Research Brief

Carbon export by rivers draining the conterminous United States

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Abstract

Material exports by rivers, particularly carbon exports, provide insight to basin geology, weathering, and ecological processes within the basin. Accurate accounting of those exports is valuable to understanding present, past, and projected basin-wide changes in those processes. We calculated lateral export of inorganic and organic carbon (IC and OC) from rivers draining the conterminous United States using stream gaging and water quality data from more than 100 rivers. Approximately 90% of land area and 80% of water export were included, which enabled a continental-scale estimate using minor extrapolation. Total carbon export was 41–49 Tg C yr^{-1}. IC was >75% of export and exceeded OC export in every region except the southeastern Atlantic seaboard. The 10 largest rivers, by discharge, accounted for 66% of water export and carried 74 and 62% of IC and OC export, respectively. Watershed carbon yield for the conterminous United States was 4.2 and 1.3 g C m^{-2} yr^{-1} for IC and OC, respectively. The dominance of IC export was unexpected but is consistent with geologic models suggesting high weathering rates in the continental United States due to the prevalence of easily weathered sedimentary rock.

Key words: biogeochemistry, carbon cycle, inorganic carbon, load estimation, organic carbon, rivers

Introduction

Carbon export in rivers draining continents is gaining interest and importance because of its relevance to properly constraining other components of the global carbon cycle, most notably terrestrial net ecosystem production (Cole et al. 2007). Aquatic ecosystems process carbon rapidly, transforming up to 50% of the gross carbon input between the headwaters and coastal rivers (Cole et al. 2007). Land use and climate change may alter the hydrologic conditions and processes governing carbon cycling in rivers (Striegl et al. 2007, Barnes and Raymond 2009); therefore, baseline estimates of carbon transport in rivers at large scales are needed. Studies examining this question at a global scale have made necessarily broad assumptions about carbon yield from various landcover types (Schlesinger and Melack 1981, Meybeck 1982, Ludwig et al. 1996, Aitkenhead and McDowell 2000, Mayorga et al. 2010), have depended on aggregating former syntheses to foster greater confidence in overall numbers (Stallard 1998, Cole et al. 2007), or have depended on long-term (i.e., monthly) average values of chemistry and modeled runoff to determine constituent fluxes (Moosdorf et al. 2011, Lauerwald et al. 2012). However, the data exist within the United States (US) to assess continental carbon export from stream gaging and water quality data using highly refined methodologies such as maximum-likelihood regression based on daily streamflow values (Runkel et al. 2004).

The US Geological Survey maintains a large network of river sampling stations throughout the US. The National Stream Quality Accounting Network (NASQAN) currently monitors rivers comprising 80% of the total discharge from the land to the ocean, and the National Monitoring Network monitors several other large coastal rivers (http://water.usgs.gov/nasqan); therefore, carbon export from the conterminous US can be estimated with relatively minor extrapolations. We compiled the data needed to assess the carbon export from the conterminous US and used a multiple linear regression approach to relate streamflow with carbon export. This study is intended to serve as an empirical assessment of carbon fluxes to the coastal ocean under baseline modern conditions.

Methods

"Export" in this study refers to the lateral transport of the dissolved load of organic and inorganic carbon (IC and OC) and the suspended load of particulate organic carbon. It excludes bed load of organic particles as well as carbon gas efflux from rivers, both of which are substantial (Syvitski et al. 2005, Butman and Raymond 2011).

All streamflow and water quality data were taken from the US Geological Survey (USGS) National Water Information System (NWIS, http://waterdata.usgs.gov/nwis/). We present the results as an estimate of contemporary carbon (C) export because 77% of the basin area covered in this study had samples collected after 2000, and 96% of the basin area had samples collected after 1990, although for some smaller rivers the only data available were collected much earlier.

Our final database contained more than 5000 observations of total organic carbon (TOC) and alkalinity along with over 3000 dissolved organic carbon (DOC) observations. About half of the TOC observations were used directly from NWIS and half were calculated as the sum of dissolved and particulate OC. Virtually all DOC data were taken directly from NWIS. We calculated IC concentration from pH, temperature, and either filtered or unfiltered alkalinity (see Supplemental Information for detailed information about the constituents used and their frequency in our database).

For any given river, we selected the farthest downstream station that had both stream water quality and streamflow data. Ultimately, we included 123 sites for TOC, 134 sites for IC, and 95 sites for DOC. Coincident estimates of IC, TOC, and DOC export were possible from the largest rivers, but some of the smaller coastal streams lacked sufficient data for at least one carbon constituent. Our final dataset covered approximately 90% of the total drainage area and 80% of the total discharge from the conterminous US (see Supplemental Information for a complete list of sites included in our analysis).

Our IC calculations required 2 principal assumptions. First, particulate IC concentrations are small enough that filtered and unfiltered alkalinity measurements are nearly equivalent. Mean and median particulate IC concentration, measured at several of the sites in our database, were each <0.2 mg C L^{-1} and only exceeded 1 mg L^{-1} at one station (San Bernard River near Boling, TX, 08117500); therefore, particulate IC was a small part of alkalinity. Second, IC is the major source of alkalinity in water samples. In typical, unpolluted, fresh surface water, IC accounts for most of the alkalinity, but titratable organic functional groups (RCOO$^-$) can contribute substantially to alkalinity in dilute waters with high OC concentrations (Driscoll et al. 1989, Hunt et al. 2011). We examine this

assumption in greater detail in the Supplemental Information and discuss how it may have affected the interpretation of our results.

We calculated C export using the USGS Load Estimator (LOADEST; Runkel et al. 2004). This approach uses measured concentration values to calibrate a maximum likelihood regression between constituent load, streamflow, and seasonality. Daily streamflow values are then used to calculate a daily flux, which were summed and expressed as annual C export. LOADEST requires at least 12 water quality observations matched with daily streamflow in the calibration dataset, although most of our streams had more than 12 observations. In order for a stream to be included in our dataset, we required that water quality observations were collected within 4 years and that no year have fewer than 3 observations. We present the adjusted maximum likelihood estimate (AMLE) results. Watershed C yields were calculated as the annual C export divided by the entire watershed area and were expressed as g C m^{-2} watershed area yr^{-1}.
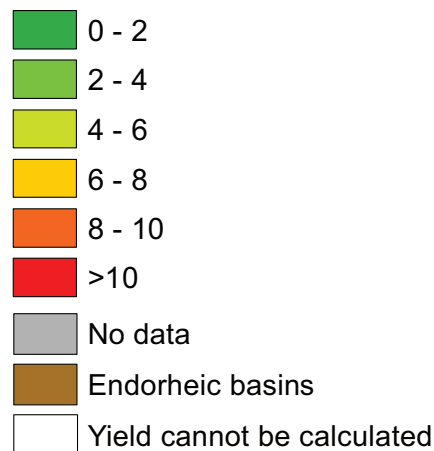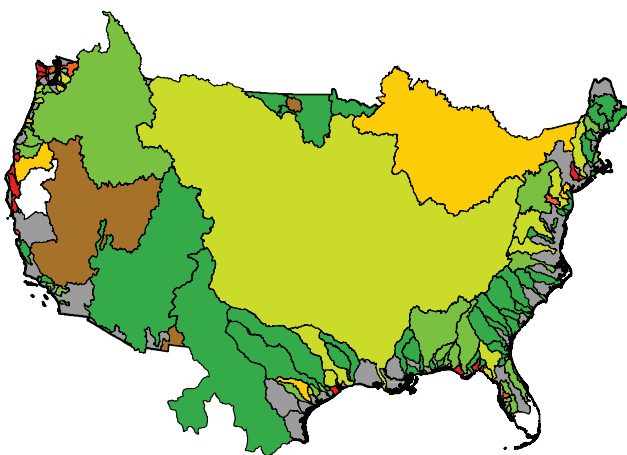
We summed the observed mean C export from all sites and then corrected for the drainage area and discharge known to be missing from our database. For missing exorheic drainage area, the total C export estimate (Total E$_C$) was calculated as

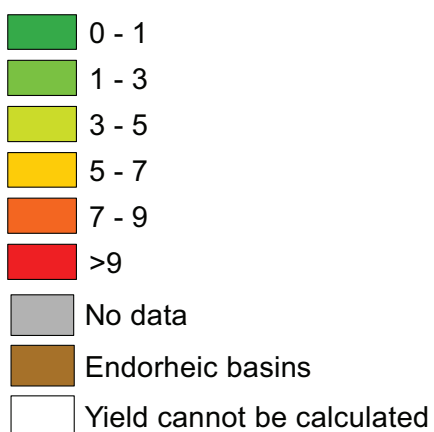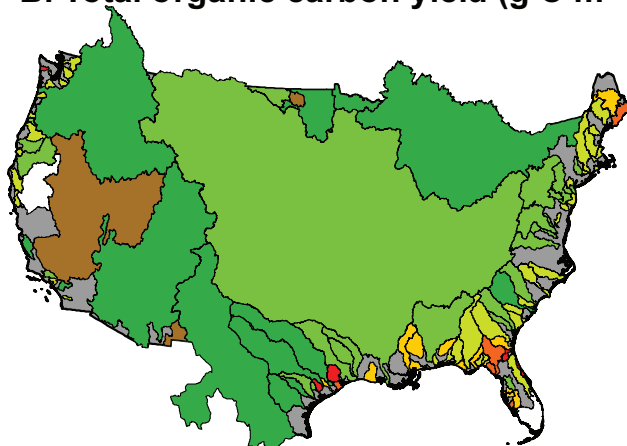$$\text{Total } E_C = E_{C\ (IN)} \text{ x } (A_{TOT} / A_{IN}) \qquad (1)$$

where E$_{C\ (IN)}$ is the C export estimated from sites included in our database, A$_{TOT}$ is the total exorheic drainage area for rivers draining the conterminous US, and A$_{IN}$ is the total drainage area in our dataset. This correction assumes an equivalent watershed C yield from the remaining (unmeasured) exorheic drainage area. For missing discharge, we adapted equation 1 by substituting Q$_{TOT}$, the long-term average total stream discharge from rivers draining the conterminous US (http://water.usgs.gov/nasqan), and Q$_{IN}$, the stream discharge included in our dataset. The discharge correction assumes an equivalent flow-adjusted C concentration from the remaining discharge.

We present results for the entire conterminous US and for 10 geographic regions (Fig. 2). The regions were selected based on geography, runoff characteristics, and coastal receiving waters. The St. Lawrence, Mississippi-Atchafalaya, and Colorado river basins were each considered as separate regions. Regional average watershed C yields and flow adjusted concentration (FAC) were calculated by weighting each stream by its drainage area. FAC for a basin is defined as C export divided by the water export (mass/volume) and provides a comprehensive summary of chemical concentration in the basins and regions of interest. We were unable to calculate watershed
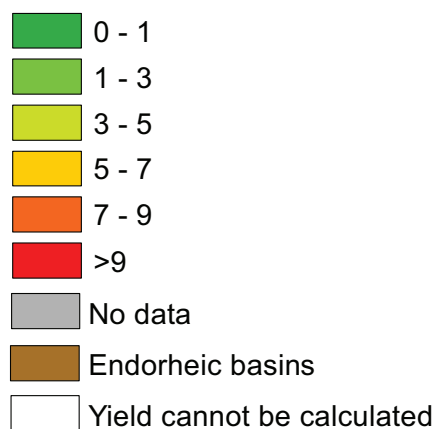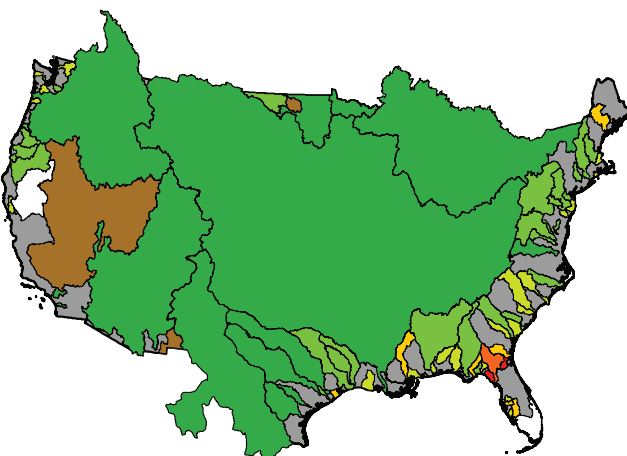
Fig. 1. Watershed carbon yield (g C m⁻² yr⁻¹) for all river basins included in this study. Gray areas indicate endorheic basins and areas not covered in this study.

C yield for several rivers because the basins were poorly defined. The largest of these were the Sacramento River and several canals draining southern Florida. Several rivers have watersheds that extend into Canada or Mexico. For these, we included the entire basin area in our export and watershed yield calculations because the intent of this study was to report values for riverine C export from rivers draining the conterminous US whether the basin lies entirely within the US or not. Confidence intervals on the aggregate flux estimates were calculated by summing variance from each individual basin and using this to calculate an aggregate standard deviation, and then estimating confidence intervals as 1.96 × standard deviation. Error expressed by LOADEST assumes no error in the discharge record, and therefore the calculated confidence intervals may be underestimated (see Supplemental Information for more details).
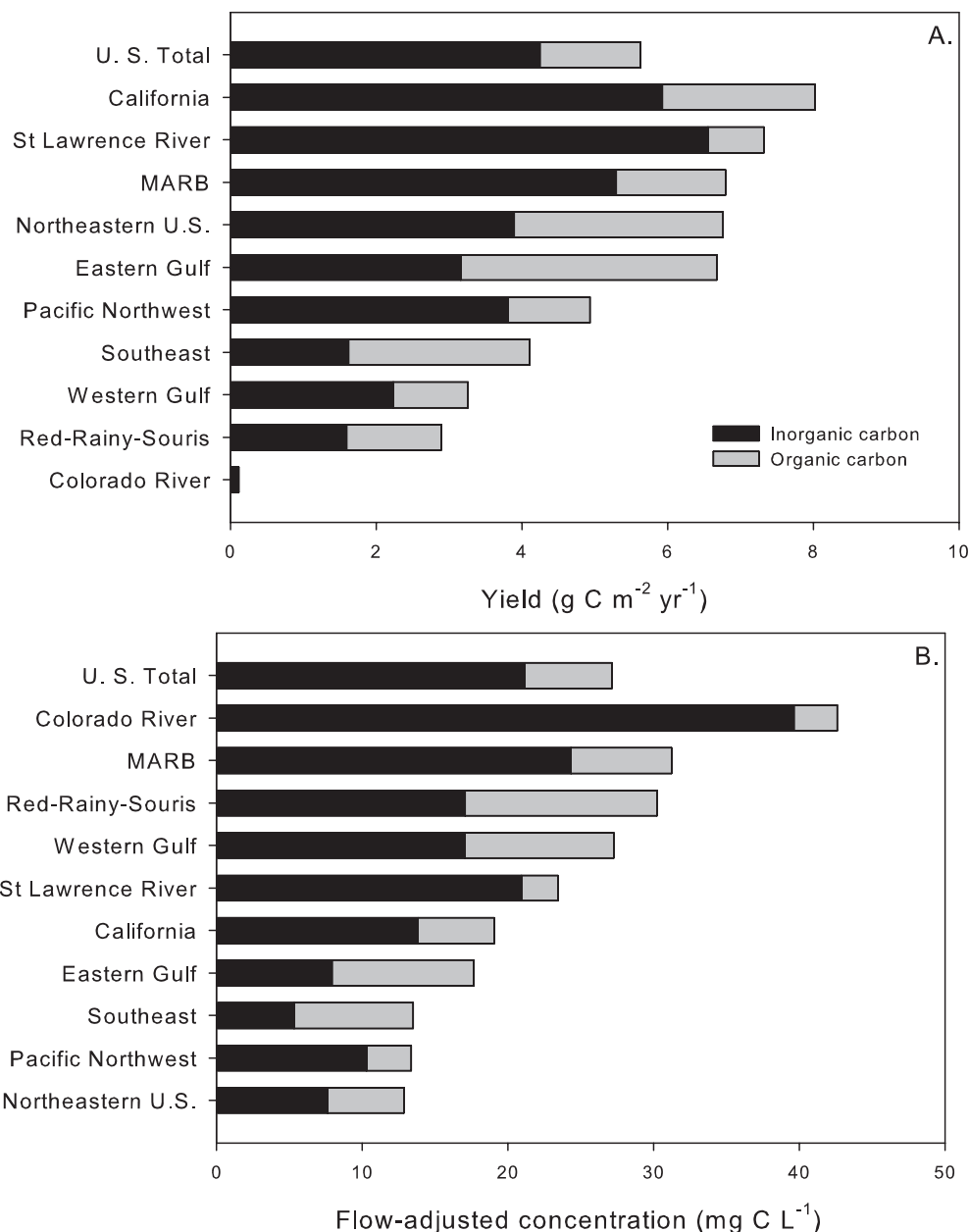

Fig. 2. (A) Watershed carbon yield and (B) flow adjusted concentration from the 10 regions defined in this study. The Mississippi-Atchafalaya River basin is displayed as MARB.

Results

For all constituents, the database covered nearly 90% of the drainage area in the conterminous US, after subtracting noncontributing endorheic basins, and 80% of the known water discharge (Table 1). Our raw observations for constituent flux were 29.0, 9.3, and 6.3 Tg C yr^{-1} for IC, TOC, and DOC, respectively (Table 1). Correcting for drainage area missed in our database yielded an E_C of 43 Tg C yr^{-1} with 95% confidence intervals of 41–45 Tg C yr^{-1}. Correcting for missing runoff yielded an E_C of 47 (45–49) Tg C yr^{-1}; therefore, our overall estimate of E_C ranged from 41–49 Tg C yr^{-1} with IC comprising 76% of the total carbon flux (Table 1). DOC fluxes were comparatively small, 7–9 Tg C yr^{-1}, but were 68% of the TOC flux (Table 1).

We estimate that RCOO^{-} contributed little to overall alkalinity concentrations and probably had a minor influence on our estimated IC flux. RCOO^{-} exceeded 20% of reported alkalinity in some small, low-alkalinity rivers, but IC export from these rivers totaled only 0.4% of the IC export in our overall dataset. The effect was most important in the Northeastern US and Southeast regions, but even in those regions rivers with >20% of the reported alkalinity potentially attributable to RCOO^{-} accounted for only 5.2 and 6.8% of the total IC export, respectively.

The largest rivers were most important in terms of overall C fluxes as well as total water discharge. The 10 largest rivers (defined by discharge) carried 66% of the total water discharge, 74% of the IC, and 62% of the TOC flux (Table 1).

For the entire dataset, total watershed yield was 5.5 g C m^{-2} yr^{-1}. Of this, 4.2 g C m^{-2} yr^{-1} was IC and 1.3 g C m^{-2} yr^{-1} was TOC. Watershed IC yield varied regionally from 0.1 to 6.6 g C m^{-2} with the highest yield in the St. Lawrence River basin (Fig. 1 and 2A). TOC yield varied from <0.1 to 3.3 g C m^{-2} yr^{-1} and was highest in rivers draining to the Gulf Coast east of the Mississippi River (Fig. 1 and 2A.). DOC yield ranged from <0.1 to 2.9 g C m^{-2} yr^{-1} and showed a spatial pattern similar to TOC (Fig. 2A.). Watershed total C yield (IC + TOC) was greatest in basins located in California draining to the Pacific Ocean (Fig. 2A.). The watershed yield calculation for the California region excluded the Sacramento and San Joaquin rivers and was influenced by several rivers having high runoff, including the Elder, Eel, Mad, and Smith rivers; therefore, calculated watershed yield for this particular region may not provide an adequate representation. Other regions with high watershed total C yield included the Mississippi-Atchafalaya and St. Lawrence river basins, with IC comprising 75% of the watershed total C yield in both cases (Fig. 2A.).

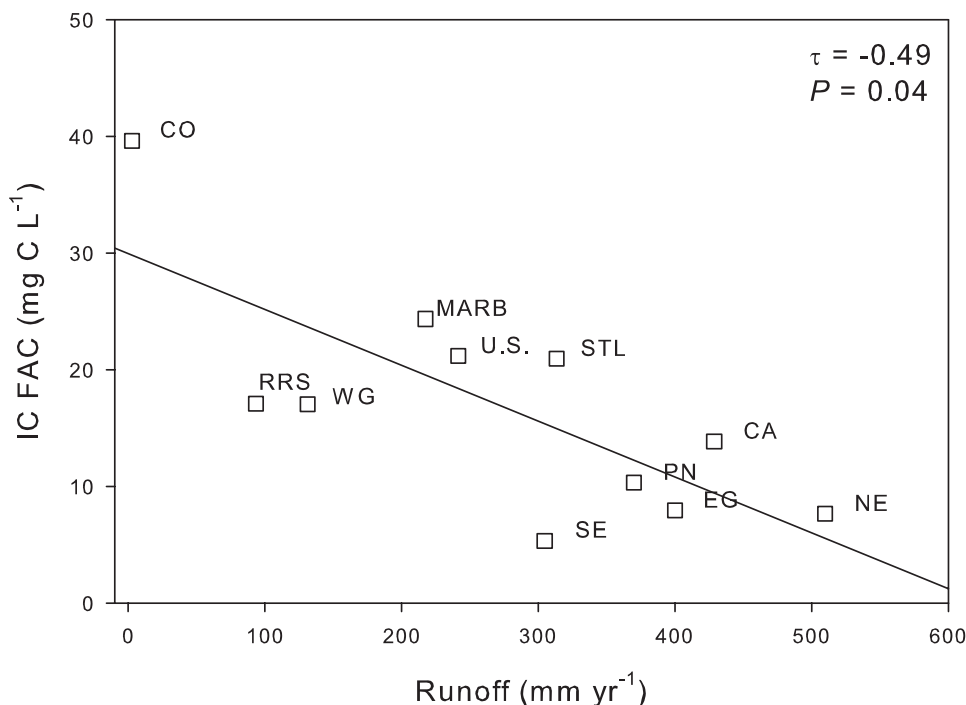**Fig. 3.** Flow-adjusted concentration (FAC) for inorganic carbon (IC) vs. annual runoff for the 10 regions in this study. The regional abbreviations are: California (CA), Colorado River (CO), Eastern Gulf of Mexico (EG), Mississippi-Atchafalaya River basin (MARB), Northeastern US (NE), Pacific Northwest (PN), Red-Rainy-Souris (RRS), Southeast (SE), St Lawrence River (STL), U.S. Total (U.S.), and Western Gulf of Mexico (WG).

Table 1. Carbon flux for the entire database with details for the 10 largest rivers. 95% confidence intervals are shown in parentheses.

Continental carbon flux calculations					
Constituent	Observed flux (Tg C yr^{-1})	Drainage area covered (%)	Flux corrected for drainage area	Discharge included (%)	Flux corrected for discharge
Inorganic carbon (IC)	29.0 (27.8–30.2)	89	32.6 (31.2–34.0)	82	35.4 (33.9-36.9)
Total organic carbon (TOC)	9.3 (8.6–10.0)	89	10.4 (9.7–11.2)	81	11.5 (10.6-12.3)
Dissolved Organic Carbon (DOC)	6.3 (5.8–6.8)	87	7.2 (6.6–7.9)	78	8.1 (7.4-8.8)
Total carbon flux (IC + TOC)	38.3 (36.4–40.2)		43.0 (40.9–45.2)		46.8 (44.5-49.2)
Carbon and water fluxes in the 10 largest rivers					
River	IC flux (Tg C yr^{-1})	TOC flux (Tg C yr^{-1})	DOC flux (Tg C yr^{-1})	Mean discharge (m^3 s^{-1})	
Mississippi-Atchafalaya River	17.39	5.05	2.79	21,391	
St. Lawrence River	5.15	0.60	0.54	7,733	
Columbia River	2.43	0.66	0.63	6,638	
Mobile River	0.38	0.20	0.21	1,167	
Susquehanna River	0.27	0.14	0.09	837	
Connecticut River	0.10	0.08	0.05	634	
Apalachicola River	0.16	0.15	0.14	576	
Altamaha River	0.06	0.12	n/a	467	
Skagit River	0.07	0.03	0.03	466	
Klamath River	0.20	0.06	0.06	463	
Total, top 10 rivers	26.2	7.09	4.5	40,372	

Total US FAC was 21.2, 6.0, and 4.2 mg L^{-1} for IC, TOC, and DOC, respectively (Fig. 2B.). Among the regions, IC FAC was highest in the Colorado River and lowest in the Southeast regions, 39.6 and 5.3 mg L^{-1}, respectively (Fig. 2B.). FAC for TOC and DOC were both highest in the Red-Rainy-Souris region, 13.2 and 12.1 mg L^{-1}, respectively; and lowest in the St Lawrence River region, 2.5 and 2.3, respectively (Fig. 2B.). There was a weakly significant negative correlation between IC FAC and runoff among the regions (Kendall τ = −0.49, P = 0.04; Fig. 3a) but no correlation between TOC FAC and runoff (Kendall τ = −0.24, P = 0.31; not shown) or DOC FAC and runoff (Kendall τ = −0.09, P = 0.69; not shown). Total C FAC was highest in the Colorado River basin and lowest in basins draining the Northeastern US (Fig. 2B). Higher IC FAC in basins with low runoff could be a result of (1) increased water residence time within the watershed, which allows greater contact time between water and weatherable substrates (Amiotte Suchet et al. 2003); or (2) evaporative concentration of stream solutes in drier watersheds (White and Blum 1995).

Discussion

The USGS NWIS database covered a large portion of the conterminous US and allowed estimates of lateral C fluxes to be made using only minor extrapolation. It is difficult to find a point of comparison with our results because other large-scale C export studies have been continental or global in scale. The most direct comparison can be drawn between our study and that of Mulholland and Watts (1982), which estimated riverine TOC flux from the US and Canada to be 39 Tg C yr^{-1}. Their estimates for Canada and Alaska totaled 25 Tg C yr^{-1}, leaving approximately 14 Tg C yr^{-1} TOC export from the conterminous US, which is similar to our estimate of 9–12 Tg C yr^{-1} (Table 1). Mayorga et al. (2010) estimated that 46 Tg OC yr^{-1} are exported from North America, suggesting slightly higher TOC export values for the conterminous US than our calculations.

Carbon dioxide (CO_2) release from rivers and streams in the conterminous US has been estimated to be 97 Tg C yr^{-1} (Butman and Raymond 2011), roughly

double that of lateral C export (Table 1). Regional estimates of both lateral C export and CO_2 emission are not common, but several existing studies offer a point of comparison with our findings for the conterminous US. In the Amazon River basin, CO_2 emission is more than 6 times larger than lateral C export (Richey et al. 2002), while in the Yukon River basin CO_2 emission and lateral C export are nearly identical (Striegl et al. forthcoming). An estimate developed for Sweden indicates that CO_2 emission from streams and rivers is approximately one-fifth that of lateral C export (Humborg et al. 2010). Thus, the ratio of CO_2 emission to lateral C export seems to be lower at higher latitudes, which would be consistent with a lower respiration rate in either the terrestrial or aquatic environment. Lower temperatures and lower terrestrial net primary production could both contribute to lower ecosystem respiration at high latitudes.

Global TOC and IC export to the oceans are believed to be about equal (Meybeck 1982, Amiotte Suchet and Probst 1995), so finding that IC export from the conterminous US was 3 times greater than TOC export (Table 1) was somewhat unexpected. OC has nonconservative behavior in rivers and streams, with net OC consumption likely in most systems (Lauerwald et al. 2012). Using data from the most downstream station could have reflected net OC mineralization occurring in the rivers; however, geologic models suggest that weathering rates in the conterminous US are high due to the presence of karst and sedimentary deposits, which are particularly susceptible to weathering reactions (Amiotte Suchet and Probst 1995). Spatial analysis of weathering in North America shows elevated weathering rates in much of the eastern US (Moosdorf et al. 2011). Agriculture in the US may elevate IC export, but the identified mechanism, increased water export (Raymond et al. 2008), would presumably also increase TOC export; therefore, we do not believe the relatively high IC export is due to perturbances, but rather to the underlying geology of the conterminous US.

Acknowledgments

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