by 140% (Table 2). There were no obvious increases in NO_3^- export during 1901–1960 even though there were large interannual variations. However, after the late 1960s, a rapid increase of NO_3^- export was seen in the river basin with even larger interannual variations through 2014; the largest annual NO_3^- export (1,730 Gg N/year) was found in 1993, while the lowest amount (315 Gg N/year) occurred in 2000. Annual NH_4^+ export showed variations similar to NO_3^- and increased by 30% over the same time period. The highest amount of NH_4^+ export (76 Gg N/year) was in 1993 and the lowest amount (12 Gg N/year) was in 2000. There was a slight increase in TON export during the study period (Figure 4). The TON load increased from 243 Gg N/year in the 1900s to 368 Gg N/year during 2000–2014 with large interannual variations. Similar to the DIN load, the highest amount (549 Gg N/year) of TON load was observed in 1993 and the lowest value (219 Gg N/year) was recorded in 2000.

3.3. Seasonal Patterns in N Loading

The comparisons of seasonal DIN and TON exports based on DLEM simulations agreed with the LOADEST estimates for the entire study region during 1990–2014 (Figure 5). River discharge was largest in the spring and least in the autumn. The largest seasonal DIN export occurred during the spring period (March–May) and accounted for an average of ~39% of annual total during 1990–2014, followed by winter (December–February, ~29%) and summer (June–August, ~21%). However, for some years (i.e., 1990, 1995, 1998, 2000, 2008, 2011, and 2013), the DIN export was higher during summer than during winter. The DIN export during autumn contributed least to the total annual export for the 1990–2014 period. Similarly, spring had the highest TON export (~36%), while autumn had the lowest (~15%). The TON export during winter was the second largest, except for some years (i.e., 1990, 1995, 1996, 1998, 1999, 2000, 2002, 2008, 2011, and 2013) that had higher export during summer.

We further studied the impact of extreme events on seasonal N export from 1990 to 2014. We found that the sum of DIN and TON export for the period (684 and 219 Gg N, respectively) peaked between May and September 1993, which was also the period of greatest flooding in the Mississippi River basin, within the same decade of 1990–1999. Summer 2013 was also characterized by record floods, and the corresponding DIN and TON export was 123% and 70% higher, respectively, as compared to the average DIN and TON export during 2000–2014.

Table 2
DLEM Simulated Average DIN (NH_4^+ and NO_3^-) and TON Fluxes in the Mississippi River Basin During the 1900s and 2000–2014

River basins	Drainage area (km^2)	NH_4^+ (Gg N/year) 1900s	NH_4^+ (Gg N/year) 2000–2014	NO_3^- (Gg N/year) 1900s	NO_3^- (Gg N/year) 2000–2014	TON (Gg N/year) 1900s	TON (Gg N/year) 2000–2014
UM	489,086	6.5	8.1	63.9	171	69.7	99.1
MI	1329,662	3.8	4.9	73.8	187.0	31.8	47.6
OH	376,290	5.6	8.7	126.2	275.1	77.2	119.5
AR	408,566	0.19	0.37	6.3	16.8	13.3	26.0
Red	178,226	0.38	0.74	3.7	11.1	7.5	18.9
TNS	104,676	0.32	0.33	13.4	19.0	15.8	19.8
LM	189,653	9.0	12.88	76.4	194.7	27.7	39.7
MRB	3,193,302	25.8	36.0	363.7	874.4	243.0	378.5

Note. UM represents Upper Mississippi River basin, MI represents Missouri River basin, OH represents Ohio River basin, AR represents Arkansas River basin, Red represents Red River basin, TNS represents Tennessee River basin, LM represents Lower Mississippi River basin, and MRB represents Mississippi River basin.

3.4. Spatial Patterns in N Loading

Although all subbasins have experienced increases in DIN and TON export (Table 2), the spatial pattern and magnitude of DIN and TON loads varied dramatically among the seven subbasins of the entire Mississippi River basin during the past 114 years (Figure 6). The OH was the largest contributor to the total N loads in the entire basin, followed by the UM and LM subbasins. In contrast, the TNS subbasin accounted for the lowest total N load.

Compared with the first decade of the twentieth century, our estimate showed that NH_4^+ export during 2000–2014 from the OH and LM subbasins increased by 55% (3.1 Gg N) and 44% (3.9 Gg N), respectively, which was the largest increase among all subbasins. The UM and MI contributions increased by 25% and 30% corresponding to amounts of 1.6 and 1.1 Gg N, respectively. A significant increase in NH_4^+ export was observed for the AR and Red subbasins even though their baseline values were much lower compared to those from the OH, UM, LM, and MI subbasins. NH_4^+ export

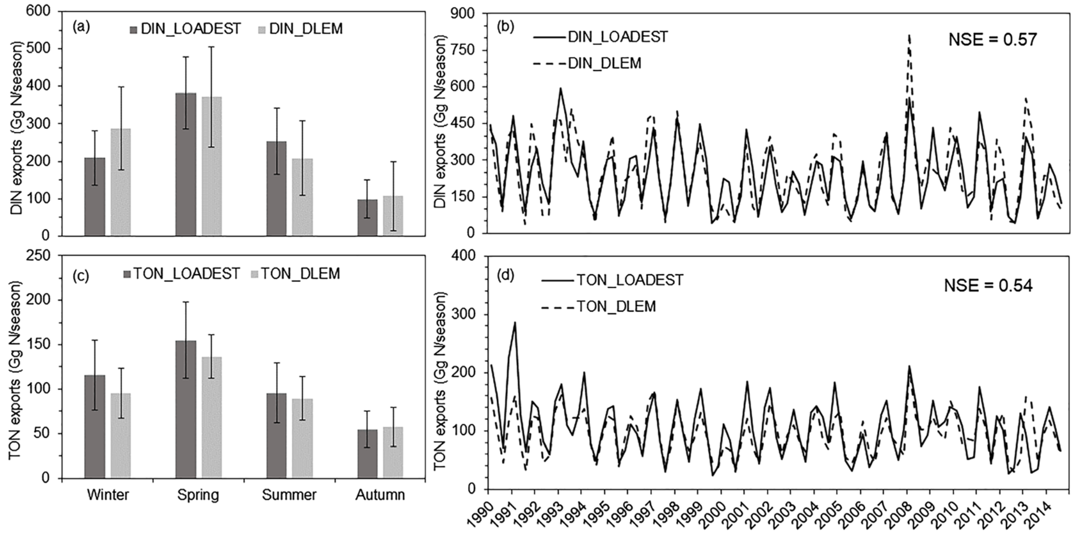

Figure 5. Comparison of long-term average and seasonal DIN (NH_4^+ and NO_3^-) export with LOADEST estimates (a and b); comparison of long-term average and seasonal TON export with LOADEST estimates from the Mississippi River basin during 1990–2014. Note that LOADEST estimates are obtained from the United States Geological Survey Open File Report (https://toxics.usgs.gov/pubs/of-2007-1080/index.html). Winter includes December–February; spring includes March–May; summer includes June–August; autumn includes September–November. Note that the error bars show the annual variability of seasonal DIN or TON exports during 1990–2014 (1± standard deviation). The tick marks in (b) and (d) correspond to winter.

from the TNS River subbasin contributed least to the overall Mississippi River basin export and the increase over time was negligible (<5%).

Compared to the beginning of the twentieth century, the increase in NO_3^- load from the OH, averaging 148 Gg N during 2000–2014, was largest among all subbasins, followed by the LM and MI with values of 118.3 and 113.2 Gg N, respectively. The AR and Red River subbasins also experienced significant increases, 167% and 200%, although the absolute amounts were smaller compared to other subbasins. NO_3^- loads from the TNS River subbasin increased by 42% with a value of 5.6 Gg N, which was considerably less than the increases seen for the UM, MI, and OH River subbasins.

The increases in TON export from four major subbasins (i.e., LM, UM, MI, and OH) were much lower than those for NO_3^-. The greatest increase in TON export was from the OH of 42.3 Gg N. The UM, MI, and LM all experienced large increases in TON export with corresponding values of 29.4, 15.8, and 12 Gg N, respectively. Similar to the increase in NH_4^+ export, TON export increased dramatically in the AR and Red subbasins. However, trends were undetectable in the TNS subbasin.

3.5. N Loading Responses to Multiple Environmental Factors

During the period 1901–2014, the substantial increases in DIN (~2,935 Gg N) and TON (~633 Gg N) export from the Mississippi River basin were attributable to a number of factors (Figure 7). Synthetic N fertilizer application and atmospheric N deposition were the two major factors that caused the rapid DIN export increases, accounting for 71% and 20%, respectively, of the total increase. LUC and synthetic N fertilizer are two primary contributors to the total TON increase, accounting for 51% and 35%, respectively, of the overall increase. The increasing atmospheric CO_2 and LUC had a small effect on DIN export throughout the 114 years. The impact of LUC on TON export was dominant before the 1960s when synthetic N fertilizer was not widely used but became less important during the last five decades. The interactive effect of all factors was positive and increased total DIN export by ~11%, while it was slightly negative and reduced total TON export by ~2% during the past 114 years.

The interannual variations in DIN and TON export were largely due to climate variability, which was reflected in the specific hydrological conditions in different years. After the 1990s, climate exhibited a

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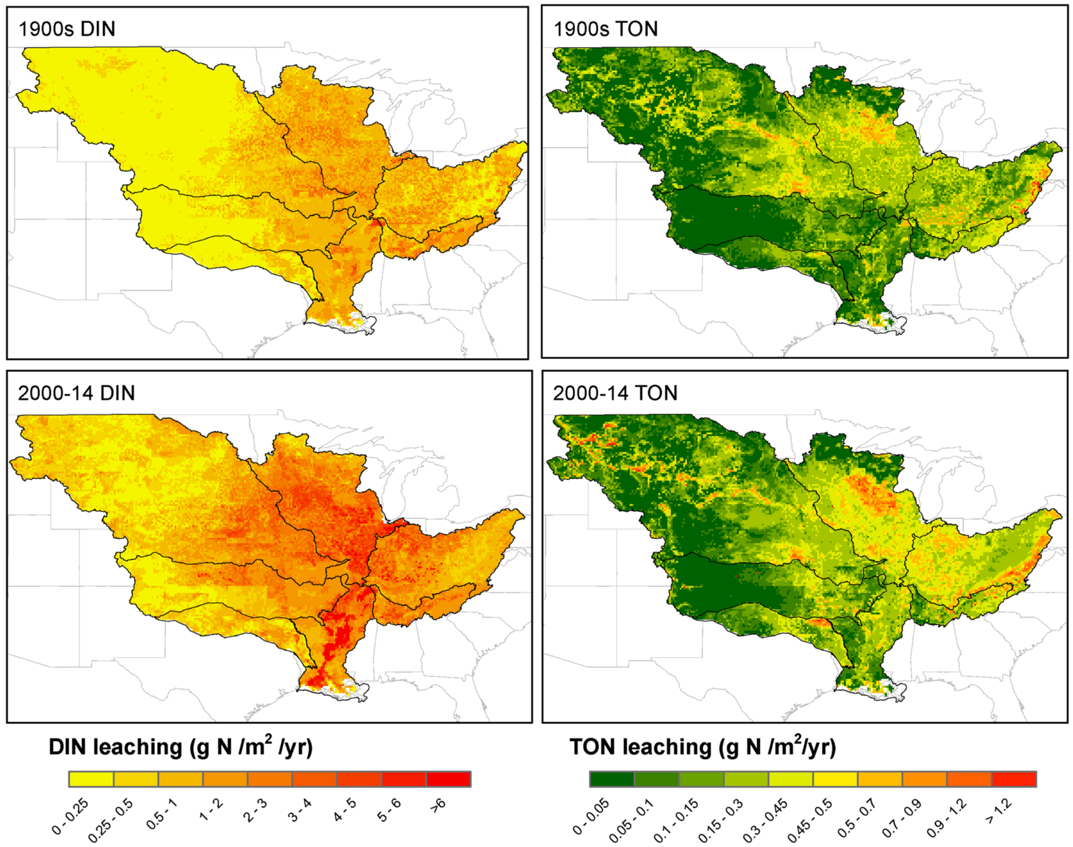

Figure 6. The spatial distribution of simulated DIN (NH_4^+ and NO_3^-) and TON leaching (g N/m^2/year) from the Mississippi River basin during the 1900s and 2000–2014.

positive impact on DIN export. In contrast, climate change resulted in a reduction of ~62 Gg N of TON export between 1901 and 2014. This negative impact of climate variability on TON export was in sharp contrast with climatic effects on DIN export, particularly during years with extreme weather conditions. For example, during a wet year (2008), both DIN and TON export were relatively higher in most areas with a larger increase in the central Mississippi River basin (Figure S6). During a dry year (2006), however, DIN export was notably lower in the central basin, while TON export was smaller across most parts of the basin with a notably large decrease in the central and southern basins of the Mississippi (Figure S6).

4. Discussion

4.1. Comparison With Previous Studies

Nitrogen, especially NO_3^-, is the major driving factor affecting the size of the dead zone in the northern Gulf of Mexico (Turner et al., 2006). Thus, it is particularly important to investigate the long-term trends and interannual variations in DIN and TON loads delivered from the river basin. Previous estimates of N loads in this region have been conducted using various models, including simple statistical models (Goolsby et al., 1999), semimechanistic simulation models (the Soil and Water Assessment Tool; Gassman et al., 2007), and a hybrid statistical/mechanistic model (SPARROW; Smith et al., 1997; Nutrient Export from WaterSheds, Mayorga et al., 2010). The regional comparisons with previous estimates confirm that DLEM is able to reasonably represent N fluxes from the Mississippi River basin (Table S2). DLEM 2.0-based estimates of NO_3^- are in good agreement with estimates from Goolsby et al. (2000) and the LOADEST AMLE Predicted Load, while TON estimates are 37% and 23% lower than their estimates, respectively. Alexander et al. (2007) and Robertson et al. (2014) provided TN estimates of 1,461 (527–3,492) during 1975–2000 and

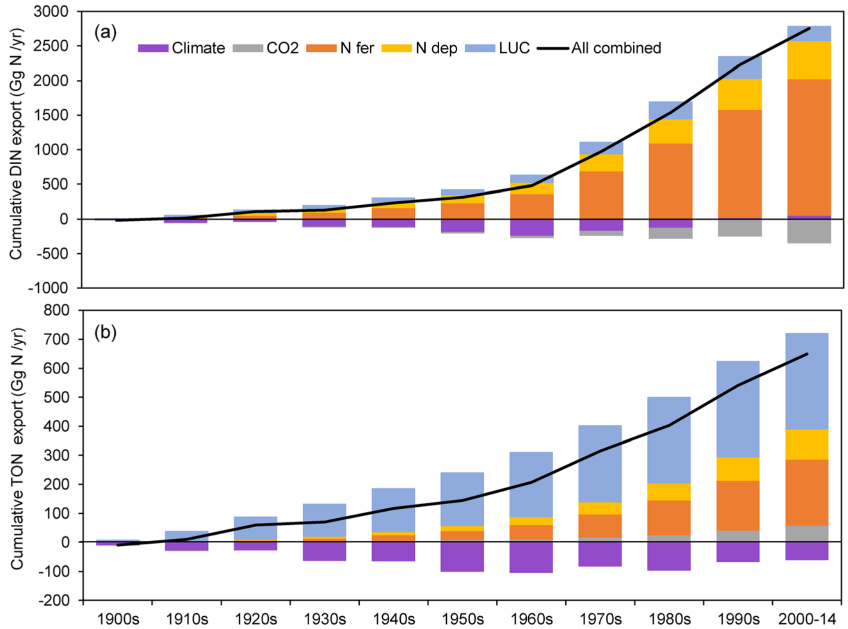

Figure 7. Changes in decadal mean DIN (a, NH_4^+ and NO_3^-) and TON (b) exports in response to multiple environmental factors including climate variability (climate), atmospheric CO_2, atmospheric N deposition (N dep), synthetic N fertilizer use (N fer), and land use change (LUC) during 1901–2014. Decadal changes were the cumulative difference between S1 and each counterfactual scenario (see section 2.3 and Table 1). The experiment S1 is a representation of real world considering the changes of all factors. In counterfactual scenarios (S2–S6), we hold one of factors at the level of 1900 while changing all other factors during 1901–2014. The all-combined line represents the overall change (the difference between S1 and S0), which is not equal to the summed effect from counterfactual experiments due to the interactive effect (see section 2.3).

1,351 Gg N year^{-1} in 2002 in the Mississippi River basin, respectively, with the SPARROW model. Our results for the same time period are 11% lower and 9% higher than these two estimates, respectively. Through using the USGS Weighted Regressions on Time, Discharge, and Season model, Oelsner et al. (2017) found NO_3^- contributed ~60% to the TN load during 1972–2012, which is consistent with the estimate by *An Integrated Assessment of Hypoxia in the Northern Gulf of Mexico* (2000). In contrast, the contribution of NO_3^- to TN load in this study (~66%) is higher than these previous estimates due to the underestimate of TON loads. As shown in Table S2, our estimates of NO_3^- load are comparable to LOADEST and previous studies, but our TON load was 23% and 37% lower than LOADEST and Goolsby et al. (2000), respectively. The annual difference between regression models and DLEM is possibly associated with model biases. The underestimate of TON during winters is probably due to less TON production in DLEM (Figure 5). In contrast, despite the high TON production in spring and summer, the fast removal processes through decomposition due to synthetic fertilizer N inputs may result in this underestimate.

For comparisons among different subbasins, our simulations are relatively consistent with the results of Alexander et al. (2007) and Robertson et al. (2014) suggesting that the UM and OH plus TNS subbasins are the major contributors to the total TN loading in the entire river basin (Tables S3). The third contributor in our study is the LM subbasin, while the MI subbasin ranks higher in their studies. Through the examination of spatial patterns of DIN export (Figure 6), we found that the LM subbasin was also one of the major TN sources. In this study, it was challenging to separate N export from the LM subbasin in DLEM. The N load from the LM subbasin was estimated by merely using the total DIN/TON fluxes in the entire Mississippi River basin to subtract the sum of DIN/TON values from the six upper subbasins (Tables 2 and S3). This calculation remains a large source of uncertainty since N export from other small rivers was also included in the LM subbasin, which would lead to an overestimation of N load from the LM subbasin. Moreover, inorganic and organic N exports from the six upper subbasins flow together into the LM and experience physical and chemical transformations, thus introducing additional uncertainty in the reported N load in the LM subbasin. Our estimate of TN export in the UM subbasin is lower by 17% and 12%, respectively than estimates from the two previous studies referenced above, while the estimates from the OH and TNS subbasins agree with previous estimates. However, our simulations at multiple sites within the UM are consistent with the USGS observations (Figures S2–S4).

4.2. Environmental Controls on N Export

Multiple environmental factors influence N loading in the Mississippi river basin. In our study, we found that synthetic N fertilizer input accounted for 71% and 40% of the increase in DIN and TON, respectively, since the 1970s. McIsaac et al. (2001) found that ~80% increase of net anthropogenic nitrogen inputs led to the large increase of riverine NO_3^- flux in the Mississippi during 1960–1998. Alexander et al. (2007) and McIsaac et al. (2001) pointed out that 52% of the N exported from the river basin to the Gulf originated from the cultivation of corn/soybean concentrated in the central Mississippi and Ohio River basins. Other studies have also reported that agricultural activities involving large N applications of organic and inorganic fertilizer, along with legume crops, were the dominant sources of N loading in the entire river basin (Hong et al., 2013; McCrackin et al., 2017; Robertson et al., 2014; White et al., 2014). Also, it was reported that N deposition is one of the major sources for N export in the Mississippi River basin (Alexander et al., 2007; Booth & Campbell, *2007*; Hong et al., 2013; Lawrence et al., 2000) and our study is in line with their findings. Booth and Campbell (2007) found that atmospheric nitrate deposition accounted for 17% of spring NO_3^- flux. Moreover, ammonia volatilization from synthetic N fertilizer application (particularly urea) is one of the primary sources for the atmospheric NH_x; therefore, the partial effect of N deposition on N export can be an indirect effect of fertilization. The annual N deposition showed a rapidly increasing trend, from 1.46 to 3.39 Tg N/year during 1901–2014, with a rate of 0.02 Tg N/year^2 (Wei et al., 2014). In our study, we found that N deposition accounted for 20% and 16% of DIN and TON flux increases, respectively, in the entire Mississippi river basin since the 1970s.

It has been a point of contention of prior studies that the effects of climatic variability, especially precipitation, have a significant impact on N loading (Sinha et al., 2016; Sinha et al., 2017). Donner and Scavia (2007) indicated that winter and spring precipitation variations in the central United States could serve as a strong predictor of spring NO_3^- flux in the Mississippi River. Pellerin et al. (2014) concluded that the seasonality in precipitation, snowmelt runoff, N fertilizer application, and relative groundwater contributed to high NO_3^- loads during summer and low NO_3^- loads during autumn. They also found that the 2012 drought and the 2013 flood events resulted in large leaching of stored NO_3^- from soils. Consistent with these findings, our DLEM simulations show that the relatively dry autumn period had the lowest relative contribution to the annual total NO_3^- load in 2012 and 2013, while summer had the largest contribution. Consistent with these previous estimates, we found a peak in NO_3^- loading (537 Gg N/season) during the spring 2013 flood and a low (282 Gg N/season) during the spring 2012 drought. The interannual variability of inorganic and organic N fluxes as simulated by DLEM were largely due to the short-term annual variations in precipitation. For example, a year with severe drought resulted in the reduced N exports from soils, while a flood year had the opposite effect. Similar findings were reported by previous studies on N and carbon loadings in various river basins of the USA based on DLEM simulations (Ren et al., 2016; Tian, Ren, et al., *2015*; Yang et al., 2015). In addition, temperature exhibited a positive impact on DIN export after the 1970s since temperature increased. It is evident that climate warming together with more N inputs intensified DIN export in the Mississippi River basin. The short-term variations in the magnitude and spatial patterns of precipitation and temperature have a major influence on N export and such variations are projected to increase with increasing climate change.

LUC is another major factor that influenced N export from the land. The Mississippi River basin is one of the most productive agricultural regions in the United States and has been significantly influenced by LUCs (Foley et al., 2004; Ren et al., 2016). A recent study found that the conversion of natural vegetation to croplands led to a significant increase in N loading above baseline levels in the Mississippi River basin before the intensive use of synthetic N fertilizer (Van Meter et al., 2017). Their study also shows that about 55% of the current annual N loads are from synthetic N fertilizer that was applied to cropland over 10 years ago. Raymond et al. (2008) argue that LUC along with agricultural practices increased river discharge in the Mississippi beyond that resulting from precipitation changes. These two factors have a greater impact on long-term trends, comparing to CO_2 fertilization and climate effects. DLEM simulations suggest that LUC slightly increased DIN fluxes during 1901–2014 (<10%), while it resulted in a relatively greater increase in TON export, especially before the 1970s when synthetic N fertilizer was not widely used (Figure 7). Interaction of LUC with other factors can affect N load to the river. For example, a recent study indicated that interaction of urbanization and climate variability amplifies watershed nitrate export (Kaushal et al., 2008).

4.3. Uncertainty and Future Work

This study considered major N inputs to the watershed and environmental factors that have impacted seasonal and annual N export in the Mississippi River basin over the past 114 years. DLEM simulations of water discharge and N export are in line with observations and other empirical and modeling studies. However, low correlations are shown at several sites (Table S1). For example, the negative NSEs at Missouri River at Hermann, Mo. (USGS Station ID 06934500) are associated with an overestimate of DLEM-simulated water discharge and NH_4^+ export from the Missouri River. DLEM simulations of NO_3^- and TON loads show good correlations with the LOADEST model in subbasins of Mississippi River basin, yet for NH_4^+ load with negative NSEs shown at most sites. This is largely due to measurements variability from field experiments (Figure S3). In addition, USGS water monitoring stations sample the water quality for a certain period (e.g., once a month) and provide us with discrete water quality observations. The LOADEST model that generates time series of N export was used to make comparison with DLEM simulations. Low NSEs between the comparison in some sites may be due to the autocorrelation issue in the LOADEST model that may substantially hinder its performance in changing environmental conditions. Thus, large uncertainty remains in evaluating process-based model performance through the comparison with the regression estimator.

There still remain several important factors affecting N fluxes from soils that were not considered in this study. The watershed inputs of N are strongly coupled with the watershed N export. In our study, we mainly focused on two sources of N input: synthetic N fertilizer use and atmospheric deposition. In reality, other than these two factors, the watershed inputs include animal manure application and human sewage, although their contributions are significantly smaller than N fertilizer (Alexander et al., 2007; Booth & Campbell, 2007). It has been suggested that tile drained regions can increase the transport efficiency of N fluxes to streams resulting in higher N export, especially in regions with high N inputs (McIsaac & Hu, 2004). David et al. (2010) found that tile drainage explained 17% of the spatial variation in winter–spring NO_3^- yield in the Mississippi River basin. Thus, the tile drainage effect should be included in future modeling studies. Further, there are thousands of constructed dams in the Mississippi River basin that could have important effects on water discharge and N exports (Strauss et al., 2011), which were not considered in this study. As multiple input data sets drive model simulation (e.g., climate, LUC, and synthetic N fertilizer), the quality and accuracy of these data sets will ultimately affect the accuracy of the N export estimates and associated temporal and spatial changes. For example, we used HYDE 3.2 LUC data to drive our simulations. Recently, Yu and Lu (2018) compared different existing LUC data sets for the continental United States and showed that a large discrepancy exists regarding the temporal changes in the cropland area. The steady or increasing N concentration in surface waters may be associated with the time lags due to legacy N in the watershed despite implementing conservation strategies. Although DLEM has included the legacy N from previous years during the simulation period from 1900 to 2014, the quantification of its contribution to N export from the Mississippi River basin will be considered in greater detail in our future studies. In addition, it would be important to consider other data sets for conducting analyses and evaluating associated data uncertainties. For example, Sinha et al. (2017) found that future precipitation changes under the "business-as-usual" scenario could increase riverine TN loads for the continental United States by 19% by the end of the 21st century. Thus, future work should include a focus on improved understanding on how climate-related changes may affect N export in the Mississippi River basin by the end of this century for different scenarios indicated in the fifth assessment report of the Intergovernmental Panel on Climate Change (AR5).

5. Conclusions

A process-based model, DLEM, was used to simulate DIN and TON export from the Mississippi River basin over the period 1901–2014. Our results show that DLEM is capable of simulating the monthly and annual N export dynamics from the entire basin as well as individual subbasins. Factorial experiments show that the increasing atmospheric CO_2 and LUC had a relatively small effect on DIN export throughout the entire

114 years of simulation. In contrast, the impact of LUC on TON export was dominant before the 1960s, when mineral N fertilizer was not widely used, but became less important during the last five decades. We found a substantial increase in DIN and TON export in the study region, most notably in the OH subbasin. This significant increase in N export is primarily due to heavy use of synthetic N fertilizer in crop production, with corresponding peak N export in the spring. In addition, DLEM captures N dynamics as influenced by extreme weather in the Mississippi River basin. In addition, the interannual variation in simulated DIN and TON exports was affected by variability in climate-related conditions, including increasing frequency of extreme climate events during the study period. We found low NO_3^- loading during the spring 2012 drought followed by a peak in NO_3^- loading during the spring 2013 flood. Thus, short-term variations in the magnitude and spatial patterns of rainfall have a major influence on N export and such extreme rainfall are projected to increase with increasing climate change. Although the implementation of N reduction has been carried out for the past three decades, total N loading to the Gulf of Mexico from Mississippi River basin has not decreased significantly. Due to the legacy effect from historical N accumulation in soils and riverbeds, both a reduction in synthetic N fertilizer inputs and improved N management practices for effectively preserving and restoring water quality in the northern Gulf of Mexico.

Acknowledgments
This study was supported in part by the National Science Foundation grant 1903722, the National Aeronautics and Space Administration grants NNX12AP84G, NNX14AO73G, and NNX10AU06G, the National Oceanic and Atmospheric Administration grant NA16NOS4780204, and the OUC-AU Joint Center Program. We are grateful to Robert D. Sabo, Luis Lassaletta, and an anonymous reviewer for their very constructive comments that have helped to significantly improve the paper. The model input and output data used in this study are archived in International Center for Climate and Global Change Research at Auburn University (https://wp.auburn.edu/cgc/). Model outputs are also archived in the Oak Ridge National Laboratory Distributed Active Archive Center (https://doi.org/10.3334/ORNLDAAC/1699).

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