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Key Points:
- Wintertime DOC export to the Gulf of Maine increased from 1930 to 2013
- Earlier snowmelt and spring runoff are leading to changes in the timing of DOC export
- In the 21st century it is likely that DOC export will increase in winter and decrease in summer

Supporting Information:
- Supporting Information S1

Correspondence to:
T. G. Huntington,
thunting@usgs.gov

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Climate change and dissolved organic carbon export to the Gulf of Maine

Thomas G. Huntington[1], William M. Balch[2], George R. Aiken[3], Justin Sheffield[4], Lifeng Luo[5], Collin S. Roesler[6], and Philip Camill[6]

[1]New England Water Science Center, U.S. Geological Survey, Augusta, Maine, USA, [2]Bigelow Laboratory for Ocean Sciences, East Boothbay, USA, [3]National Research Program, U.S. Geological Survey, Boulder, Colorado, USA, [4]Department of Civil and Environmental Engineering, Princeton University, Princeton, New Jersey, USA, [5]Department of Geography, Environment and Spatial Sciences, Michigan State University, East Lansing, Michigan, USA, [6]Department of Earth and Oceanographic Science, Bowdoin College, Brunswick, Maine, USA

Abstract Ongoing climate change is affecting the concentration, export (flux), and timing of dissolved organic carbon (DOC) exported to the Gulf of Maine (GoM) through changes in hydrologic regime. DOC export was calculated for water years 1950 through 2013 for 20 rivers and for water years 1930 through 2013 for 14 rivers draining to the GoM. DOC export was also estimated for the 21st century based on climate and hydrologic modeling in a previously published study. DOC export was calculated by using the regression model LOADEST to fit seasonally adjusted concentration discharge (C-Q) relations. Our results are an analysis of the sensitivity of DOC export to changes in hydrologic conditions over time since land cover and vegetation were held constant over time. Despite large interannual variability, all rivers had increasing DOC export during winter and these trends were significant ($p < 0.05$) in 10 out of 20 rivers for 1950 to 2013 and in 13 out of 14 rivers for 1930 to 2013. All rivers also had increasing annual export of DOC although fewer trends were statistically significant than for winter export. Projections for DOC export during the 21st century were variable depending on the climate model and greenhouse gas emission scenario that affected future river discharge through effects on precipitation and evapotranspiration. The most consistent result was a significant increase in DOC export in winter in all model-by-emission scenarios. DOC export was projected to decrease during the summer in all model-by-emission scenarios, with statistically significant decreases in half of the scenarios.

1. Introduction

There is great concern about and research interest in how climate and land use change may be affecting carbon cycling in and transport from terrestrial ecosystems. Hydrologic changes can influence terrestrial carbon cycling, affecting net exchanges between vegetation, soils, atmosphere, and rivers [*Worrall and Burt*, 2007; *Williamson et al.*, 2008; *Bianchi and Allison*, 2009]. Dissolved organic carbon (DOC) export to surface waters is a small term in regional carbon budgets compared with gross primary productivity and respiration, but it is an important term compared with net changes in terrestrial carbon storage and for assessing sensitivity of carbon cycle processes to changes in climate and land use [*Buffam et al.*, 2011; *Christensen et al.*, 2007; *Jonsson et al.*, 2007; *Kindler et al.*, 2011]. Changes in DOC export may also reflect changes in terrestrial organic carbon cycling that affect net ecosystem exchange [*Pumpanen et al.*, 2014; *Clark et al.*, 2007] and DOC concentration in surface waters.

There have been many reports of increasing DOC concentrations in surface waters (streams, rivers, and lakes) over the last few decades in northern Europe [*Freeman et al.*, 2001; *Worrall et al.*, 2004b; *Evans et al.*, 2006; *Erlandsson et al.*, 2008; *Sarkkola et al.*, 2009; *Monteith et al.*, 2014]. Similar trends in DOC concentrations in surface waters in eastern North America have also been reported, but the results are more mixed and the trends are weaker than for most of Europe [*Monteith et al.*, 2007]. It is also noteworthy that many of the increasing trends in DOC concentration in surface waters in eastern North America are for lakes rather than streams and rivers [*Driscoll et al.*, 2003; *Stoddard et al.*, 2003]. However, some studies have reported weak trends or no increases in DOC concentration over time in northern Europe [*Oni et al.*, 2012; *Jennings et al.*, 2010; *Rodríguez-Murillo et al.*, 2014] and the northeastern United States [*Navrátil et al.*, 2010]. One study in eastern Canada [*Clair et al.*, 2008] and one in the northeastern United States [*Fahey et al.*, 2005] reported trends toward decreasing DOC concentrations in rivers. In major rivers in Switzerland an increasing trend was observed (1974 to 1999) but then reversed (2000 to 2010) resulting in a weak or no trend for the longer-term period [*Rodríguez-Murillo et al.*, 2015]. *Räike et al.* [2016] found increasing concentrations in 12 rivers and decreasing concentrations in 2 rivers, and no significant trends in 15 rivers in Finland from 1975 to 2014.

Recent reviews [*Clark et al.*, 2010; *Filella and Rodríguez-Murillo*, 2014] consistently support the finding that increases have been observed in many systems but that they cannot be considered "universal," nor is there any consensus that observed increases are due to a common driver [*Pagano et al.*, 2014; *Räike et al.*, 2016]. In some cases, reported increases in DOC concentration may be due to increases in discharge if the concentrations are not discharge weighted [*Eimers et al.*, 2008].

Understanding how climate change may have affected stream DOC concentration and export in the past, or may affect it in the future, is a complex problem. Many processes have been proposed to explain the observed temporal trends toward increasing DOC concentrations in streams. Changes in precipitation and runoff regimes [*Tranvik and Jansson*, 2002; *Erlandsson et al.*, 2008; *Striegl et al.*, 2005; *Lepistö et al.*, 2008] and drought [*Worrall et al.*, 2004a] have been suggested as possible direct drivers for observed trends toward increasing DOC concentration in some streams. Other indirect drivers for observed increases in DOC concentrations have included increases in temperature [*Freeman et al.*, 2001; *Worrall and Burt*, 2007; *Preston et al.*, 2011] decreases in acidic deposition [*Monteith et al.*, 2007] increasing atmospheric CO_2 concentration [*Fenner et al.*, 2007; *Freeman et al.*, 2004], and increasing nitrogen enrichment [*Findlay*, 2005].

Climate warming can affect vegetation composition and productivity, and soil biotic and abiotic processes [*Bates et al.*, 2008; *Iverson et al.*, 2008; *Melillo et al.*, 1993; *Bond-Lamberty and Thomson*, 2010; *D'odorico et al.*, 2010]. Climate warming has also been associated with higher precipitation intensity [*Westra et al.*, 2013]. Historical records indicate increasing rainfall amount and intensity in northern temperate latitudes [*Westra et al.*, 2013] and, specifically, in the northeastern U.S. [*Kunkel et al.*, 2013]. Higher precipitation intensity could result in flashier streams and rivers characterized by greater day to day variation in runoff and DOC export. *Baker et al.* [2004] defined a flashiness index as a measure of the differences in daily flow relative to the total flow over a specified period of record

$$\text{R-B Index} = \frac{\sum_{i=1}^{n} |q_i - q_{i-1}|}{\sum_{i=1}^{n} q_i}$$

where q_i is the mean daily flow on any given day and q_{i-1} is the mean daily flow on the previous day and n is the number of days in the specified period. These authors found statistically significant increased flashiness in 22% and decreased flashiness in 9% of 515 streams in the Midwestern U.S. from 1975 to 2001; the flashiness index ranged from 0.45 to 0.75 and was positively correlated with increasing frequency and magnitude of storm events.

Changes in hydrologic conditions affect wetland abundance, type, and connectivity to streams [*Dick et al.*, 2015], and because wetlands are positively related to the amount of DOC in streams [*Frost et al.*, 2006; *Creed et al.*, 2008; *Huntington and Aiken*, 2013], DOC export could be affected. Process-based modeling of stream DOC concentration and export in a changing climate requires integrated climate and hydrologic models that are coupled with dynamic vegetation and biogeochemical models. This type of modeling is relatively new and is usually applied to small watersheds where extensive data exist for calibration and validation [e.g., *Oni et al.*, 2014; *Wu et al.*, 2014; *Tang et al.*, 2015]. However, uncertainty is propagated from climate-to-hydrologic-to-vegetation-to- biogeochemical modeling and can yield a broad range of model-specific outcomes for even a single emission scenario [*Oni et al.*, 2014].

The fundamental importance of hydrologic conditions relative to other processes over the intermediate term (decades to a century) in determining DOC export to the Gulf of Maine (GoM) is apparent from a recent study by *Tian et al.* [2015]. They applied a model to estimate DOC export from eastern North America during 1901 to 2008 and reported that changes in DOC export to the GoM were related to hydrologic changes rather than changes in land use or land cover or to increases in temperature and resulting DOC production, for which they reported low sensitivity. This study did not include changes in acidic deposition that might have affected sensitivity over time.

Because of the absence of integrated models for the GoM watershed and the overriding importance of hydrologic conditions controlling DOC export to the GoM [*Huntington and Aiken*, 2013; *Tian et al.*, 2015; *Balch et al.*, 2016], we have chosen to evaluate the sensitivity of DOC export to runoff only. Runoff has increased in northern New England in the 20th century [*Huntington and Billmire*, 2014] and is projected to increase further in the 21st century [*Hayhoe et al.*, 2007; *Thibeault and Seth*, 2014]. Because of observed and projected increases in runoff, it is important to attempt to assess the sensitivity of DOC export to changes in hydrologic condition. Our objective was to calibrate regression models that would allow us to estimate the sensitivity of DOC export to measured historical and projected future variations in runoff using our short-term record of water chemistry and runoff. We acknowledge that while the magnitude and timing of runoff are the primary drivers of DOC export, our approach is limited in that we assume that other variables are constant.

2. Methods

2.1. Description of Study Area

The total area of the watershed draining into the GoM is ~179,000 km^2, and the total average discharge into the GoM is estimated to be ~3000 m^3 s^{-1} [*Meade and Emery*, 1971]. The major rivers in this study (St. John, St. Croix, Penobscot, Kennebec, Androscoggin, Saco, and Merrimack) have a combined discharge-gauged area of 75,622 km^2 (Figure 1). The climate of the study area is humid continental [*Peel et al.*, 2007] and precipitation ranges from about 0.9 m to 1.2 m yr^{-1} with the highest precipitation in coastal areas. Precipitation is relatively evenly distributed seasonally, and annual snowfall ranges from about 1.5 to 2.0 m in southern and coastal areas to 2.5 to 3.0 m in northern and inland areas [*Cember and Wilks*, 1993]. The typical seasonal pattern of streamflow shows a distinct spring peak during snowmelt, with lowest flows during late summer and early fall followed by a small peak in late fall [*Hodgkins and Dudley*, 2005]. Runoff ranges from about 55% to 63% of precipitation inputs [*Huntington and Billmire*, 2014].

The GoM watershed in Maine is primarily composed of forest land (~89%) [*Griffith and Alerich*, 1996]. Of the remaining land coverage, 5% is covered by ~5700 lakes and ponds $>$0.4 ha, and 4% is in agriculture. Palustrine wetlands occupy ~12% of the land area in Maine, 60% of these wetlands are forested, and the remainder are scrub/shrub or emergent vegetation [*Armstrong*, 1996]. About 90% of the organic carbon transported in major rivers in the northeastern U.S. is in the form of DOC based on U.S. Geological Survey (USGS) National Water Information System (NWIS) data for the Androscoggin, Merrimack, Penobscot, and Connecticut Rivers and reported by *Roesler et al.* [2006]. This DOC fraction is similar to that reported for temperate forested rivers [*Schlesinger and Melack*, 1981]. DOC concentrations in these rivers in Maine typically range from 4 to 15 mg C/L, lowest in winter and spring regardless of level of discharge, higher in summer (low- or high-flow periods) and highest in fall (high-flow periods) [*Cronan*, 2012; *Huntington and Aiken*, 2013].

2.2. Data Sources, Collection, and Analyses

All basins draining to the GoM that had daily discharge records beginning in 1951 or earlier and that had DOC data for export computations were included in the historical analysis (Figure 1 and Table 1). Daily average and instantaneous (at time of sample collection) streamflow data for each river were obtained from the National Water Information System (NWIS) online database (10.5066/F7P55KJN). Streamflow data quality, record extension techniques used to estimate daily streamflow, and methods for estimating instantaneous discharge have been previously described [*Huntington and Aiken*, 2013; *Huntington and Billmire*, 2014].

The Penobscot, Kennebec, and Androscoggin Rivers were chosen for analysis of trends in DOC export during the 21st century because they are the largest rivers for which DOC data and flow projections were available. Together, these three basins drain a gauged area of about 42,000 km^2 or 47% of the State of Maine. We used climate and hydrologic projections for 2014 to 2099 for the northeastern U.S. that were derived by using the UK Meteorological Office Hadley Centre (HadCM3) and the U.S. Department of Energy/National Center for Atmospheric Research Parallel Climate Model (PCM) coupled atmosphere-ocean general circulation models (AOGCMs) and that represented the lower (B1) and higher (A1FI) emission scenarios [*Hayhoe et al.*, 2007]. The B1 scenario can be seen as a proxy for stabilizing atmospheric CO_2 concentrations at or above 550 ppm, as levels reach this value by 2100. The corresponding atmospheric CO_2 concentrations for the higher A1FI scenario are 970 ppm by 2100. Details of the model evaluation and implementation are described in *Hayhoe et al.* [2007]. Briefly, for the hydrological projections, monthly AOGCM temperature and precipitation fields were first statistically downscaled to daily values with a spatial resolution of 1/8°. Downscaled temperature and precipitation were then used as input to the Variable Infiltration Capacity (VIC) land surface hydrological model [*Liang et al.*, 1994, 1996; *Cherkauer et al.*, 2002], to calculate future changes in hydrology.

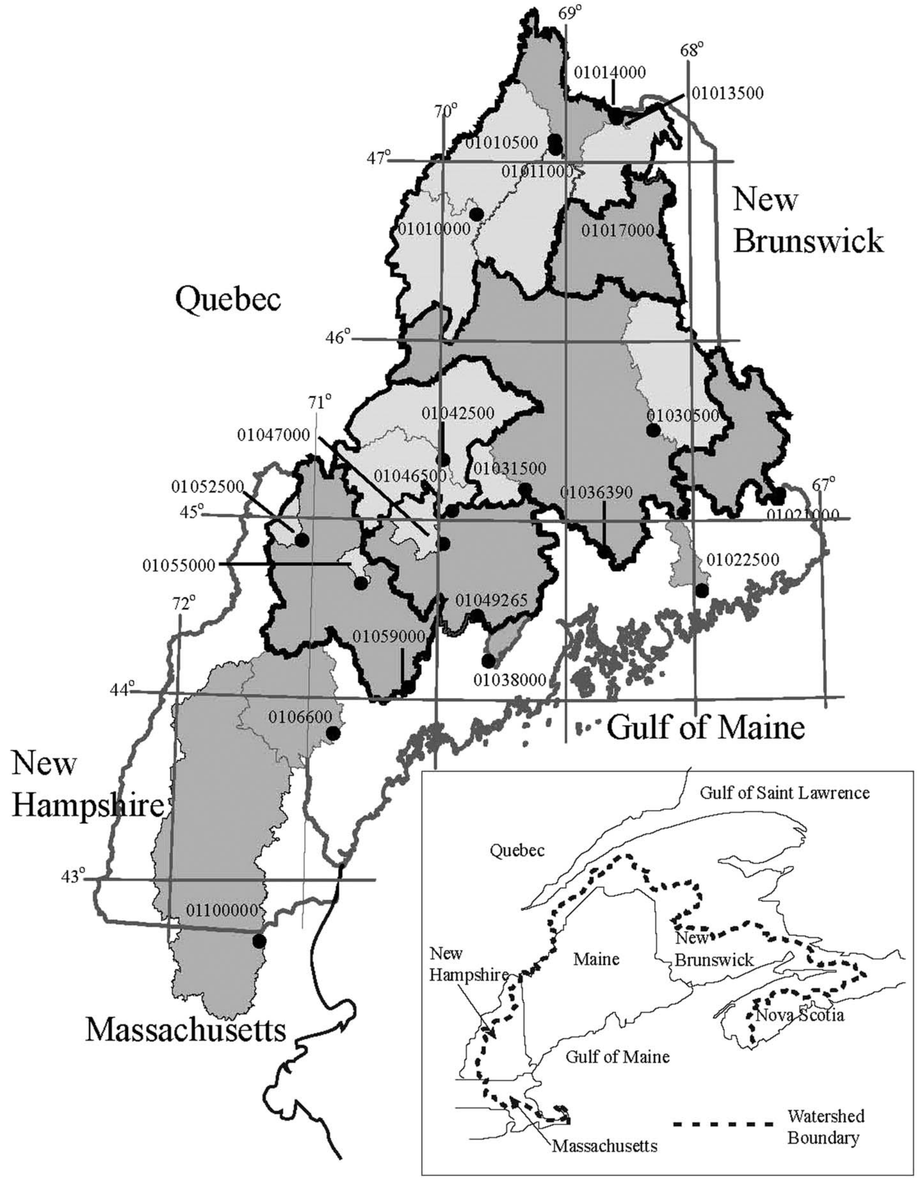

Figure 1. River basins in the study with numbers identifying the USGS stations where these basins are gauged (Table 1). Basins in lighter gray are nested within larger basins in bold outlines with the same first three digits in station IDs. The inset shows the approximate boundary for the drainage area of the Gulf of Maine.

Details of the VIC model simulation, scaling to match the gauged watershed areas, and the bias corrections that were employed for this study are described in the supporting information.

Grab samples were collected periodically throughout the years shown in Table 1 from fast-flowing river sections for DOC using precleaned (acid and deionized water rinsed) high-density polyethylene bottles and refrigerated immediately. Samples were filtered within 1 to 24 h through 32 mm diameter, 0.45 μm Supor® membrane syringe filters in polypropylene housings and maintained refrigerated in the dark in amber glass bottles. DOC concentrations were measured within 1 to 2 weeks of sample collection using the platinum catalyzed persulfate wet oxidation method on an O.I. Analytical Model 700 TOC Analyzer™ [*Aiken*, 1992] or using high-temperature catalytic oxidation followed by nondispersive infrared detection on a Shimadzu TOC-V_{CSH} analyzer [*Dickson et al.*, 2007].

The number of samples collected from each river varied from 13 to 175 (median 28). Sample collections were evenly distributed over the range of river flows (e.g., Figure S1 in the supporting information). The average

Table 1. River Basins, USGS Station IDs, Basin Area, Number of DOC Samples, and Date Ranges of Sample Collections[a]

Station Name	USGS[b] Station ID	Bowdoin Station ID[c]	Latitude of Basin Centroid	Basin Area (km^2)	No. Samples	Date Range of Samples
St. John at Ninemile	01010000	NS	46.4577	3,473	13	2011–2012
St. John at Dickey	01010500	S01	46.7489	6,941	22	2011–2013
Allagash near Allagash	01011000	S02	46.6558	3,828	22	2011–2013
Fish near Fort Kent	01013500	S04	47.0078	3,168	30	2011–2013
St. John near Fort Kent	01014000	S03	46.8462	14,711	22	2011–2013
Aroostook at Washburn	01017000	S13	46.5288	4,284	22	2011–2013
St. Croix at Baring	01021000	NS	45.4397	3,559	30	2011–2013
Narraguagus at Cherryfield	01022500	NS	44.7811	588	23	2011–2013
Mattawamkeag at Mattawamkeag	01030500	P03	45.8044	3,673	54	2004–2013
Piscataquis at Dover-Foxcroft	01031500	NS	45.2354	776	37	2004–2012
Penobscot at Eddington	01034500	P08	45.6700	20,109	175	2004–2013
Sheepscot near Pittsfield	01038000	NS	44.3464	376	19	2011–2013
Kennebec at Bingham	01046500	K05	45.4524	7,032	23	2011–2013
Carrabassett at N. Anson	01047000	K06	44.9879	914	34	2011–2013
Kennebec at The Forks	01042500	K03	45.6021	4,118	22	2011–2013
Diamond at Wentworth, NH	01052500	A01	44.9622	394	36	2011–2013
Swift near Roxbury	01055000	A04	44.7518	251	23	2011–2013
Androscoggin at Auburn	01059000	A13	44.6246	8,451	91	2004–2013
Saco at Cornish	01066000	NS	43.9793	3,349	39	2007–2013
Merrimack at Lowell, MA	01100000	NS	43.1788	11,450	28	1998–2000
Kennebec at North Sidney	01049265	K10	45.1224	13,993	55	2004–2013

[a]NS, not sampled by Bowdoin College, sampled by USGS only. All locations in Maine unless otherwise noted.
[b]Data collected and analyzed by the USGS is associated with the indicated USGS Station ID and is available through the National Water Information System (NWIS) 10.5066/F7P55KJN.
[c]Data collected and analyzed by Bowdoin College is associated with the indicated Bowdoin College Station ID and is available through the NASA SeaBASS data archive http://seabass.gsfc.nasa.gov/seabasscgi/archive.cgi?q=BOWDOIN/camill/3rivers/archive.

river discharge was slightly higher during the study period compared with the long-term (1949 to 2013) average flows but sampling during the study period covered the range of discharges observed during both periods (e.g., Figure S1). To address the possibility of bias associated with sampling during a shorter time interval for some sites compared with the full time period for others we performed additional regression analyses to estimate DOC concentration and export for the study period 1949 to 2013 by splitting the sampling period used in the LOADEST regression modeling, described below, into 2004 to 2008 and 2009 to 2013 for two rivers that had been sampled over the entire period. This analysis showed that there were only minor differences (<5%) in mean daily DOC concentration and DOC export model estimates for the entire 1949 to 2013 period regardless of the period in which the samples were collected (Table S1 in the supporting information). It is also evident that the results were not particularly sensitive to the number of samples since similar results were obtained when only half as many samples were included in the analyses (Table S1). Additionally, the fact that there were only minor differences in estimated concentration and export between the models based on the two different time periods, in spite of the fact that in the early period the samples were collected at substantially higher (36%) average discharge rates, indicates that the model was similarly not overly influenced by the discharges at which samples were collected. The standard errors of prediction were higher when fewer samples were included indicating that, not surprisingly, the confidence in each model is improved with more samples.

River flashiness was determined by using the Richards-Baker flashiness index (FI) [*Baker et al.*, 2004] to quantify the annual average day-to-day variation in modeled DOC export for rivers having a minimum of 80 years of discharge records. The FI measures differences in daily flow relative to the total flow over a specified period of record. In our application of the index we have substituted DOC export (kg C/d) for daily discharge volume in the original index.

$$\text{R-B Index} = \frac{\sum_{i=1}^{365} \left| E_{\mathrm{DOC}_i} - E_{\mathrm{DOC}_{i-1}} \right|}{\sum_{i=1}^{365} E_{\mathrm{DOC}_i}}$$

where E_{DOC} is daily DOC export, Σ is summation, and i is the day of the year where the summation is for the entire year (leap years have 366 days in the summation).

Low FI values indicate a less-flashy stream DOC export, and higher values indicate a flashier stream. FIs range from about 0.45 to 0.75 for most sites studied by *Baker et al.* [2004].

Statistical analysis for testing of significance of temporal trends was performed by using MAKESENS software [*Salmi et al.*, 2002] to compute the nonparametric Mann-Kendall test and the magnitude of the trend (slope) by using Sen's method. Locally weighted scatterplot smoothing (LOWESS) curves were plotted by using S-Plus 5.0 software.

2.3. Estimation of Historical and Projected DOC Concentration and Export

Mean daily DOC concentrations and export for the historical and projected periods were estimated by using site-specific regression models developed by using Load Estimator (LOADEST) regression software [*Runkel et al.*, 2004]. We use the term export in this paper, in units of mass per unit time, which is synonymous with the terms flux and load; when export is scaled to drainage area, in units of mass per unit time per unit area, we use the term yield. The models were calibrated by busing discrete pairs of DOC concentration and instantaneous discharge values. LOADEST determines the "best" regression model based on Akaike information criterion; the Approximate Maximum Likelihood Estimator is used with LOADEST for calibration and estimation of daily export and uncertainty. For this analysis, we used the best model that explicitly maintained the same seasonally dependent C-Q relation over the entire estimation period. The regression model implements sine and cosine terms to reflect the seasonality of constituent export. A model with an invariant seasonally dependent C-Q relation was required in order to extrapolate beyond the brief period of sample collection. We have observed short-term interannual changes in C-Q relations that we believe are related to major differences in rainfall and runoff between years rather than fundamental changes that would persist over time [*Huntington and Aiken*, 2013]. In this case, the model is constrained to predict the same concentration for a given discharge for a given time of year. If the model were allowed to adjust the concentration over time based on the short-term sampling period, the model would assume that observed trends would persist, potentially resulting in unrealistic long-term projections. The site-specific discharge models are reported in Table S2.

Application of the LOADEST model as a hindcast or forecast outside the period of record for DOC concentration data requires an assumption of stationarity in the C-Q relation observed during the sampling period. As noted in the introduction, while there are many reports of increasing DOC concentration in rivers and streams, particularly in northern Europe, other reports, particularly in eastern North America, indicate that trends are mixed or nonexistent. Although lack of clear trends in DOC concentration is not evidence that there is no trend in C-Q relation over time, it does suggest that there have not been major changes in these relations during a time when temperature, precipitation, and runoff have generally increased in eastern North America [*Huntington and Billmire*, 2014]. Over the long-term, forest response to climate change will likely include changes in forest composition, growth rate, phenology (in response to a longer growing season [*Rustad et al.*, 2012]), and hydrologic conditions that affect wetland extent [*Kayranli et al.*, 2010]. Many of these responses could lead to increased forest growth and carbon sequestration, but other factors such as increasing drought, insect and disease pressures, invasive species, and increased rates of microbial decomposition of soil organic matter may balance or outweigh trends toward increases in net carbon storage, i.e., affecting the status of the forest as a carbon sink or source. Given these uncertainties, the assumption of stationarity in the DOC C-Q relation will permit only a first approximation of the changes in DOC export that would result from changes in hydrology alone. In this sense we are conducting sensitivity analyses of DOC export to changes in runoff as opposed to trend analyses incorporating changes in all of the variables that will be affected by climate change. A similar approach, assuming stationarity in most variables, was adopted by *Sebestyen et al.* [2009] for projections of long-term stream nitrate and DOC responses to climate change in a small watershed in Vermont, USA.

LOADEST model output includes estimates of daily DOC export (kg C/d) and regression statistics that include correlation, mean load estimates, 95% confidence intervals, standard error, and bias diagnostics for both export and concentration. Descriptions of the bias diagnostics were included in model updates in 2013 [*Runkel*, 2013] that can be accessed from the URL http://water.usgs.gov/software/loadest/doc/. Bias diagnostics include concentration bias (%), partial concentration ratio, and Nash Sutcliffe efficiency index. A summary of model bias diagnostics for each basin is presented in Table S3. The LOADEST model cannot simulate hysteresis during storm responses if it is present in the data. Export calculations will be more accurate if samples are collected on both rising and falling limbs of the hydrograph to obtain representative concentrations at

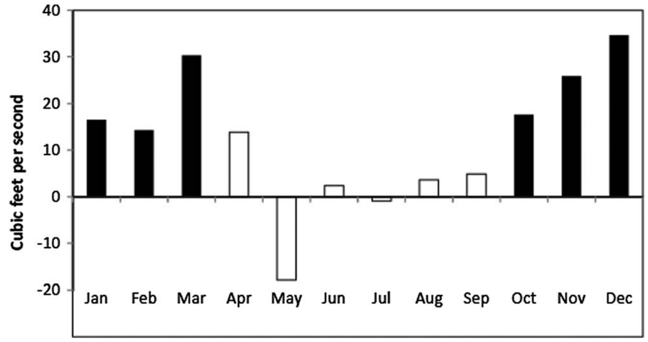

Figure 2. Basin area-weighted trends in monthly runoff from the Allagash, Androscoggin, Aroostook, Carrabassett, Fish, Kennebec, Mattawamkeag, Merrimack, Penobscot, Piscataquis, Saco, St John, and Swift rivers from 1930 to 2013. The solid bars indicated statistically significant ($p < 0.05$) trends.

given discharges. The LOADEST model assumes that the residuals are independent and homoscedastic (having constant variance) [*Runkel et al.*, 2004]. This assumption was investigated and validated by plotting model residuals versus export (e.g., Figure S2). Similarly, we tested the model assumption of a normal distribution of model residuals for each model, and we have not found any evidence that this assumptions of normality is violated (e.g., Figure S3). The LOADEST model can be subject to a seasonal bias due to the model's fixed shape of the C-Q relation among seasons when in reality the shape may be different [*Hirsch*, 2014]. We tested for seasonal bias by plotting the seasonal distribution of residuals in boxplots as described in *Hirsch* [2014]. This type of plot will identify periods where the model may be biased due the fixed shape of the seasonally varying C-Q relation. This test revealed a seasonal bias whereby estimates of DOC concentration and associated export have a small positive bias in the wintertime. Biases in other seasons were smaller than that observed in winter (e.g., Figure S4).

3. Results

3.1. Historical Trends in Runoff, DOC Concentration, and DOC Export: A Sensitivity Analysis

Basin area-weighted runoff increased significantly in fall and winter months, and there were no significant changes in spring or summer months for the 14 rivers having discharge data back to about 1930 (Figure 2). The estimated average DOC yield for the period 1950 through 2013 varied from 27 to 85 kg C/ha/yr among rivers with the highest yields generally in the most northern watersheds and the lowest yields in the southernmost watersheds (Table 2). The median concentration as determined from the LOADEST model among these rivers during this period varied from 3.3 to 12.0 mg C/L. Estimated DOC concentration in winter (January through March) increased in all but one river, and the increases were statistically significant ($p < 0.05$) in 7 out of 20 rivers (Table 2). Estimated annual DOC concentration increased in all rivers, and the increases were statistically significant ($p < 0.05$) in 10 out of 20 rivers. Estimated DOC export in winter increased in all rivers and the increases were statistically significant ($p < 0.05$) in 10 out of 20 rivers. Estimated annual DOC export also increased in all rivers, and the increases were statistically significant ($p < 0.05$) in only three rivers and with the trends having p-values of <0.1 in four rivers. The ratio of DOC export in May to the export in March plus April (a proxy for a shift to earlier seasonal peak export) decreased in all but three rivers, and the decreases were statistically significant ($p < 0.05$) in 6 out of 20 rivers. Trends toward increasing DOC concentration and export in winter and decreases in the ratio of DOC export in May to the export in March plus April were strongest in more northerly basins (Table 2).

An analysis of trends for 14 of the rivers having discharge data back to about 1930 indicated that there were significant ($p < 0.05$) increases in estimated DOC concentration in winter in 12 out of 14 rivers (Table 3). Estimated annual DOC concentration increased significantly in all rivers. Estimated DOC export in winter increased in all rivers, and the increases were statistically significant ($p < 0.05$) in 13 out of 14 rivers. Estimated annual DOC export increased in all rivers, and the increases were significant in 11 out of 14 rivers.

Estimated DOC export generally increased from 1930 to the late 1970s, then remained steady or decreased until the early 1990s, and has increased rapidly since then (Figure 3). Interannual variability in DOC export was substantial in all rivers. For example, annual DOC export from the Penobscot River at Eddington varied by a factor of about 3 and winter DOC export varied by a factor of about 5 from 1930 to 2013. For the 1930 to 2013 period the ratio of DOC export in May to the export in March plus April decreased significantly ($p < 0.05$) in 6

Table 2. Median DOC Concentrations, Loads, Yields, and Trends in Concentration and Export as Estimated Using the LOADEST Model for 1950 to 2013

Station Name	Median DOC Conc.[a] (mg/L)	Median DOC Load (kg/d)	Std. Err. Pred. (kg/d)	DOC Yield[b] (kg/ha/yr)	Trend in Winter DOC Export (% Change)	Trend in Annual DOC Export (% Change)	Trend in May/(March + April) DOC Export (% Change)	Trend in Winter DOC Concentration (% Change)	Trend in Annual DOC Concentration (% Change)
St. John at Ninemile	11.9	81,000	4,900	85.3	222***	29.5*	−63.9***	22.9*	8.00*
St. John at Dickey	9.7	160,000	12,000	84.3	148**	14.8	−66.1**	22.4**	5.56
Allagash near Allagash	7.8	44,000	1,700	41.9	135**	19.0	−3.07	16.9*	7.9*
Fish near Fort Kent	5.9	23,000	420	27.0	51.1*	13.2	−55.3**	2.57^{+}	2.54*
St. John near Fort Kent	7.9	260,000	20,000	65.1	130**	13.3	−68.0***	19.6*	7.72
Aroostook at Washburn	7.2	60,000	2,500	51.1	90.0*	13.6	−66.6***	14.1^{+}	8.96
St. Croix at Baring	9.4	62,000	1,700	63.3	5.51	1.31	−0.44	−0.47**	0.34***
Narraguagus at Cherryfield	9.6	13,000	410	79.0	17.1	17.0	−3.07	0.80	5.30^{+}
Mattawamkeag at Mattawamkeag	9.5	66,000	2,700	65.9	58.6*	16.4	−31.3	2.94	2.86
Piscataquis at Dover-Foxcroft	6.2	11,000	410	52.4	36.4	7.77	−26.6	1.00	1.50
Penobscot at Eddington	8.4	326,000	4,105	59.2	31.1	16.0	−29.1	1.95	2.75
Sheepscot near Pittsfield	7.1	4,900	220	48	19.8	23.3	26.7	0.33	4.62
Kennebec at Bingham	6.0	74,000	1,600	38.3	49.8 *	19.5	−30.8^{+}	5.03*	1.98
Carrabassett at N. Anson	5.0	12,000	650	49.1	56.2	32.8^{+}	−29.0	7.06	8.45*
Kennebec at The Forks	6.0	42,000	1,200	37.1	39.8*	24.2^{+}	3.94	0.33*	0.26*
Diamond at Wentworth, NH	4.0	5,300	350	48.8	142**	14.4^{+}	−56.8**	3.35**	5.13*
Swift near Roxbury	2.8	2.200	140	33.5	82.8^{+}	45.4*	−36.6	12.2^{+}	13.8**
Androscoggin at Auburn	6.4	100,000	1,400	43.8	17.4	21.8^{+}	−17.2	1.14	1.17*
Saco at Cornish	3.7	29,000	780	32.1	21.3	21.4	−18.5	2.63	7.44*
Merrimack at Lowell, MA	4.0	88,000	4,500	28.1	22.4	36.2*	4.70	3.26	8.07

[a]As estimated using the LOADEST model for water years 1950–2013.
[b]All locations in Maine unless otherwise noted.
*$p < 0.05$.
**$p < 0.01$.
***$p < 0.001$.
$^{+}p < 0.1$.

out of 14 rivers (Table 3). A statistically significant increase in estimated flashiness in DOC export was observed for eight rivers, and a significant decrease was observed in three rivers out of the 14 rivers tested for the period 1930 to 2013 (Table 3).

Analysis of monthly trends in the area-weighted estimated average DOC yield for five rivers draining directly to the GoM that have discharge records from 1930 to 2013 indicated that DOC yield increased in all months except May and July and these trends were significant ($p < 0.05$) for January, February, March, October, and December (Figure 4). For this longer period the magnitude of the trends in winter DOC concentration and export were greatest in the more northerly watersheds, but the magnitude of the trends in annual export generally were greatest in the central and more southerly watersheds (Table 3).

3.2. Projected Future Trends in Climate

In the 21st century, temperatures across the northeast U.S. are projected to increase with greater increases under the higher emission scenario (A1FI) compared with the lower emission scenario (B1) [*Hayhoe et al.*, 2007]. Projected increases in annual regional surface air temperature average 5.3°C by 2070–2099 relative to 1961–1990 under A1FI as compared with 2.9°C under B1 based on an ensemble of nine GCMs [*Hayhoe et al.*, 2007]. The *Hayhoe et al.* [2007] climate projections based on HadCM3 and A1FI and B1 emission scenarios are generally consistent with projections from the higher-resolution Hadley Centre regional climate model using the A2 (high emission) and B2 (low emission) employed by *Fan et al.* [2014].

Precipitation projections are less certain and more variable among models and emission scenarios. Projections for changes in precipitation and evapotranspiration for three river basins in this study between 2015 and 2099 expressed as percentages are shown in Table 4. The HadCM3 model projects a substantially

Table 3. Trends in Percent Change ~1930 to 2013 in Winter and Annual Export of DOC, DOC Concentration, and Richards-Baker Flashiness Index

Station Name[a]	Start of Discharge Record	Trend in Winter DOC Export (% Change)	Trend in Annual DOC Export (% Change)	Trend in May/ (March + April) DOC Export (% Change)	Trend in Winter DOC Concentration (% Change)	Trend in Annual DOC Concentration (% Change)	Trend in Richards-Baker Flashiness Index ($\times 10^{-3}$)
Allagash near Allagash	10/1/1931	195***	10.6	−71.8***	18.7***	5.50*	0.054
Fish near Fort Kent	10/1/1929	99.2***	20.6*	−52.5**	3.57***	2.01**	0.056
St. John near Fort Kent	10/1/1929	185***	12.5	−54.9**	20.9***	6.34*	0.085+
Aroostook at Washburn	10/1/1930	225***	24.0+	−55.9***	29.6***	9.36**	0.396***
Mattawamkeag at Mattawamkeag	10/1/1934	91.0**	34.6*	−42.8*	5.34*	3.38*	0.390***
Piscataquis at Dover-Foxcroft	10/1/1929	70.4*	29.1*	−35.3+	3.60+	3.12*	1.476***
Penobscot at Eddington	10/1/1929	57.4**	32.1**	−24.8	6.06**	3.66**	0.344***
Kennebec at Bingham	10/1/1930	74.1***	30.8*	−40.7*	5.63***	3.23**	−0.472**
Carrabassett at N. Anson	10/1/1929	105**	52.2**	−33.7+	11.0**	8.87***	1.512***
Kennebec at The Forks	10/1/1929	54.8***	39.8**	−16.7	0.31**	0.22**	0.778*
Swift near Roxbury	10/1/1929	112**	46.7**	−41.6+	13.6**	11.8***	2.467***
Androscoggin at Auburn	10/1/1929	44.2*	31.5**	−23.5+	1.45**	1.21***	−0.555***
Saco at Cornish	10/1/1929	41.1+	31.9*	−20.8	4.90	5.58**	0.262***
Merrimack at Lowell, MA	10/1/1929	40.7*	47.0**	7.49	4.84*	6.63***	−0.616***

[a]All locations in Maine unless otherwise noted.
*$p < 0.05$.
**$p < 0.01$.
***$p < 0.001$.
+$p < 0.1$.

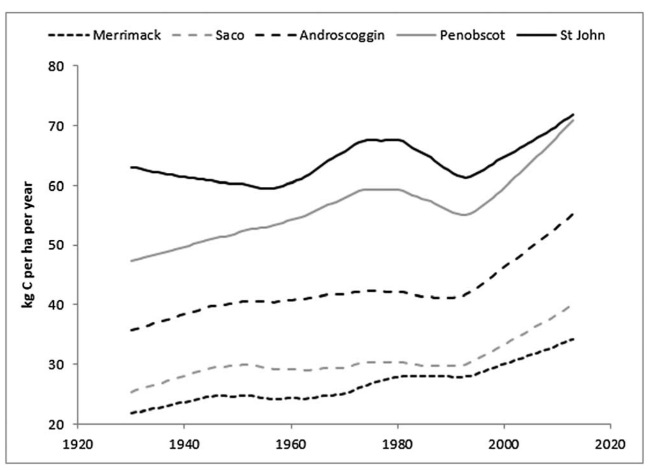

Figure 3. Locally weighted scatterplot smoothing (LOWESS) time series of LOADEST estimated DOC export from major rivers draining to the Gulf of Maine estimated by using the LOADEST model from measured daily discharge and discrete water sampling for DOC concentration.

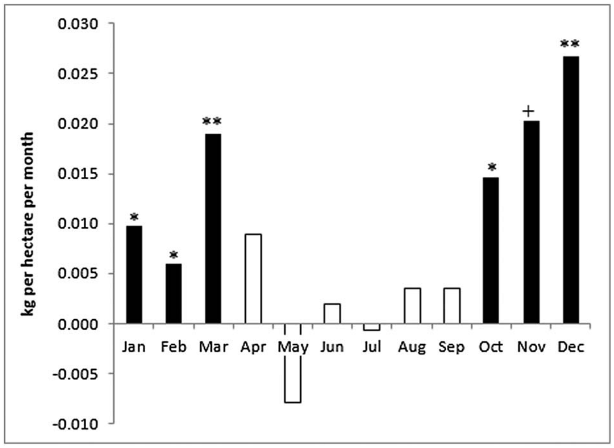

Figure 4. Area-weighted average trends (Mann Kendall trend) in monthly LOADEST estimated DOC export for Penobscot, Androscoggin, St. John at Fort Kent, Merrimack, and Saco for the water years 1930 to 2013. The solid bars with double asterisks, asterisk, and plus sign indicate statistical significance at $p = 0.01$, 0.05, and 0.1, respectively, and the white bars indicate lack of significance. From Excel files (Weighted Average Monthly DOC Export 5 Rivers.xlsx and MAKESENS Monthly Trends 1930–2013.xlsm).

larger increase in precipitation than the PCM model for the A1FI scenario and a similar increase as the PCM model for the B1 scenario. Evapotranspiration increased under the HadCM3 model but generally decreased under the PCM model, consistent with higher temperatures projected under the HadCM3 compared with the PCM model. There were minor differences among river basins whereby increases in precipitation and evapotranspiration were moderately higher in the more southerly basins.

3.3. Projected Future Trends in DOC Yield and DOC Concentration: Sensitivity to Changes in Runoff

Estimated annual average DOC yield is projected to increase significantly ($p < 0.05$) in all three major rivers under the high emission scenario (A1FI) and HadCM3 climate projections (Table 5). The modeled DOC yield (for water years 2015 to 2099) based on the HadCM3 and PCM models and the A1FI and B1 emission scenarios for the Penobscot River (Figure 5) is representative of the projections for all three rivers. Under the HadCM3-by-A1FI DOC yield remains at about 65 kg C/ha/yr from 2015 to about 2045 and then increases to about 75 kg C/ha/yr by 2099. Under the HadCM3-by-B1 DOC yield decreases from 71 kg C/ha/yr in 2015 to 63 kg C/ha/year in 2055, then increases to about 73 kg C/ha/yr by 2099. Under the PCM-by-A1FI DOC yield varies from about 58 to 61 kg C/ha/yr from 2015 to 2070 and then decreases to 55 kg C/ha/yr by 2099. Under the PCM-by-B1 DOC yield varied between 60 and 67 kg C/ha/yr following the pattern of the PCM-by-A1FI simulation but with higher yield projected throughout the period.

All GCM-by-emission scenarios for all three rivers projected increases in DOC yield in winter with most trends being highly significant ($p < 0.001$) (Table 5 and Figure 5). The HadCM3-by-A1FI simulation projects the largest increase in wintertime DOC yield from about 12 to 22 kg C/ha/yr and a constant rate of increase over time. The other model-by-emission simulations project relatively constant DOC yield in the range of 12 to 14 between 2015 and 2050 followed by increasing yield to 18 to 24 kg C/ha/yr by 2099 (Figure 5). Significant decreases in DOC yield during spring were projected for all rivers for the A1FI emission scenario under the PCM (Table 5). Trends in DOC yield in spring were negative but not significant for most other model-by-emission combinations. DOC yield during the summer was projected to decrease in all model-by-emission scenarios for all rivers although the trends were significant in only half of the combinations including all of the PCM-by-A1FI scenarios. Trends in summer DOC yield were largest and most significant in the most northerly river, the Penobscot River. The PCM-by-B1 scenario for the Penobscot River projected a significant increase in DOC yield during the fall but none of the other simulations projected significant changes in the fall.

Table 4. Projected Changes in Precipitation and Evapotranspiration in Percent From 2015 to 2099 for the HadCM3 and PCM Models and for the A1FI and B1 Emission Scenarios for Three Rivers in Maine

	HadCM3				PCM			
	A1FI		B1		A1FI		B1	
	Precip	ET	Precip	ET	Precip	ET	Precip	ET
Penobscot	19.9	9.33	4.98	2.65	−0.99	−3.34	4.51	−2.26
Kennebec	20.7	9.23	7.50	3.81	−1.57	−3.30	5.96	−0.66
Androscoggin	21.1	11.0	8.63	5.21	−0.99	−1.22	7.10	1.62

Table 5. Sen's Slope Estimates (kg C/ha/yr or kg C/ha/Season) and Mann Kendall Trend Tests for LOADEST Estimated DOC Yield 2015 to 2099 for the Penobscot (Pen), Kennebec (Ken), and Androscoggin (And) Rivers in Maine[a]

River by GCM-by- Emission Scenario	Annual		Fall		Winter		Spring		Summer	
Pen.Had.A1	0.242	**	0.041	NS	0.266	***	−0.033	NS	−0.026	*
Pen.Had.B1	0.089	NS	−0.008	NS	0.147	***	−0.042	NS	−0.009	NS
Pen.PCM.A1	0.022	NS	0.021	NS	0.172	***	−0.103	***	−0.041	**
Pen.PCM.B1	0.134	+	0.082	*	0.128	***	0.006	NS	−0.013	NS
Ken.Had.A1	0.219	*	0.086	NS	0.225	***	−0.090	NS	−0.009	*
Ken.Had.B1	0.029	NS	0.018	NS	0.053	**	−0.032	NS	−0.001	NS
Ken.PCM.A1	−0.017	NS	−0.001	NS	0.088	***	−0.054	**	−0.020	*
Ken.PCM.B1	0.079	+	0.036	NS	0.067	***	0.001	NS	−0.005	NS
And.Had.A1	0.130	**	0.019	NS	0.139	***	−0.022	NS	−0.019	+
And.Had.B1	0.042	NS	0.019	NS	0.059	**	−0.007	NS	−0.009	NS
And.PCM.A1	−0.024	NS	−0.006	NS	0.082	***	−0.058	**	−0.020	*
And.PCM.B1	0.082	NS	0.034	NS	0.062	***	0.005	NS	−0.005	NS

[a]For the HadleyCM3 (Had) and Parallel Climate Model (PCM) GCMs for the A1FI and B1 emission scenarios.
*$p < 0.05$.
**$p < 0.01$.
***$p < 0.001$.
+$p < 0.1$.

Projections for trends in DOC concentrations during the 21st century for the Penobscot River were representative of those for the Kennebec and Androscoggin Rivers. Estimated average annual DOC concentration was projected to remain relatively constant at about 8.6 mg/L for all model-by-emission scenarios with the exception of the PCM-by-A1FI simulation, which projected a constant DOC concentration of 8.4 mg/L until 2070 and a decline after that reaching 8.1 mg/L by 2099 (Figure 6). However, average wintertime DOC concentration increased in all model-by-emission scenarios from about 7.2 to 7.9 mg/L in 2015 to between 8.2 to 8.7 mg/L in 2099 (Figure 6). The PCM-by-A1FI and PCM-by-B1 simulations projected an initial decline in DOC concentration from 2015 to 2037 followed by increases until 2099. The HadCM3-by-A1FI simulation projects increasing winter DOC concentration throughout the 21st century but with the rate of increase decreasing over time. The HadCM3-by-B1 simulation projects and initial slow rate of increase in winter DOC concentration until about 2055 followed by a substantially faster rate of increase. In all simulations, with

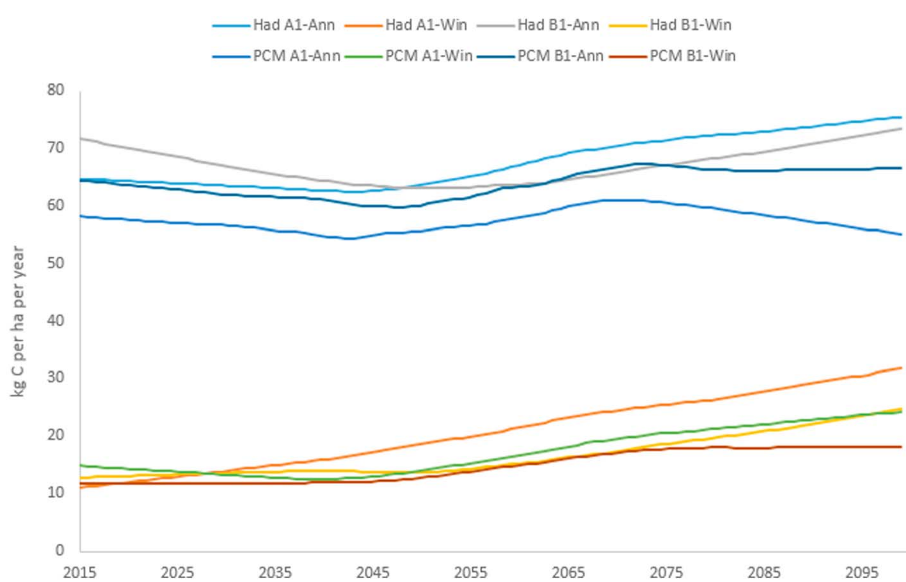

Figure 5. LOADEST-modeled DOC yield for HadCM3 and PCM GCM climate simulations and VIC model runoff simulations for A1FI (high) and B1 (low) emission scenarios for annual and winter periods for the Penobscot River at Eddington, Maine, for the period of 2015 to 2099. The graphs are smoothed with locally weighted scatterplot smoothing (LOWESS).

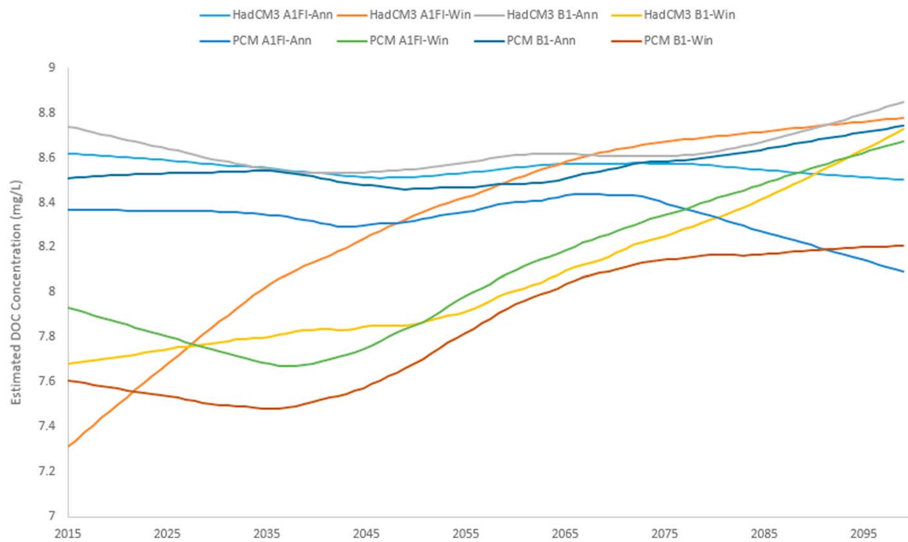

Figure 6. LOADEST-modeled DOC concentration for HadCM3 and PCM GCM climate simulations and VIC model runoff simulations for A1FI (high) and B1 (low) emission scenarios for annual and winter periods for the Penobscot River at Eddington, Maine, for the period of 2015 to 2099. The graphs are smoothed with locally weighted scatterplot smoothing (LOWESS).

the exception of the PCM-by-B1, DOC concentrations in winter are projected to increase to the same level as the average annual concentrations by late in the 21st century.

4. Discussion

4.1. Trends in Annual DOC Export and Concentration: Sensitivity to Changes in Runoff

The estimated increase in annual DOC export from 1930 to 2013 (Table 3) was expected because of the previously reported increase in precipitation and runoff across the region during the historical period [*Huntington and Billmire*, 2014]. The largest trends in annual DOC export tended to be in the more southerly basins where trends toward increasing annual runoff were also greater [*Huntington and Billmire*, 2014]. The Kendall's tau correlation between the latitude of the river basin geographic centroid and average annual runoff for the period 1930 to 2013 was negative and statistically significant ($p = 0.03$).

Our results showing historical increases in riverine DOC export are consistent with the results from studies in North America [*Findlay*, 2005] and Western Europe [e.g., *Worrall and Burt*, 2007]. Our results are also consistent with *Tian et al.* [2015] where the process-based Dynamic Land Ecosystem Model was used to simulate increasing DOC export to the Gulf of Maine during 1901 to 2008 in association with increasing discharge. In some studies, an historical increase in DOC export is implied based on an increase in both DOC concentration and river discharge [e.g., *Freeman et al.*, 2001; *Tranvik and Jansson*, 2002; *Erlandsson et al.*, 2008; *Monteith et al.*, 2014]. Other studies have reported no significant increases, or decreases, in DOC export over time [e.g., *Striegl et al.*, 2005; *Eimers et al.*, 2008; *Sarkkola et al.*, 2009; *Räike et al.*, 2016]. There have been fewer reports of trends in DOC export compared with DOC concentration. Several factors can influence trends in riverine DOC concentration and export including climate, hydrologic conditions, acidic deposition, changes in land cover, and atmospheric CO_2. In most cases multiple factors may explain observed trends and the importance of any given factor can vary over time or have variable influence depending on the season of the year [*Pagano et al.*, 2014; *Räike et al.*, 2016].

The estimated increases in DOC concentration, particularly over the long-term period (1930 to 2013) in our study (Table 3), are consistent with reports from many studies in northwestern Europe. Our study assumed a constant C-Q relation, so that the estimated increases in DOC concentration were a result of increases in discharge alone. If other factors, such as the decrease in atmospheric acidic deposition over this region [*Lawrence et al.*, 2015], resulted in increases in DOC concentration over time [*Monteith et al.*, 2007], then the estimated increases could be biased low. Our results over the long-term period (1930 to 2013) generally showing larger estimated percentage increases in DOC concentration in winter compared with annual periods are consistent with the results for Finnish Rivers over the last three decades [*Räike et al.*, 2016].

Climate and hydrologic projections for the three large river basins from 2015 to 2099 indicated continued statistically significant increases in estimated annual DOC export under only four of the 12 climate model-by-emission scenarios. Climate projections for the 21st century forecast substantially larger increases in mean annual temperature than observed in the historical period [*Hayhoe et al.*, 2007], but generally smaller increases (except under the HadCM3-by-A1FI scenario), or decreases (PCM-by-A1FI) in precipitation, compared with the increases observed for this region in the historical record period [*Huntington and Billmire*, 2014]. Taken together, this indicates that estimated DOC export increased substantially more per degree Celsius warming in the 20th century than it is projected to do in the 21st century for these model-by-emission combinations based on hydrologic changes only. This can be explained by the fact that future warming will either be accompanied by increases in ET that compensate for increases in precipitation, thereby reducing potential increases in runoff and DOC export, or that future warming will not cause an increase, or may cause a decrease, in precipitation in the 21st century. The overall pattern where the Penobscot River generally had more significant and larger-magnitude changes in annual spring and summer DOC yield and export is consistent with this river basin's higher latitude and greater ratio of snow-to-total annual precipitation than the other two rivers. Similar geographic trends in hydrologic sensitivity to warming have been shown for observed changes in the ratio of liquid to solid precipitation [*Huntington et al.*, 2004] and changes in streamflow timing [*Hodgkins et al.*, 2003] where trends are more pronounced where snowmelt is a more important feature of the annual hydrograph.

4.2. Trends in Seasonal DOC Export: Sensitivity to Changes in Runoff

The estimated historical increase in DOC export during winter is a consequence of regional trends toward increasing winter runoff [*Hodgkins and Dudley*, 2005], increasing precipitation in winter [*Huntington and Billmire*, 2014], increasing ratio of liquid to solid precipitation [*Huntington et al.*, 2004], and earlier snowmelt and high spring flow [*Hodgkins et al.*, 2003]. The increasing trends in wintertime DOC export were strongest (a higher proportion of sites showing significant trends and greater statistical significance) for the longer period of record, 1930 to 2013. The main reason for the stronger trends for the longer period of record is that the average winter runoff was substantially lower during the early part of the record (i.e., 1930 to 1950) than it was following that period. The median percent increase in winter runoff was 49% between 1950 and 2013, but it increased to 70% between 1930 and 2013 for those 14 rivers with runoff data back to about 1930.

The strongest trends, and largest percentage increases, in estimated wintertime DOC export tended to be in more northerly basins based on the latitude of the basin's geographic centroids (Table 1). The correlation (Kendall's tau) between the latitude of the geographic centroid and average annual wintertime DOC export for the period 1930 to 2013 was positive and statistically significant ($p = 0.01$). Hydrographs in the more northerly basins are more influenced by changes in snowfall and snowmelt regimes that are sensitive to climate warming.

The general trend toward an earlier export of DOC during the spring as shown by the decrease in the ratio of DOC export in May to that in March plus April in the historical period (Table 3) was expected based on previous studies that have shown earlier high spring flows in the region [*Hodgkins et al.*, 2003]. These trends were greatest in more northerly basins that tend to have higher snow accumulations. Earlier high spring flows are associated with warmer spring temperatures, earlier snowmelt, and more liquid precipitation in late winter and early spring.

The projections for decreasing DOC export in spring and summer for most model-by-emission scenarios indicate increases in evapotranspiration and little change or decreases in precipitation during these seasons [*Hayhoe et al.*, 2007; *Fan et al.*, 2014]. Spring and summer DOC export decreases are generally larger and have greater statistical significance for the PCM-by-A1FI emission scenario compared with the HadCM3-byA1FI scenario because the PCM-by-A1FI scenario projects less precipitation and runoff compared to the HadCM3 model. Little change is projected in DOC export in the fall because small increases in precipitation are partially compensated for by higher evapotranspiration. The projections for changes in annual export of DOC reflect the influence of winter, and to a lesser extent fall, increases in precipitation that are partially offset by decreases in spring and summer precipitation, resulting in significant changes largely restricted to the HadCM3-by-A1FI scenarios where increasing runoff dominates the signal.

The estimated increase in flashiness in DOC export for most rivers for the period 1930 to 2013 is associated with an increase in day-to-day variation in streamflow that is consistent with that reported for many streams in the Midwestern U.S. [*Baker et al.*, 2004]. The increase in flashiness has resulted in more pulsed inputs of DOC to the near coastal ocean. For the future hydrological projections, we use climate model projections of changes in monthly temperature and precipitation that are then scaled to daily variations based on past observations. Therefore, potential changes in precipitation frequency or intensity and thus, potential future changes in flashiness of DOC export, are not taken into account. Changes in future precipitation are expected to manifest as more intense and, to a lesser extent, fewer events [*Sun et al.*, 2007] so it is likely that DOC export will become flashier in the future.

Significant increases in projected 21st century winter DOC concentration and export are associated with increasing wintertime precipitation and runoff, and a decreasing solid-to-liquid precipitation ratio [*Hayhoe et al.*, 2007]. The overall pattern of increasing winter and decreasing spring and summer DOC export indicates a major temporal shift in the timing of the delivery of DOC to the near-coastal ocean. The projected decreases in spring and summer are smaller than the projected increases in winter DOC export; therefore, on an annual basis, DOC export is projected to increase. Projected decreases in DOC export during spring and summer could affect stream metabolism by reducing labile carbon for heterotrophic bacterial respiration in benthic and pelagic environments [*Meyer et al.*, 1988; *Volk et al.*, 1997] and hence the supply of energy to higher trophic levels.

Changes in the timing and amount of DOC exported to the near coastal ocean may influence marine biogeochemistry including the development of nuisance and harmful algal blooms [*Hayes et al.*, 2001] and carbon sequestration [*Schlünz and Schneider*, 2000]. In the near-coastal ocean colored dissolved organic matter (CDOM), which is a component terrestrially derived DOC, can lower the accuracy of satellite-derived chlorophyll concentrations. CDOM strongly absorbs in the blue wavelengths, thus lowering the water-leaving radiance in those wavelengths that the satellite sensor's chlorophyll algorithm mistakenly interprets as chlorophyll absorption [*Dierssen*, 2010; *Sauer and Roesler*, 2013]. Terrestrially derived DOC exported to the marine environment could also decrease phytoplankton productivity through increases in light attenuation [*Balch et al.*, 2012; *Balch et al.*, 2016].

5. Summary

Using long-term historical and future projected runoff for several rivers in the GoM drainage basin and our measurements of DOC concentration in recent years, we investigated how hydrologic changes have, and may, affect DOC export. This analysis used the assumption that the seasonally variable relation between DOC concentration and discharge was stationary through time. Because of the uncertainty in the assumption of stationarity in the C-Q relation, our findings represent a sensitivity analysis of DOC export to changes in hydrologic conditions alone, assuming that changes in other factors controlling DOC are of little importance. With sufficient long-term concentration and discharge data or biogeochemical models that can represent change in C-Q relations, future analyses will be able to distinguish between changes in export that result from changes in C-Q relations versus hydrologic conditions. Our results suggest large increases in estimated DOC concentration and export during winter in the historical period (1930 to 2013) and increasing, but weaker trends in annual DOC export, following the pattern of increasing runoff over this period. Using climate and hydrologic projections for the 21st century and the assumption of stationarity, our results suggest continuing trends toward increasing DOC export in winter and likely new emerging trends toward decreasing DOC export in summer.

Acknowledgments
The historical hydrologic data used in this study are available from the U.S. Geological Survey NWIS database (10.5066/F7P55KJN). The 21st century hydrologic data are available from the corresponding author. The DOC data collected by the USGS are available from the U.S. Geological Survey NWIS database (10.5066/F7P55KJN), and the data collected by Bowdoin College are available from the NASA SeaBass archive (http://seabass.gsfc.nasa.gov/seabasscgi/archive.cgi?q=BOWDOIN/camill/3rivers/archive). This work was supported by NASA grants NNYH04AA661 and NNH08A1571 and the U.S. Geological Survey funds for climate research. W.M.B. was supported by NASA grants NNX11AQ70G and NNX14AM77G. We thank hydrologic technicians with the USGS Water Science Center in Augusta, Maine, for their support in the maintenance of discharge records and their assistance with sampling, and we thank Kenna Butler, chemist with the USGS, for her assistance with chemical analysis and database management. We also thank Anna Bourakovsky and students of Bowdoin College for the sampling and analysis of water samples from several of the rivers included in this study. We thank Robert Runkel (USGS, Boulder, CO) and Timothy Cohn (USGS, Reston, VA) for the assistance with the application of the LOADEST model. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the USGS.

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