



Global Biogeochemical Cycles

RESEARCH ARTICLE

10.1002/2016GB005395

Key Points:

- A century-long increase in dissolved organic carbon export occurred from the Mississippi River basin
- Land use and land management practices dominated DOC export increase
- Climate change/extremes controlled interannual and decadal variations in DOC export

Supporting Information:

- Supporting Information S1

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Citation:

Ren, W., H. Tian, W.-J. Cai, S. E. Lohrenz, C. S. Hopkinson, W.-J. Huang, J. Yang, B. Tao, S. Pan, and R. He (2016), Century-long increasing trend and variability of dissolved organic carbon export from the Mississippi River basin driven by natural and anthropogenic forcing, *Global Biogeochem. Cycles*, 30, 1288–1299, doi:10.1002/2016GB005395.

Received 17 FEB 2016

Accepted 11 AUG 2016

Accepted article online 15 AUG 2016

Published online 5 SEP 2016

Century-long increasing trend and variability of dissolved organic carbon export from the Mississippi River basin driven by natural and anthropogenic forcing

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Abstract There has been considerable debate as to how natural forcing and anthropogenic activities alter the timing and magnitude of the delivery of dissolved organic carbon (DOC) to the coastal ocean, which has ramifications for the ocean carbon budget, land-ocean interactions, and coastal life. Here we present an analysis of DOC export from the Mississippi River to the Gulf of Mexico during 1901–2010 as influenced by changes in climate, land use and management practices, atmospheric CO₂, and nitrogen deposition, through the integration of observational data with a coupled hydrologic/biogeochemical land model. Model simulations show that DOC export in the 2000s increased more than 40% since the 1900s. For the recent three decades (1981–2010), however, our simulated DOC export did not show a significant increasing trend, which is consistent with observations by U.S. Geological Survey. Our factorial analyses suggest that land use and land cover change, including land management practices (LMPs: i.e., fertilization, irrigation, tillage, etc.), were the dominant contributors to the century-scale trend of rising total riverine DOC export, followed by changes in atmospheric CO₂, nitrogen deposition, and climate. Decadal and interannual variations of DOC export were largely attributed to year-to-year climatic variability and extreme flooding events, which have been exacerbated by human activity. LMPs show incremental contributions to DOC increase since the 1960s, indicating the importance of sustainable agricultural practices in coping with future environmental changes such as extreme flooding events. Compared to the observational-based estimate, the modeled DOC export was 20% higher, while DOC concentrations were slightly lower. Further refinements in model structure and input data sets should enable reductions in uncertainties in our prediction of century-long trends in DOC.

1. Introduction

Dissolved organic carbon (DOC) flux from terrestrial landscapes to rivers and further to the ocean is a fundamental component of the global carbon cycle [Butman *et al.*, 2016; Dai *et al.*, 2012; Meybeck, 1993; Schlesinger and Melack, 1981; Smith and Hollibaugh, 1993]. DOC produced in terrestrial, riverine, and ocean ecosystems is the major source of organic carbon fueling microbial food webs, and DOC in marine and freshwater systems represents one of the greatest cycled reservoirs of organic matter on Earth [Butman and Raymond, 2011; Cole *et al.*, 2007]. Small changes in the carbon balance of the terrestrial biosphere could result in large changes in riverine DOC flux [Aitkenhead and McDowell, 2000] and hence could alter DOC concentrations in freshwater and marine systems [Hedges, 1992]. It is imperative to investigate the variations in the timing and magnitude of DOC export and explore the underlying mechanisms to increase our ability to predict biogeochemical consequences of natural and anthropogenic changes.

Changes in the terrestrial environment, both natural (e.g., climate change, atmospheric CO₂, and fire) and anthropogenic (e.g., deforestation, cropland expansion, agricultural land management, and urbanization), have greatly altered carbon production, stocks, decomposition, movement, and export from land to river and ocean systems [Bengtson and Bengtsson, 2007; Canuel *et al.*, 2012; Christ and David, 1996; Liu and Greaver, 2010; Zhang *et al.*, 2013]. For example, recent synthesis studies revealed a large increase in carbon

transport from land to ocean caused by human activities since preindustrial times (e.g., land use changes, soil erosion, liming, and fertilizer and pesticide application), which had been ignored in estimating the global carbon budget [Regnier *et al.*, 2013]. Climate change also plays an important role in altering DOC production and turnover in soil and DOC sources and fates in coastal ecosystems [Bengtson and Bengtsson, 2007; Canuel *et al.*, 2012]. Extreme climate events can lead to increases in riverine DOC export [Dhillon and Inamdar, 2013; Tian *et al.*, 2015]. Yet it remains unclear how natural and anthropogenic factors individually and interactively contribute to carbon transport, which can considerably hinder our efforts to assess the global carbon budget as well as to effectively manage coastal ecosystems and water quality.

As the third largest drainage basin area in the world, the Mississippi River basin contains one of the most productive agricultural regions in the world, and has been profoundly influenced by rapid changes in land use and human activity over the past century [Chen *et al.*, 2006; Foley *et al.*, 2004; Mackenzie *et al.*, 2000; Zhang *et al.*, 2012]. These changes have greatly altered the magnitude, annual and decadal variations, and centennial trend of DOC fluxes from land to the Gulf of Mexico. In this study, we first analyzed the observed DOC concentration from the United States Geological Survey (USGS) gauging station (St. Francisville, LA) for the last three decades. We then used a process-based, coupled hydrological/biogeochemical model [Liu *et al.*, 2013; Tian *et al.*, 2010], in combination with spatially explicit historical environmental information (see section 2), to investigate the spatial and temporal patterns of riverine DOC fluxes from the Mississippi River basin to the Gulf of Mexico from 1901 to 2010. We then conducted factorial simulation experiments to examine the effects of major natural and anthropogenic factors on DOC export over the study period. This study illuminates how climate and land use changes likely alter DOC export from land to the ocean on a centennial time scale.

2. Methods and Data

2.1. Data Sources

The data sets used for synthesis, analysis, and model evaluation were compiled from long-term observational data of water discharge and DOC concentration provided by the USGS Water Quality Samples for the Nation (<http://www.usgs.gov/water/>) at Mississippi River subbasin and whole basin levels. Two DOC data sets derived from unfiltered (1981–1995) and filtered (1996–2010) water samples were compiled into continuous time series of DOC flux for further analysis and model evaluation (see Text S2 in the supporting information). The model was calibrated against a database collected from published field experiments and metadata analyses (e.g., the amount of DOC leached per unit area in diverse ecosystems such as cropland, grassland, and forest). Details regarding calibration procedures can be found in our previous publications [Tian *et al.*, 2015; Liu *et al.*, 2013].

To examine the controls and causes of temporal and spatial variability in DOC flux, we developed historical gridded data sets with a spatial resolution of 5×5 arc min (approximately 9.2×9.2 km at the equator) that characterize changes in climate conditions (temperature, precipitation, radiation, humidity, etc.), atmospheric CO_2 , nitrogen deposition, and anthropogenic perturbations including land cover patterns and land management practices in terrestrial ecosystems of the Mississippi River basin for the period 1901–2010. These data sets were developed from multiple sources, and detailed information about data development was reported in our previous work [Liu *et al.*, 2013; Tian *et al.*, 2010].

2.2. The Coupled Hydrologic/Biogeochemical Modeling Approach

The Dynamic Land Ecosystem Model (DLEM), a coupled hydrological/biogeochemical land model provides daily, spatially explicit estimates of carbon, nitrogen, and water fluxes and pool sizes in terrestrial ecosystems and continental margin. It consists of five core components: biophysical characteristics, hydrological and biogeochemical cycles, plant physiological processes, vegetation dynamics, and land use and management. The DLEM 2.0 uses a cohort structure and is characterized by multiple soil layer processes, coupled carbon, water and nitrogen cycles, enhanced land surface processes, and dynamic linkages between terrestrial and riverine ecosystems [Liu *et al.*, 2013; Tao *et al.*, 2014; Tian *et al.*, 2015; Yang *et al.*, 2015; Ren *et al.*, 2015]. In this study, the DLEM simulates the production, consumption, and transport of dissolved organic carbon in soils and surface waters. It does this by incorporating multiple effects derived from the spatial heterogeneity in climate change (e.g., precipitation and temperature), atmospheric CO_2 , nitrogen deposition, and land cover change and land management practices (e.g., irrigation, nitrogen fertilizer, and harvesting). An illustration of the key processes

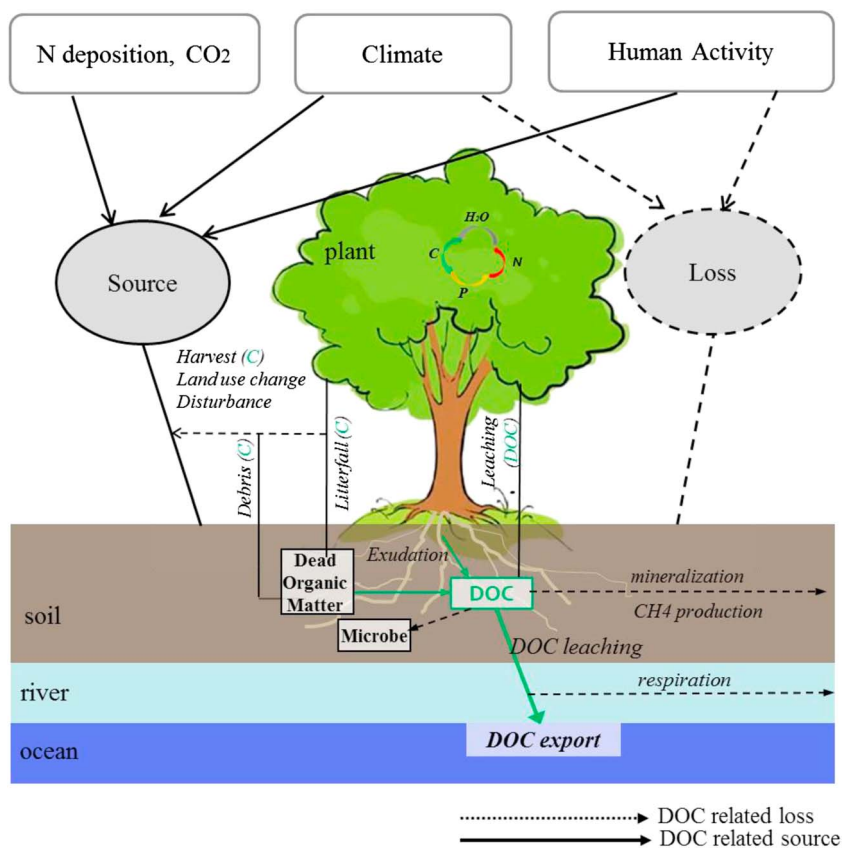


Figure 1. Key compartments, processes, and driving forces associated with production, consumption, storage, and transport of dissolved organic carbon (DOC) in the Dynamic Land Ecosystem Model (DLEM).

influencing DOC production, loss and transports in the DLEM model, and the mechanistic control by changes in natural and anthropogenic factors is given in Figure 1. Details regarding model simulations and the key processes controlling DOC production [Liu *et al.*, 2005; Parton *et al.*, 1993; Petersen *et al.*, 2005], transformation, loss [Chantigny, 2003], and transport [Coe, 2000] can be found in the supporting information for this article (Text S1) and a recent publication [Tian *et al.*, 2015].

2.3. Model Evaluation

In our previous work, key biogeochemical parameters were calibrated against field observations at multiple sites throughout North America, including the Mississippi River basin [Chen *et al.*, 2012; Ren *et al.*, 2015; Tian *et al.*, 2010; Tian *et al.*, 2012; Xu *et al.*, 2012]. In particular, hydrologically related parameters and key variables (runoff, evapotranspiration, river discharge, etc.) were calibrated and evaluated in our recent publications [Liu *et al.*, 2013; Pan *et al.*, 2015; Tao *et al.*, 2014]. Our recent study [Tian *et al.*, 2015] evaluated DOC fluxes against USGS water quality data at the subbasin levels (including sites along the Missouri River at Omaha (site No. 6610000) and Hermann (site No. 6934500), the Mississippi River at Grafton (site No. 5587450), and the Arkansas River near Little Rock (site No. 7263450)) during 2001–2010.

In this study, we collected more data and further evaluated the simulated DOC fluxes at the whole basin level (Mississippi River at St. Francisville). We consider the effect of sampling period on DOC flux estimation and apply Weighted Regressions on Time, Discharge, and Season (WRTDS) [Hirsch, 2014] with an R package (Exploration and Graphics for RivEr Trends) to estimate monthly and annual DOC fluxes (see details in Text S2). We used the most reliable data (since 1996) to evaluate model-simulated DOC concentration values (Figure 2) and also examined the temporal patterns of DOC flux and river discharge since 1981 (Figure S2). Finally, we compared model results with estimates of mean annual DOC export reported in other studies, including field observations [Trefry *et al.*, 1994; Benner and Opsahl, 2001; Bianchi *et al.*, 2004; Shen *et al.*, 2012;

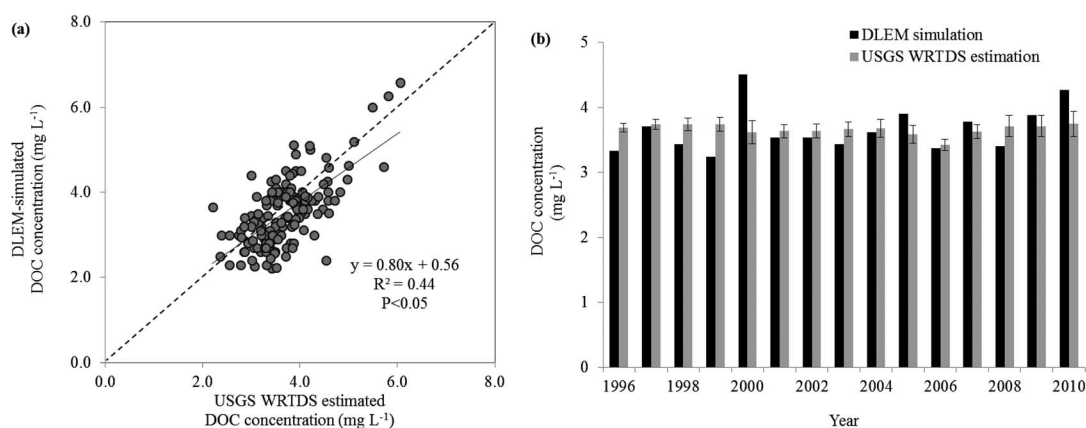


Figure 2. Comparisons of (a) monthly dissolved organic carbon (DOC) concentrations (mg L^{-1}), (b) annual mean DOC concentrations (mg L^{-1}) between DLEM simulations and station observations from the Mississippi River at St. Francisville (USGS site No. 07373420) during 1996–2010. Note: USGS values were estimated by the WRTDS approach and the error bars represent standard deviations around the annual means of USGS WRTDS estimates.

Lohrenz *et al.*, 2014], gauging stations [Smith *et al.*, 2005], empirical estimates [Ludwig *et al.*, 1996], and other process-based modeling approaches [Harrison *et al.*, 2005] (see Table S1 in the supporting information).

In general, our simulated mean DOC concentrations are comparable to observations. The DLEM-simulated average DOC export for 1971–2000 ($2.6 \pm 0.4 \text{ Tg C yr}^{-1}$) is comparable to a variety of other estimates such as Load Estimator (LOADEST) data (2.5 Tg C yr^{-1}) [Stets and Striegl, 2012], model-based estimates from the Global Nutrient Export from WaterSheds (NEWS) model (2.6 Tg C yr^{-1}) [Harrison *et al.*, 2005], and a synthesis of field observations (2.6 Tg C yr^{-1}) [Lohrenz *et al.*, 2014] (Table S1).

We found that DLEM-simulated DOC concentrations were comparable to observations (Figure 2). The model also captured most temporal patterns of DOC flux and of river discharge in recent decades (Figure S2). However, our simulated DOC export was higher than observations (over 20% for a 30 year average) (Figure S2b), while simulated DOC concentrations were lower than observed (root-mean-square deviation or RMSD between simulated and observed DOC concentrations was 0.5 mg L^{-1} for seasonal and 0.4 mg L^{-1} for annual (Figure 2). This was mainly a consequence of model estimates of river discharge being higher than observations (about 16% on 30 year average) (Figure S2a). One potential reason that our modeled estimates of river discharge were greater than observations is because the drainage basin in our simulation is about 10% larger than that defined by USGS. We also found a notable discrepancy between modeled and observed DOC fluxes in some years. For example, DLEM-simulated DOC concentration did not reflect high values around 1981 as observed by USGS but showed much higher value in 2000 than that observed. Therefore, in addition to uncertainty caused by input data, some missing or misrepresented mechanisms in DLEM model may introduce biases and variance in model results. For example, dam effects can sustainably influence river discharge and associated DOC concentration and export. Additional explanations for the differences in DOC fluxes between DLEM and other studies include differences in study periods, different methods used in various empirical studies, and different model approaches (statistical, biogeochemical and physical, and process-based ecosystem models; Table S1).

2.4. Numerical Simulation Experiments

The model was initiated with an equilibrium run, which used mean climate data sets to develop the simulation baselines for carbon, nitrogen, and water pools. Then a 90 year spin-up simulation (three spin-ups each of a 30 year period) was conducted using the detrended climate data to eliminate noise caused by the simulation shift from the equilibrium to the transient mode. Subsequently, the model was implemented using the time series of input data sets in the transient mode.

We designed 10 numerical experiments to investigate the causes of spatial and temporal patterns of DOC behavior in the context of multiple global changes (Table 1). To examine model fluctuation resulting from internal system dynamics, we first performed DLEM simulation (1: Reference) driven by all factors remained at 1900 levels through 1901–2010, including climate, land cover/land use change (LCLUC), land conversion

Table 1. Simulation Design^a

Numerical Experiments	Climate				LCLUC	
	Temperature	Precipitation	CO ₂	NDEP	Land Conversion	Management Practices
1: Reference	1900	1900	1900	1900	1900	1900
2: All	1901–2010	1901–2010	1901–2010	1901–2010	1901–2010	1901–2010
3: Climate	1901–2010	1901–2010	1900	1900	1900	1900
4: LCLUC	1900	1900	1900	1900	1901–2010	1901–2010
5: CO ₂	1900	1900	1901–2010	1900	1900	1900
6: Ndep	1900	1900	1900	1901–2010	1900	1900
7: PRECIP	1900	1901–2010	1900	1900	1900	1900
8: T	1901–2010	1900	1900	1900	1900	1900
9: LC	1900	1900	1900	1900	1901–2010	1900
10: LMPs	1900	1900	1900	1900	1900	1901–2010

^aSimulation experiments include the following: Reference: all environmental factors remain unchanged from 1900 levels; All: climate, carbon dioxide (CO₂), nitrogen deposition (Ndep), and land cover and land use (LCLUC) change during 1901–2010; Climate: only climate changes during 1901–2010 while other factors are kept constant at 1900 levels; LC and LMPs: only land cover and land management practices (fertilizer, irrigation, etc.) change, respectively, while other factors are constant at 1900 levels; Two additional simulations are designed to examine the relative role of temperature (T) and precipitation (PRECIP).

(LC), and land management practices (LMPs), and atmospheric chemical components (atmospheric CO₂ concentration and nitrogen deposition (Ndep)). Then we conducted a combined simulation (2: All) with DLEM driven by all factors varied during 1901–2010 in order to simulate the effects of temporal and spatial dynamics of all five environmental factors on DOC fluxes from the Mississippi River basin.

To attribute the relative contributions of these factors to annual variations of C export, we then designed a series of factor-specific simulation experiments, which included: 3: Climate, 4: LCLUC, 5: CO₂, and 6: Ndep. For example, to determine the effects of climate variability alone, we ran the model using the gridded historical daily data for air temperature (including maximum, minimum, and average air temperatures), relative humidity, solar radiation, and precipitation, but kept all other factors at 1900 levels.

To determine the relative role of precipitation (PRECIP) and temperature (T) in DOC export variations, we conducted additional simulations to examine which climate-related variable was the dominant factor controlling the variability of DOC export: 7: PRECIP and 8: T.

Finally, we conducted simulations to distinguish the effects of land conversion (LC) and land management practices (LMPs) from the combined effects of LCLUC: 9: LC and 10: LMPs.

To calculate the relative contributions of these factors, we used simulation attribution analysis. We defined the overall change caused by multiple environmental factors ($\Delta\text{DOC}_{\text{all}}$) as the difference between the All simulation and the Reference baseline simulation; and the change due to each factor ($\Delta\text{DOC}_{\text{factori}}$) as the difference between the factor-specific experiment and the baseline. The relative contribution (percentage) of each factor to the overall change in DOC flux can then be estimated as $\Delta\text{DOC}_{\text{factori}}/\Delta\text{DOC}_{\text{all}}$ and the interactive effect calculated as $(\Delta\text{DOC}_{\text{all}} - \sum\Delta\text{DOC}_{\text{factori}})/\Delta\text{DOC}_{\text{all}}$. Simulation attribution analysis has been widely used and details can be found in recent publications [Tao *et al.*, 2014; Tian *et al.*, 2012; Xu *et al.*, 2012].

3. Results

3.1. Environmental Changes Across the Mississippi River Basin

The Mississippi River basin has experienced substantial changes and variability in climate (i.e., temperature and precipitation), atmospheric CO₂ concentration, nitrogen (NO_x and NH₃) deposition, and land use and land cover since 1901 (Figures 3 and 4). We found large year-to-year variations in precipitation and mean air temperature, although no significant long-term trends were evident in the past 110 years (Figure 3a). There were three severe droughts (large increase in temperature and decrease in precipitation) that occurred in the 1930s, 1950s, and 2000s and two exceptionally wet periods (large increase in precipitation and small change in temperature) in the 1940s and 1970s. Atmospheric CO₂ concentration increased from 296 ppm to 385 ppm and nitrogen deposition (g N m⁻²) nearly doubled (Figure 3b). Land use and land cover also changed substantially. Cropland expanded at the expense of natural ecosystems across the entire basin. While grasslands were continually lost during the interval, cropland abandonment and reforestation occurred since

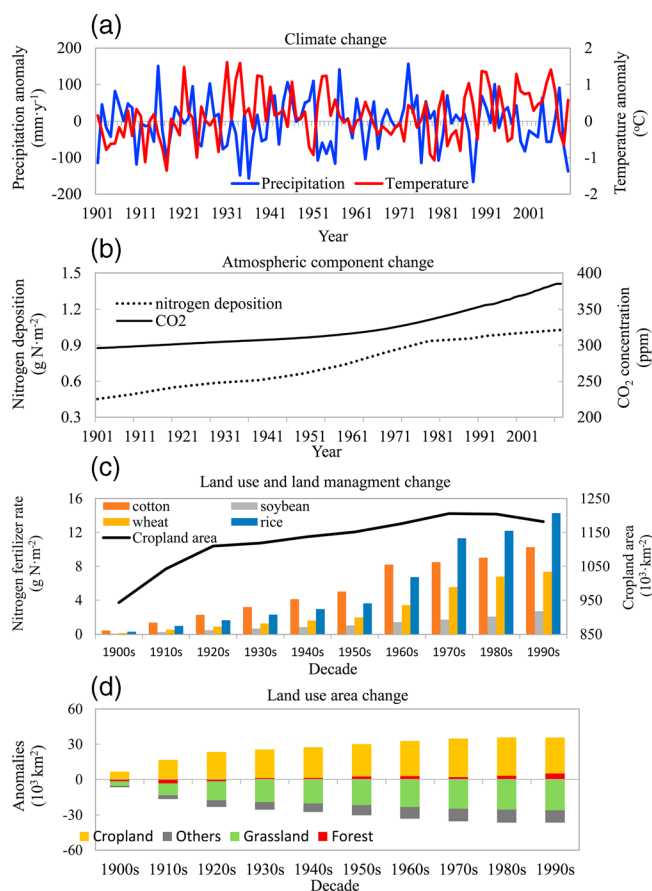


Figure 3. Temporal changes in multiple environmental factors during 1901–2010. (a) Climate (average temperature and precipitation); (b) atmospheric components (CO₂ and nitrogen deposition); (c) land use and land management (cropland area and nitrogen fertilizer rate); (d) decadal mean of changes in cropland, forest, grassland, and other types relative to the initial year (1900) across the Mississippi River basin over the 20th century.

2010) (Mann-Kendall trend test, $p < 0.001$) (Figure S1). The modeled temporal patterns were consistent with observations (Figures 2 and S2). In recent decades since 1981, both model simulations and USGS WRTDS estimations show large variations in annual water discharge and DOC export with slightly decreasing trends, while annual DOC concentration remained relatively stable.

3.3. Spatial Patterns of DOC Fluxes During 1901–2010

Large spatial variations in riverine DOC flux were found between the various subbasins of the Mississippi River system (Figures 6a and 6b). In general, DOC export was relatively high in the eastern area (Ohio and Mississippi Rivers) and low in the western part of the basin (Arkansas and Missouri Rivers). Substantial temporal increases in DOC export were attributable to the eastern basins, specifically the upper Mississippi River basin, upper and lower Ohio River basins, and eastern parts of the Arkansas and Ouachita River basins. We further examined the variations of riverine DOC export in specific years over the 20th century that coincided with severe droughts and heavy flooding events (Figure 6). We found dramatic differences in DOC export between wet and dry intervals that differed among regions. In drought years (Figures 6c, 6e, and 6g), riverine DOC export was quite low across the whole basin (approximately 12% lower relative to the 110 year average). In flood years (Figures 6d, 6f, and 6h), relatively high riverine DOC export was found, but in different flooded areas (approximately 54% higher compared to the 110 year average). For example, high riverine DOC export was found in the central Mississippi River basin in 1993 (Figure 6h), and in the north-eastern Mississippi River basin in 1973 (Figure 6f).

the 1930s in the upper and lower Ohio River basins (Figures 3c, 3d, and 4) [Liu *et al.*, 2013]. Cropland was managed very intensely, especially through the increased application of nitrogen fertilizers (Figure 3c).

3.2. Long-Term and Recent Trends in DOC Concentration and Flux

Simulation results show significant, long-term increases in both DOC concentration and export during 1901–2010 (Mann-Kendall trend test, $p < 0.001$). Mean annual export of DOC averaged over decadal intervals increased by over 40% from 1.8 ± 0.3 Tg C yr⁻¹ in the 1900s to 2.6 ± 0.4 Tg C yr⁻¹ in the 2000s (Table 2), albeit with large interannual variations (Figure 5). Furthermore, DOC concentrations in the estuary increased by approximately 70% over the study period, with small interannual variations. Seasonality analysis for the entire period shows that 75% of total annual export occurred over just half the year, in winter (37% of total export) and spring (37% of total export) (Table 2 and Figure S3). USGS observations derived from the WRTDS estimation also showed increasing trends in annual DOC concentration and DOC export (DOC concentration multiplied by water discharge) for the period 1931–

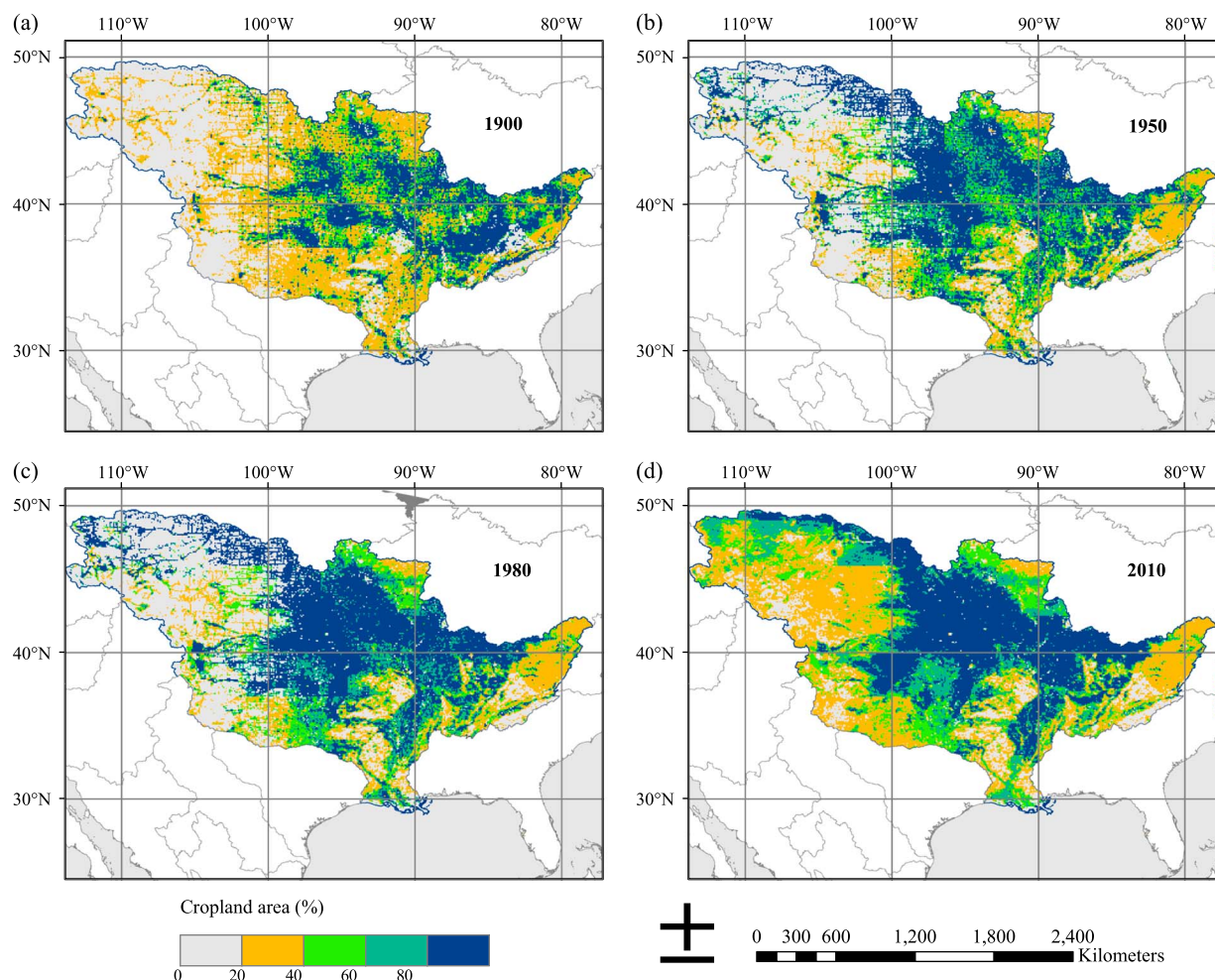


Figure 4. Fractional area of each 5 min grid cell used for cropland (%) in (a) 1900, (b) 1950, (c) 1980, and (d) 2000.

3.4. DOC Export Responses to Multiple Environmental Factors

Numerical simulations presented here provide evidence that human activities were the dominant factor contributing to the long-term increase in riverine DOC export. Land use management was responsible for 43% of the long-term increase, while land conversion contributed another 33% (76% collectively). CO₂, Ndep, and Climate increased DOC export by 25%, 18%, and 9%, respectively. The interactive effect of all the above

Table 2. Decadal Mean of Annual and Seasonal DOC Export from the Mississippi River Basin and Magnitude of Changes in Export Relative to Decadal Mean Export in the 1900s (1900–1910)^a

	Winter	Spring	Summer	Fall	Annual
<i>Decadal Mean DOC Export (Tg C yr⁻¹)</i>					
1900s	0.66 ± 0.14	0.66 ± 0.14	0.30 ± 0.09	0.19 ± 0.05	1.81 ± 0.32
1950s	0.69 ± 0.20	0.82 ± 0.16	0.31 ± 0.09	0.19 ± 0.08	2.01 ± 0.43
1990s	1.03 ± 0.30	0.99 ± 0.28	0.45 ± 0.10	0.28 ± 0.11	2.75 ± 0.67
2000s	0.98 ± 0.24	0.94 ± 0.20	0.41 ± 0.12	0.29 ± 0.10	2.62 ± 0.45
110 Year Average	0.83 ± 0.16	0.84 ± 0.12	0.34 ± 0.06	0.21 ± 0.05	2.23 ± 0.38
<i>Change in Export Relative to the 1900s Decadal Mean</i>					
1950s–1900s	5%	22%	3%	–4%	10.5%
1990s–1900s	58%	47%	47%	42%	51.1%
2000s–1900s	50%	41%	33%	44%	43.8%

^aThe ± values reflect the average variation in DLEM simulations during the decade for each season and year due to variations in streamflow and other forcing data.

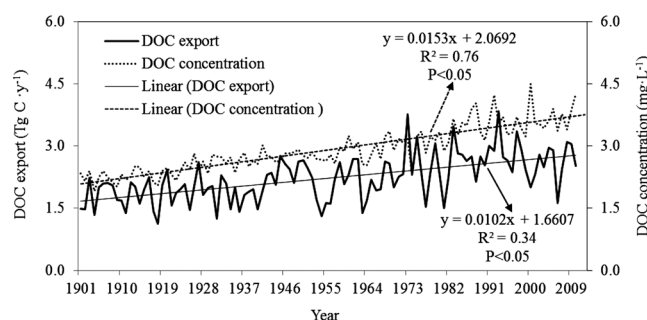


Figure 5. Simulated annual changes in dissolved organic carbon (DOC) export (Tg C yr^{-1}) and DOC concentration (mg L^{-1}) during 1901–2010.

study period. LC also contributed to increasing DOC export in the 1950s; however, its contribution to DOC export leveled off over the past 40 years.

4. Discussion

The increase in riverine DOC export from land to ocean can be caused by increased river discharge, increases in the concentrations of DOC, or both. A variety of studies have been conducted to distinguish the roles of natural and anthropogenic factors contributing to DOC flux [Christ and David, 1996; Harley *et al.*, 2006; Monteith *et al.*, 2007; Oh *et al.*, 2013; Pandey and Pandey, 2013; Tian *et al.*, 2013], in the context of rapidly changing environmental conditions that influence global water and biogeochemical cycles. Yet debates still exist regarding the roles of these factors in increasing or decreasing DOC export. A recent synthesis concluded that anthropogenic perturbations involving land use change, soil erosion, fertilizer use, and municipal sewage water inputs were major factors in stimulating DOC export through enhancement of both DOC source inputs and river discharge [Regnier *et al.*, 2013]. It is often difficult to separate the influence of natural carbon dynamics from human perturbations on carbon export. Our simulation “experiments” provide a means to separate the influences of these factors.

Our results shed light on the contribution of various factors affecting DOC export as well as offering insights into the mechanisms contributing to system responses. Human activities including LC and LMPs (fertilization, irrigation, tillage, etc.) accounted for the largest increase, more than 76%, in DOC export. Based on our LCLUC simulation experiments, we conclude that the combined effects of land cover change and management practices have led to a large increase in DOC sources and consequently DOC export, even though river discharge has decreased slightly. Based on single-factor simulations (LC and LMPs), we further separated the effects of land cover change from management practices. On average, LC alone contributed 33% to the total increase in DOC export, peaking in the 1950s as rapid crop expansion and reforestation occurred in the Mississippi River basin [Foley *et al.*, 2004; Turner and Rabalais, 2003]. One explanation is that land conversion from forests (or grassland) to cropland reduces water loss to the atmosphere through evapotranspiration while increasing runoff, which in turn leads to increased DOC export [Dunn, 1996]. Alternatively, a large amount of DOC may be released through cultivation-intensified degradation of the organic matter during the initial stages of forest clearing for agriculture [Bauer and Bianchi, 2011; Delprat *et al.*, 1997]. During later stages, as the original organic matter is stabilized, DOC concentrations decrease with duration of cultivation. At the same time, reforestation in the upper and lower Ohio basins is believed to have contributed to an increase in DOC export due to higher DOC leaching in forest land compared to other systems [Delprat *et al.*, 1997; Pandey and Pandey, 2013]. Since the 1950s, LC change (changed crop expansion pace and reforestation rate) affected both water discharge and DOC sources [Foley *et al.*, 2004] but had a relatively small impact on DOC export. LMPs, particularly those associated with fertilizer use (Figure 2c), played a dominant role in enhancing DOC export through stimulation of crop net primary productivity, organic matter decomposition, and DOC production and leaching. This finding is consistent with Liu and Greaver’s conclusion that nitrogen addition generally results in an increase in the carbon content of the organic layers in soil and DOC concentration, which is associated with an increase in carbon leaching [Liu and Greaver, 2010].

We also examined the relative contributions of environmental factors including Climate, CO_2 , and Ndep to DOC export. Our findings indicate a positive effect of elevated atmospheric CO_2 concentration on DOC

factors (see the calculation in section 2.4) was negative and reduced total DOC export by approximately 28% relative to the 110 year average. In contrast to the long-term trends, interannual variability in DOC export was most affected by Climate (Figure 7a). Change in decadal mean annual DOC export (Figure 7b) was attributed to changes in LMPs, elevated CO_2 , and Ndep, which accounted for a continuously increasing rate of DOC export during the

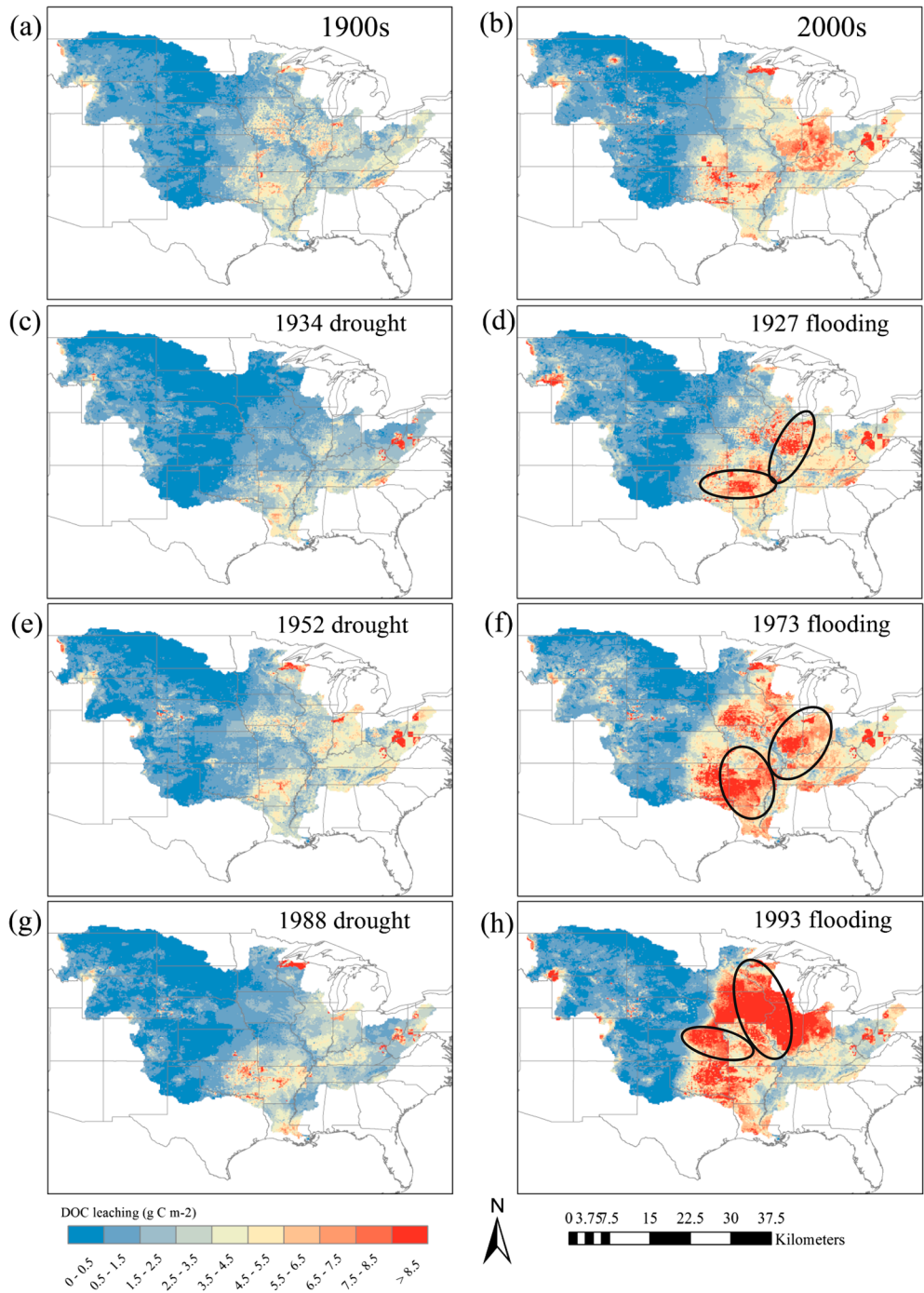


Figure 6. Spatial distributions of dissolved organic carbon (DOC) export (Tg C yr^{-1}) (a) in the 1900s and (b) in the 2000s, and in severe drought years (c) 1934, (e) 1952, and (g) 1988, and flooding years (d) 1927, (f) 1973, and (h) 1993. Black circles show flooding regions.

export, as a result of CO_2 -enhanced net primary productivity and subsequent soil organic carbon decomposition [Freeman *et al.*, 2004]. Similar to nitrogen fertilizer effects, Ndep also significantly enhanced DOC sources by influencing productivity, litter chemistry, carbon allocation, and associated microbial decomposition dynamics. Those conclusions are supported by previous studies [Findlay, 2005; LeBauer and Treseder, 2008; Monteith *et al.*, 2007; Sinsabaugh *et al.*, 2004].

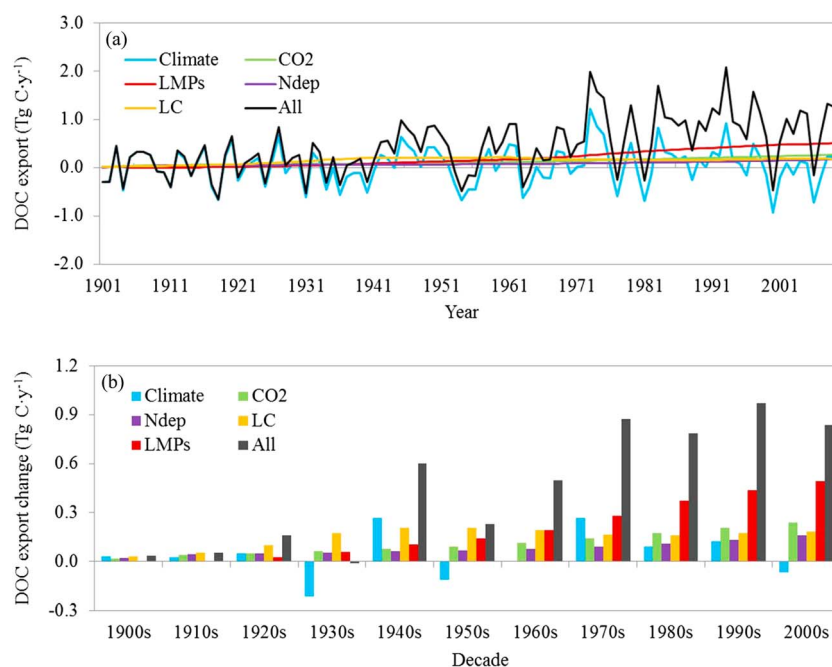


Figure 7. Changes in (a) annual DOC export and (b) decadal mean DOC export induced by multiple environmental factors including climate change (Climate), atmospheric CO₂, nitrogen deposition (Ndep), land cover change (LC), and land management (LMPs) during 1901–2010.

DOC export in our study showed substantial interannual variations in response to climate variability. DOC export increased during extreme flooding, in agreement with other studies about climate extremes (i.e., storm events) [Hood *et al.*, 2006; Inamdar and Mitchell, 2006; Jeong *et al.*, 2012]. We further isolated the effects of long-term changes in precipitation (PRECIP) from temperature (T) on DOC export using single-factor experiments. Across the entire basin, T was associated with small changes in DOC export while PRECIP accounted for the majority (over 95%) of annual DOC export variability related to climate change. Relative to other factors' contributions to DOC export, the effects of T and PRECIP were less, but a regional analysis revealed larger effects of T and PRECIP in the relatively moist eastern part of the basin. We conclude that climate effects will have a greater impact on riverine DOC yields in cooler and wetter regions [Tian *et al.*, 2013].

Our study not only investigated the magnitude and tempo-spatial patterns of riverine DOC export but also attributed the roles of natural and anthropogenic factors to increased DOC export using a spatially explicit coupled hydrologic/biogeochemical land simulation model. However, several other potentially important factors were excluded in this study and warrant further evaluation, including river engineering (e.g., dams), agronomic practices (e.g., manure application), and other DOC sources such as autochthonous DOC production from riverine algae [Bianchi *et al.*, 2007; Bianchi *et al.*, 2004]. Further improvement in model representation of additional biogeochemical processes in river systems and the spatial data sets of dams and agronomic practices are needed to reduce uncertainties.

We also conducted sensitivity analyses of key parameters related to DOC fluxes by testing the changes in simulated DOC fluxes in response to a 10% increase and decrease of each parameter. For example, we found that DOC export would be enhanced by approximately 2.6% with a 10% decrease in the soil DOC desorption coefficient, while a 10% increase in this parameter has a relatively small effect (0.4% reduction in DOC export). Parameters are a major source of uncertainty in our estimation of total DOC export. Therefore, future information obtained from site-level observations both on land and in coastal areas, and regional monitoring and observations from remote sensing, can be used for further model development, parameterization, and evaluation. In addition, higher temporal and spatial resolution regional input data (e.g., nitrogen deportation and land management practices including manure and nitrogen fertilizer use) to support ecosystem models will also improve the accuracy of regional assessments of DOC export.

5. Conclusions

Our Dynamic Land Ecosystem Model (DLEM) simulated the spatial and temporal patterns of DOC fluxes from the Mississippi River basin for the past 110 years. We found a significant trend of increasing DOC export resulting from multiple environmental changes and variations including climate change (temperature and precipitation), rising atmospheric CO₂ concentration, nitrogen deposition, land use change, and land management practices. This study provides the first characterization of DOC export dynamics from the entire basin over the past century and offers a novel attempt to quantify the relative importance of natural and anthropogenic forces to changes in DOC export through linking terrestrial and riverine biogeochemical processes. Development and improvement of the representation of additional biogeochemical processes in the linked terrestrial and riverine modeling systems and finer temporal and spatial resolution of data sets can further advance the performance of this approach for application at whole and subbasin scales.

Acknowledgments

This study has been supported by NASA Interdisciplinary Science Programs (NNX10AU06G) and Carbon System Monitoring Program (NX14AO73G and NNX12AP84G). Partial support was also provided by NSF OCE-1238212 (CSH), NSF OCE-1237140 (CSH & WJC). CSH is an affiliated member of the UGA RBC, CICR and UGAMI (Contr#1053). Data supporting Tables 1 and 2 and Figures 2–7 in the article and Table S1 and Figures S1–S3 in the supporting information are available as in section 2. We thank the U.S. Geological Survey (USGS: http://toxics.usgs.gov/hypoxia/mississippi/real_time.html) for providing open water quality data to support this study; we thank the U.S. Army Corp (<http://rivergages.mvr.usace.army.mil/WaterControl/stationinfo2.cfm?sid=01100Q>) for providing river discharge data. We also thank Jennifer Warrillow for proofreading this manuscript.

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