Spatial patterns and environmental controls of particulate organic carbon in surface waters in the conterminous United States

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February 2016

Abstract

Carbon cycling in inland waters has been identified as an important, but poorly constrained component of the global carbon cycle. In this study, we compile and analyze particulate organic carbon (POC) concentration data from 1145 U.S. Geological Survey (USGS) gauge stations to investigate the spatial variability and environmental controls of POC concentration. We observe substantial spatial variability in POC concentration (1.43 ± 2.56 mg C/ L, Mean $\pm$ One Standard Deviation), with the Upper Mississippi River basin and the Piedmont region in the eastern U.S. having the highest POC concentration. Further, we employ generalized linear models (GLMs) to analyze the impacts of sediment transport and algae growth as well as twenty-one other environmental factors on the POC variability. Suspended sediment and chlorophyll-a explain 26% and 17% of the variability in POC concentration, respectively. At the national level, the twenty-one environmental factors combined can explain ca. 40% of the spatial variance in POC concentration. At the national scale, urban area and soil clay content show significant negative correlations with POC concentration, whereas soil water content and soil bulk density correlate positively with POC. In addition, total phosphorus concentration and dam density correlate positively with POC concentration. Furthermore, regional scale analyses reveal substantial variation in environmental controls of POC concentration across eighteen major water resource regions in the U.S. The POC concentration and associated environmental controls also vary non-monotonically from headwaters to large rivers. These findings indicate complex interactions among multiple factors in regulating POC concentration over different spatial scales and across various sections of the river networks. This complexity, together with the large unexplained uncertainty, highlights the need for considering non-linear interplays of multiple environmental

45 factors and developing appropriate methodologies to track the transformation and transport of
46 POC along the terrestrial-aquatic interfaces.

47 **Key words:** Particulate organic carbon; spatial variability; environmental control; uncertainty

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1. Introduction

Carbon cycling along the terrestrial-aquatic interfaces have been identified as an important, but poorly constrained component of the global carbon cycle (Regnier et al., 2013; Butman et al., 2016). In the Fifth Assessment Report of the International Panel on Climate Change (IPCC), carbon export, burial, and outgassing from inland waters are highlighted as critical but insufficiently investigated processes that may affect the global carbon budget (Ciais et al., 2013). However, inclusion of these processes into regional and global carbon cycling investigations is jeopardized by the significant uncertainties in the magnitude, variability, and environmental controls of riverine carbon (Butman and Raymond, 2011; Regnier et al., 2013; Rodríguez-Murillo et al., 2015).

Riverine carbon is mainly composed of three groups of carbon species including dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC) (Cole et al., 2007). Synthesis of the global riverine carbon data suggests that magnitudes of riverine POC (0.2 Pg C/year) and DOC (0.18-0.33 Pg C/year) fluxes are comparable at the global scale (Cole et al., 2007; Galy et al., 2015). However, the underlying mechanisms controlling the two species are distinct from each other and vary over different spatial scales (Zhang et al., 2009). Therefore, it is necessary to explore the impacts of a wide range of environmental factors on POC concentration to discover knowledge contributing to the explanation of carbon cycling along the terrestrial-aquatic continuum.

Factors affecting POC in surface waters can be generally categorized into two groups based on their influences on the supply and/or transport of POC. POC mainly originates from two sources including erosion of soil organic carbon (Kirkels et al., 2014), and autochthonous production (Hatten et al., 2010). Impacts of these two sources on riverine POC vary with

distance from headwaters, land use types, and hydrological conditions. Soil erosion mobilizes as much as 4-6 Pg C yr⁻¹ of sequestered carbon in soils at the global scale, and plays a dominant role in POC export (Galy et al., 2015). It was estimated that autochthonous production provides approximately 8 to 28% of POC in large rivers (Howarth et al., 1996; Veyssy et al., 1998). In streams with enriched nutrients, algae growth could be the primary source of carbon input to water bodies (Royer and David, 2005). Contributions of the two POC sources vary over different temporal and spatial scales, resulting in significant variability in POC concentration.

Riverine POC is also controlled by transport-related factors. Carbon cycling is closely coupled with water cycling since water movement from soils to rivers contributes to POC transport (Kirkels et al., 2014). Rain drops provide energy and runoff for detaching and mobilizing soil organic matter through erosion, especially during heavy rainfalls (Gomez et al., 2003; Nearing et al., 2005). Meanwhile, intensive rainfalls and associated high streamflow increase the capacity of rivers in carrying high concentrations of POC (Neitsch et al., 2009). Remobilization of bottom sediment and bank erosion by floods also increase riverine POC (Adams et al., 2015; Merritt et al., 2003; Smith et al., 2003).

Human activities have dramatically altered riverine POC through land conversions, damming, and chemical fertilizer use (Butman et al., 2015; Kirkels et al., 2014; Syvitski et al., 2005; Zhou et al., 2009). Land-use change influences riverine carbon cycling either by altering water cycling or by changing the production of carbon leachates (Farley et al., 2005; Piao et al., 2007). Agricultural activities enhance soil organic carbon (SOC) erosion through mobilizing organic matter aggregates in top soils during tillage and irrigation (Kirkels et al., 2014). Dam constructions have dramatically altered the natural flow regimes and resulted in high sedimentation and burial of POC (Li et al., 2014). Excessive nutrient discharge to rivers and

lakes from urban areas and agricultural lands stimulates autochthonous POC primary production, therefore increases concentration of river carbon (Rabalais, 2002).

Recent efforts have been devoted to unraveling the complex controls of riverine POC. However, most studies examining regional scale POC dynamics were mainly focused on quantifying the magnitude of POC export (Tian et al., 2015), but paid insufficient attention to exploring mechanisms governing POC (Schlunz and Schneider, 2000). Local scale investigations provide detailed descriptions of how riverine carbon dynamics are affected by input, in-stream decomposition, and deposition (Webster et al., 1999), and demonstrate contrasting results among different watersheds (Hope et al., 1994), reflecting the complex interplays of multiple processes in controlling the generation, transport and deposition of POC. Furthermore, it is uncertain whether the mechanisms identified through watershed-scale studies are applicable and transferable to broader scales that include complex climate conditions, land use types and geophysical settings (Hatten et al., 2010). The reported large uncertainties call for comprehensive analyses of factors influencing POC in surface waters.

Investigating how POC concentration in surface waters is affected by multiple environmental factors is a necessary and critical step towards better understanding of riverine POC fluxes. In this study, we compile POC concentration data from 1145 of the U.S. Geological Survey (USGS) gauge stations. Statistical analysis is employed to explore impacts of climate factors, hydrological conditions, soil properties, and anthropogenic activities on the spatial variability of POC concentration. The objectives are to: 1) characterize the spatial patterns of POC concentration across the U.S riverine systems; 2) identify key variables controlling riverine POC concentration over different spatial scales and river orders; and (3) provide insights into future investigations of riverine POC related carbon sources and sinks.

2. Method

2.1 Data compilation and statistical analysis

[Figure 1]

We compiled field POC concentration data from 1145 USGS gauge stations (Figure 1) listed in the Geospatial Attributes of Gages for Evaluating Streamflow (GAGES-II) dataset (Falcone, 2011). The GAGES-II dataset provides geospatial attributes, such as climate conditions, geomorphological characteristics, and soil properties, for stations with long-term streamflow records (> 20 years). POC refers to carbon that cannot pass membrane filters with a 0.45um pore size (<https://water.usgs.gov/admin/memo/QW/qw00.08.html>). We first checked the availability of POC concentration data for each GAGES-II station. Stations with available suspended organic matter (with USGS water quality parameter code of 00689), or paired total organic carbon (TOC, 00680) and dissolved organic carbon (DOC, 00681), were selected for this study. For the 1145 stations, we also collected total nitrogen (00600), total phosphorus (00665), suspended sediment (00530) and chlorophyll-a (70953) observations if they are available. Water samples of these stations were mainly collected from 1973 to 2015. We downloaded these data from the USGS National Water Information System (NWIS) online database (<http://qwwebservice.usgs.gov/>). For stations with paired TOC and DOC observations, but no POC, we calculated POC concentration by subtracting DOC from TOC. Since outliers may have significant impacts on statistical analysis and interpretation of environmental controls on POC, we performed a data quality control to identify outliers according to the USGS procedure (Aulenbach et al., 2007). We screened the POC observations to remove records outside three standard deviations of the

mean (Gotway et al., 1994). Long-term average POC concentration from all valid samples at each site was calculated for the following analyses.

To analyze the influence of multiple environmental factors on riverine POC concentration, we obtained nineteen geospatial attributes for the drainage area of each station directly from the GAGES-II dataset, and two water quality variables from the NWIS water quality database. The values of the variables derived from the GAGES-II dataset represent the spatial average conditions of the drainage basin for each gauge station. Variables considered in this study include climate conditions (temperature, precipitation), hydrological factors (annual runoff), land cover information (cropland, forest, and wetlands), soil properties (soil texture, water content, bulk density, and soil organic carbon), topographic factors (slope, river order), dam density, and water quality (total nitrogen and total phosphorus). These variables were selected since they either have close connections with the hydrological cycle or with the carbon cycle, based on previous studies (Kirkels et al., 2014; Lal, 2003; Royer and David, 2005). To reduce the impacts of non-normal distribution on statistical analysis, we used log transformation to convert highly-skewed variables to approach symmetric distributions (More information is provided in the supporting document).

We divided all selected stations into 18 groups based on the delineation of the major U.S. water resources regions (Seaber et al., 1987), to account for regional variations in mechanisms controlling POC concentration. We also investigated impacts of environmental factors on POC concentration by river orders, by assigning all stations into four groups based on the river Strahler order, to explore the hierarchical patterns of POC.

We employed linear regression models to analyze the impacts of the selected environmental factors on POC concentration. First, we used bivariate regression analyses to check how the two

POC sources (suspended sediment and algae) affect POC concentration. Then we tested the linear correlation between POC concentration and each of the selected environmental factors to demonstrate the complex environmental controls on POC. Next, a general linear model (GLM) was used to quantify the interacting influences of the selected factors on POC concentration. This model provides partial correlation estimates for each independent variable by eliminating compounding impacts from other variables (Sweet and Grace-Martin, 2007). We applied the GLM across all the stations to test how environmental factors affect POC concentration at the national scale. Then, we applied the GLM analysis to each water resource region, as well as to the four river-order groups. Variables with high collinearity were checked and removed from these GLM analyses. Specifically, we checked the variance inflation factor (VIF) values of all the variables for each GLM simulation. VIF is an index of multicollinearity among independent variables in the GLM models. Variable with highest VIF value was removed until the VIF is less than 10 for all independent variables. All the statistical analyses were conducted using the R statistical software (<http://www.R-project.org>). We set the confidence level to 95% ($P < 0.05$) to detect statistically significant correlations. The GLM model equations are listed in the supporting information file.

3. Results

3.1 *Spatial patterns of POC concentration*

POC concentration demonstrates significant spatial variability (Figure 1). Average POC concentration of all stations is 1.43 ± 2.56 mg C/ L (Mean $\pm$ One standard deviation). Distribution of the POC concentration data is positively skewed, with 71.5% of all the observations having a value lower than 1.3 mg C/ L. Stations with low POC concentration are mainly located in the Eastern and Western coasts of the U.S. Stations with POC concentration

over 3.35 mg C/ L only account for 7.8% of all selected stations, and are mainly located in the upper Mississippi River basin and the Piedmont areas in the eastern U.S.

[Figure 2]

Water resources regions located in Missouri (region 2), the Upper Mississippi (Region 6), and the Lower Colorado (region 12), have higher average POC concentration than other regions (Figure 2). Specifically, average POC concentration in these three regions is 2.56, 2.24, and 2.55 mg C/ L, respectively. On the contrary, the New England region, the Mid-Atlantic region, and the Great Basin area have relatively lower average POC concentration, generally lower than 1mg C/ L. Lowest POC concentration is found in the California region (Region 8), with an average of 0.79 mg C/ L.

3.2 Contributions of suspended sediment and algae growth to POC concentration

[Figure 3]

The mean suspended sediment and its standard deviation for all selected stations is 124 ± 700 mg / L, with low-concentration stations located in the Eastern and Western Coastal areas, and high-concentration stations located in the Central and Southwestern U.S. (Figures S1 and S2 in supporting information). The mean Chlorophyll-a concentration and its standard deviation over all selected stations is 9.6 ± 13.89 μg / L (Figures S3 and S4), and stations with high chlorophyll-a concentration are mainly located in the Upper Mississippi River basin and Coastal areas in Northeastern U.S., Southern Florida, and California (> 17.6 μg / L). Correlation analysis indicates that POC concentration has positive correlations with both suspended sediment and chlorophyll-a. Specifically, suspended sediment accounts for approximately 26% of the POC variability, while chlorophyll-a concentration explains 17% of the POC variability (Figure 3).

3.3 POC concentration in relation to different environmental factors

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[Table 1]

Most of the selected environmental factors have statistically significant correlation ($P < 0.05$) with POC concentration (Table 1). POC concentration tends to increase with drainage area. Temperature and precipitation have contrasting impacts on POC concentration. POC concentration tends to be high under warm temperatures and in dry areas, but low in cold and wet regions. In line with the impacts of precipitation, runoff has negative impacts on POC concentration. Both soil water and soil bulk density show positive correlations with POC concentration. Multiple land covers contribute to the POC variability. Urban area and cropland have positive correlations with POC concentration, whereas forest, shrub land, and barren area are negatively correlated with POC concentration. Alterations to the natural regimes of river discharge affect POC concentration. For example, dam density tends to boost POC concentration, and excessive nutrient (nitrogen and phosphorus) inputs to surface waters have positive impacts on POC concentration.

Although most of the selected variables have significant correlation with POC concentration, each individual factor has a fairly low explanatory power for the POC variability. Only four variables, including total phosphorus, total nitrogen, forest land cover, and soil water content, each can explain more than 10% of the POC variability. Therefore, collective impacts from multiple factors should be considered to better explain the spatial patterns of POC concentration.

[Table 2]

[Figure 4]

The GLM model analyses suggest that POC concentration is affected synergistically by multiple variables (Table 2, Figure 4). For the entire U.S., urban extent negatively affects POC concentration ($P < 0.01$). Soil properties, such as soil water content ($P < 0.01$), bulk density ($P <$

0.01) and clay content ($P < 0.05$), show significant influences. POC concentration decreases with soil clay content, whereas the other two soil variables have positive impacts. Total phosphorus in water and dam density have positive impacts on POC concentration. No significant impacts were detected for the other variables. At the national level, our multi-variate model explains up to 40% of the POC concentration variability.

Our regional scale analyses reveal significant variation in the mechanisms regulating POC concentration across the 18 U.S. water resource regions (Table 2). For regions 4, 12, 14, and 16, the GLM model fails to provide statistically significant correlation for POC concentration due to insufficient observations. For regions 9 and 13, no variable shows significant impacts on POC. Soil organic matter content has positive impacts in regions 2 and 8, but negatively affects POC concentration in region 18. Region 3 is the only region where wetlands have positive impacts. Temperature tends to increase POC in region 11. Runoff has a dilution effect in the California region (region 8). In the Western U.S. (region 10), drainage area has positive impacts on POC. Major land covers have either negative or insignificant ($P > 0.05$) impacts on POC. Specifically, barren land negatively correlates with POC in region 18; urban extent tends to reduce POC concentration in regions 1 and 11; shrub land has negative impacts in regions 8 and 11. Although the selected soil properties (soil water, clay content, and soil bulk density) all significantly correlate with POC at the national scale, they only exert significant influences in four of the 18 regions. Clay content negatively affects POC in region 7; soil water has positive impacts in region 15; soil bulk density has positive impacts in regions 8 and 10. Percentage (length of first order streams to total stream length in the drainage area of each station) of first-order rivers correlates positively with POC concentration in region 3 and region 17. For regions in the Eastern and Mid-eastern U.S, total phosphorus shows a positive correlation with POC. In

addition, significant positive impacts ($P < 0.05$) of total phosphorus were also observed in regions 2, 3, 4, 6, and 17 ($P < 0.05$). The significant influence of total nitrogen on POC occurs in regions 6 and 18. In region 6, dam density is another variable having a significant correlation ($P < 0.05$) with POC.

3.4 Variation of POC concentration and environmental controls by river orders

[Figure 5]

[Table 3]

Average POC concentration varies by river orders (Figure 5). The 2nd order stations have higher average (1.89 mg C/ L) POC concentration, which is however not significantly different from average POC concentration of other river order groups at a significance level of 0.05. Variable(s) that correlates significantly with POC concentration varies with river order (Table 3). Since there are insufficient observations to conduct GLM modeling for the first and second order stations, we combined stations located at river orders 1 through 3 together as one group. For this combined group, soil density and dam density show significant ($P < 0.05$) and positive impacts. POC concentration of stations located at the 4th river order is sensitive to total phosphorus, wetlands, and soil water content. For stations located at the 5th river order, total phosphorus is the only factor that has significant impacts ($P < 0.05$). For stations located at the 6th and higher river orders, POC concentration is negatively impacted by runoff ($P < 0.05$) and soil clay content ($P < 0.05$), but positively affected by soil organic matter ($P < 0.05$) and total phosphorus ($P < 0.01$).

4. Discussion

4.1 Spatial patterns of POC concentration

Overall, POC concentration demonstrates significant spatial variability with high POC concentration occurring mainly in the Upper Mississippi River basin and the Piedmont area.

Average POC concentration reported in this study (1.42 mg C/ L) is comparable to the previous estimates (1.8 mg C/ L) that only used stations located close to the outlets of major U.S. river basins (Stets and Striegl, 2012). High POC concentration in the Upper Mississippi River basin may be induced by the high suspended sediment production in the Central U.S. (Smith et al., 2001), which is the home of the corn belt. High POC concentration in the Eastern U.S. may be attributable to the high carbon load from soil erosion in the mountain areas (Dosskey and Bertsch, 1994).

Apart from the two regions with high POC concentration, we did not identify any apparent patterns in POC concentration to be influenced by different climatic or hydrological conditions. Our analyses demonstrate the complexity of the mechanisms regulating POC concentration. In addition to the selected river basin properties, in-stream processes (aquatic primary production, sediment deposition, and remobilization etc.) may have further complicated the spatial patterns of POC concentration.

4.2 Contribution of multiple sources to POC concentration

Detachment of soil organic matter during physical erosion and subsequent transport through rivers has been identified as the primary control of POC export at the global scale (Galy et al., 2015). Our analyses corroborate the high correlation between suspended sediment and POC concentration based on the detailed U.S. data. Soil erosion transports a large amount of POC from land to surface waters (Smith et al., 2005). Soil erosion mobilizes 52 Tg yr⁻¹ soil organic carbon in the conterminous U.S. and may play the dominant role in regulating riverine POC cycling (Smith et al., 2001). In addition, the high correlation between suspended sediment and POC concentration may also be attributable to sediment deposition and remobilization, which affect POC dynamics in rivers (Drummond, 2014).

Contribution of algae growth to riverine POC has not been well understood yet. Most previous investigations focused on large spatial scales indicated that aquatic primary production had minor influence on riverine carbon (Cole et al., 2007). However, watershed-level studies suggest that supplier of riverine carbon shifts from terrestrial sources to in-stream algal production and from forest streams to agricultural rivers (Hagen et al., 2010). Our analyses imply that chlorophyll-a has an explanatory power that is comparable in magnitude to suspended sediment at the national scale, highlighting that algae growth may play a more important role in determining riverine POC than previous studies have suggested (Duan et al., 2007; Findlay et al., 1991). As depicted in Figures 1 and 3, high chlorophyll-a concentration occurs coincidently with high POC concentration in the Upper Mississippi River basin, illustrating that algae growth may have significant impacts on POC in areas with intensive agricultural activities (Royer and David, 2005).

Although both suspended sediment and algae growth have significant impacts on POC concentration, a large proportion of the POC variability is still not accounted for (Figures 3). Other carbon sources, such as the allochthonous input through litter fall (Hagen et al., 2010), particularly in headwaters, may need to be considered to explain the spatial patterns of POC. Due to the dense plant canopy, litter fall is the primary source of carbon input for headwater streams (Webster et al., 1997). It was estimated that plant litter input may account for roughly 69% of the carbon input to headwaters (Webster et al., 1997).

Contribution of litter fall and its interactions with other carbon sources may be responsible for the non-monotonic patterns of POC from small streams to large rivers. Headwater streams have typically high litter input and high respiration rates (Webster, 2007). In addition, high sediment input from mountainous areas may also contribute to the elevated POC concentration in

headwater rivers (Milliman and Syvitski, 1992). Reduced litter fall input may result in lower average POC concentrations in the 3rd order rivers than headwaters (Golladay, 1997). For large rivers, in-stream production tends to play a more important role than riparian litter input (Webster, 2007). In addition, input of carbon along with sediment deposition/remobilization may further complicate the contribution of different carbon sources (Blair et al., 2004; Trimmer et al., 2012).

4.3 Environmental controls on POC concentration

Divergent correlations between POC concentration and the selected variables further illustrate the complexity and nonlinearity in aquatic carbon cycling (Hanson et al., 2014), and suggest that underlying processes regulating POC maybe spatial-scale specific (Sobek et al., 2007; Jackson R. Webster, 2007). Since the partial correlation analysis (Table 2) measures impact of each factor after removing the influence of other factors, our analysis of environmental controls on POC concentration is mainly based on the GLM results.

At the national scale, soil properties show close correlations with POC concentration. Significant impacts from soil water, soil density and soil clay content imply that movement of carbon in soils plays an important role in affecting riverine POC concentration (Schlunz and Schneider, 2000). Soil properties affect POC concentration mainly through controlling water movement in soil (Price, 2011). Soils with high clay contents are characterized with low effective porosity (Rawls et al., 1982), and movement of water and soil organic particles may be jeopardized by the low connectivity. Similarly, soils with high clay content tend to have lower bulk density and that is why the two variables have opposite correlations with POC concentration (Dexter, 2004). Positive impacts of soil water content on POC concentration suggest that water availability for mobilizing POC is important for POC leaching.

Total phosphorus in surface waters is another important factor shaping the spatial patterns of POC concentration at the national scale. Since total phosphorus has a significant correlation with chlorophyll-a ($P < 0.01$), the positive correlation of total phosphorus with POC further confirms the important contribution of in-stream primary production to POC (Cole et al., 2007; Shih et al., 2010). In this study we find that phosphorus, rather than nitrogen, has a significant correlation with POC concentration at the national scale. This result is in accordance with previous findings that primary production in aquatic ecosystems is more limited by phosphorus than nitrogen (Elser et al., 2007).

At the national scale, impacts of dam density should also be taken into consideration in explaining the spatial variability of POC concentration. In contrast with studies which found dam constructions substantially reduce riverine POC (Li et al., 2014), our analyses point to a positive correlation between dam density and POC. One possible explanation is that although reduced flow velocity and sediment deposition following dam construction might reduce POC, algae growth stimulated by dam construction may offset this reduction and increase the POC concentration in surface waters (Friedl and Wüest, 2002).

Previous investigations indicate that land cover could explain a significant amount of variability in lateral carbon movement, mainly because of differences in carbon storage and hydrological conditions (Hope et al., 1994). Our analyses suggest that percentage of urban area is the only land cover showing significant impacts on POC concentration at the national scale. Discrepancies between this study and the SPATIally Referenced Regressions On Watershed attributes (SPARROW) model investigations of total organic carbon (TOC) further illustrate that riverine POC and DOC may be regulated by different process and thus need to be investigated separately, and land covers may have less significant impacts on POC than DOC (Shih et al.,

2010). The negative impacts from urban area may be attributable to the special hydrological processes and sediment transport in urban areas, but need to be further analyzed in case of non-causative correlations (Howarth et al., 1991).

The remaining factors listed in table 2 affect POC mainly on regional scales. Although many studies have underscored the importance of soil organic carbon on riverine carbon (Kalbitz et al., 2000), we find that SOC content only affects POC concentration positively in two water resource regions. This finding is consistent with the fact that riverine POC only account for a small fraction of the soil organic carbon pool, and POC generation may not be limited by soil organic carbon stock (Bauer et al., 2013). Positive impacts of wetlands on riverine POC were only found in region 3, indicating that high carbon storage in wetlands affect riverine POC only at the regional scale. Other land cover types, such as shrub land, have similar, regional-specific impacts as wetlands.

4.4 Interplays among multiple processes in regulating POC concentration

Concentration of POC in rivers reflects the interactive impacts of multiple processes during the generation, transport, and transformation of POC (Hope et al., 1994). Impacts of the selected factors on POC may be counteractive and their impacts may cancel each other out in determining POC concentration. Identifying the counteractive processes is helpful for explaining the variability in POC concentration across multiple spatial and hierarchical scales, and for providing insights into developing process-based methodologies to track the dynamics of POC.

Although suspended sediment has significant impacts on POC (figure 3), our analysis does not identify cropland area, which is usually associated with high soil erosion, as a significant factor. Possible explanations responsible for the insignificant influence of erosion may lie in the non-linear negative correlation between sediment concentration and POC concentration (Veyssy

et al., 1998). At high sediment levels, POC content tends to be diluted by soil minerals (Galy et al., 2015). In addition, suspended sediments only represent a small portion of the total eroded sediment (Smith et al., 2001), and thus result in the complex impacts of erosion on riverine POC. This result suggests that river channel's transport capacity may play an important role in POC delivery in addition to upland soil erosion.

Deposition of suspended sediment at depositional sites substantially reduces total mobilized particulate materials by soil erosion (Lal, 2003). For example, it was estimated that about 94% (49 Tg C yr⁻¹) of the eroded carbon is impounded in surface waters or other depositional sites in the U.S. (Smith et al., 2001; Stets and Striegl, 2012). Additionally, a large proportion of suspended sediment in streams is contributed by river bed or bank erosion rather than terrestrial sources (Blair et al., 2004), and partially explains the insignificant influence from cropland. Therefore, elucidating the complex mechanisms that regulate POC concentration requires improved understanding of POC production, mobilization, and transport along the coupled terrestrial-aquatic continuum. Our findings and explanations should be further tested in the future to explore the complex interplays among soil erosion, sediment deposition/mobilization, and carbon cycling.

Previous investigations have suggested that rainfall controls the detachment of soil organic matter and transport of sediment (Lufafa et al., 2003), and storm flows disproportionately contribute to lateral carbon export (Smith et al., 2003). In contrast, our analysis suggests that runoff mainly play negative roles due to the dilution of POC concentration (Findlay et al., 1991). In addition, regions receiving heavy rainfalls also tend to have dense vegetation covers, which protect soils from erosion (Durán Zuazo and Rodríguez Pleguezuelo, 2008). Note that in this study we focus primarily on the relationship between long-term average runoff and POC

concentration, instead of seasonal variability of POC and associated processes. Since hydrological and biological processes both have significant seasonal variability (Bianchi et al., 2004), how these processes regulate POC concentration over finer temporal scales awaits further exploration to improve our understanding of hydrological controls on riverine POC.

Impacts of dam construction on sedimentation and burial of organic carbon have been widely investigated (Cole et al., 2007). Due to the reduced flow velocity, dams and reservoirs can trap up to 100% of the sediment transported from upstream rivers (Toniolo et al., 2004). It was estimated that burial of carbon in reservoirs is higher than that by all natural waters (Cole et al., 2007). However, results of our correlation analyses indicate that dam density has a positive impact on POC concentration. This finding does not necessarily imply that dam has no impacts on sedimentation. Other processes associated with dam construction, such as changes in flow regime that promote algae growth, may increase POC concentration. Understanding impacts of these processes requires explicit representations of dam related alteration of hydrologic, biological, and biogeochemical processes in watershed models.

4.5 *Uncertainties in modeling riverine POC concentration*

The primary purpose of the statistical modeling analysis is to identify factors that have significant linear impacts on POC. These factors are also expected to be related to important physical processes regulating POC concentration, thereby informing future modeling efforts. Notably, a large portion (60%) of the variability in POC concentration is unexplained by the selected variables and linear models, indicating that additional factors and nonlinear processes should be considered in order to better represent the complexity of riverine POC modeling..

First, most of the selected watershed attributes have indirect impacts on POC concentration in streams. Although terrestrial sources provide large amounts of mobilized POC, only a small

portion (6%) is transported to coastal waters (Smith et al., 2001), indicating significant controls during riverine transport. As a result, including instream factors, such as flow velocity and water residence time, is expected to further constrain the uncertainties in explaining POC concentration (Blair et al., 2004; Prosser and Rustomji, 2000).

Second, linear regression models have limited powers to simulated complex biogeochemical processes. Cycling of POC along the terrestrial-aquatic interfaces is controlled by a plethora of interconnected processes (Hope et al., 1994). Our results highlight the necessity of developing and employing process-based models, which consider the key factors and processes to further improve POC modeling.

Finally, quality of the observational data also affects the analysis results. We primarily focused on the long-term patterns of POC concentration and associated river basin attributes mainly due to the limited availability of observational data, while POC and other water quality variables, such as total phosphorus and total nitrogen, have pronounced seasonal and interannual variability. Furthermore, watershed attributes, such as percentage of varying land covers, change over time. Using the long-term averages, especially for variables collected in different years, may have introduced uncertainties and caused non-causative correlations in our statistical analysis. To reduce such uncertainties, more extensive field experimental exercises with the aim of collecting concurrent environmental data over large regions are required in the future.

5. Conclusion

In this study, we investigate the spatial variability and environmental controls of POC concentration across the conterminous U.S. and 18 major water resource regions. POC concentration demonstrates significant spatial variability, with the Upper Mississippi River basin

and the Piedmont region in the eastern U.S. having the highest POC concentration. Both algae growth and sediment transport are important sources of riverine POC.

In this study, generalized multi-variate linear models can explain ca. 40% of the spatial variance of POC concentration over 1145 USGS gauge stations. At the national scale, factors that have significant impacts on POC include soil properties, drainage area, total phosphorus concentration, and dam density. Our further analyses at the regional scale show substantial variation in environmental controls of POC concentration across the 18 major water resource regions in the U.S. In addition, POC concentration and associated environmental controls also vary non-monotonically with river orders. These findings indicate complex interactions among multiple factors regulating POC production over different spatial scales and across various components of the river networks. This complexity, along with the large unexplained uncertainty, calls for the development of process-based, non-linear methodologies that consider coupled terrestrial-aquatic processes regulating supply, removal, and transformation of POC in order to better constrain this carbon flux.

485

486 **Acknowledgements:**

487 We sincerely appreciate the valuable comments provided by the anonymous reviewers. This
488 work was funded by the NASA New Investigator Award (NIP, NNH13ZDA001N) and
489 Terrestrial Ecology Program (NNH12AU03I) as part of the North American Carbon Program,
490 and the DOE Great Lakes Bioenergy Research Center (DOE BER Office of Science DE-FC02-
491 07ER64494, DOE BER Office of Science KP1601050, DOE EERE OBP 20469-19145).

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Tables

Table 1. Bivariate analysis of environmental impacts on POC concentration

	F-value	Slope	P-value	Ad-R²	Y-Intercept
POC ^T versus total phosphorus ^T	495.6	0.454	0.000**	0.306	0.886
POC ^T versus total nitrogen ^T	331.6	0.522	0.000**	0.231	-0.275
POC ^T versus total forest	165.4	-0.012	0.000**	0.126	0.287
POC ^T versus soil water ^T	162	1.405	0.000**	0.123	2.723
POC ^T versus cropland ^T	101.4	0.100	0.000**	0.092	-0.210
POC ^T versus runoff ^T	107.5	-0.284	0.000**	0.086	1.410
POC ^T versus soil sand	93.54	-0.468	0.000**	0.075	1.450
POC ^T versus slope ^T	71.94	-0.151	0.000**	0.058	0.038
POC ^T versus soil clay	57.07	0.021	0.000**	0.048	-0.664
POC ^T versus precipitation ^T	53.55	-0.472	0.000**	0.045	1.968
POC ^T versus shrub land ^T	48.61	-0.075	0.000**	0.041	-0.140
POC ^T versus soil bulk density ^T	35.77	1.932	0.000**	0.030	-2.903
POC ^T versus barren surface ^T	34.35	-0.091	0.000**	0.030	-0.331
POC ^T versus urban area ^T	22.14	0.065	0.000**	0.019	-0.156
POC ^T versus drainage area ^T	22.05	0.063	0.000**	0.018	-0.620
POC ^T versus % of 1 st order river	6.531	-0.006	0.011*	0.006	0.165
POC ^T versus dam density ^T	4.664	0.051	0.032*	0.005	-0.141
POC ^T versus water area ^T	3.514	0.032	0.061	0.002	-0.147

POC ^T versus Temperature	2.717	0.009	0.010*	0.002	-0.275
POC ^T versus wetlands ^T	0.667	0.011	0.414	<0.001	-0.182
POC ^T versus soil organic matter ^T	0.210	-0.015	0.648	<0.001	-0.178

^Tindicated that variables are Log-transformed; *: $P < 0.05$; **: $P < 0.01$ Ad-R²: adjusted coefficient of determination.

Table 2. Interactive impacts of environmental variables on POC concentration over the U.S. and 18 water resource regions

	Tp	Sd	1st	Sw	Tn	Damd	Om	Wet	T	Area	R	Barr	Shrub	Clay	Urban	Ad-R ²
The U.S.	P**	P**	P*	P**		P*								N*	N**	0.40
Region 1	P**														N*	0.59
Region 2	P**						P*									0.64
Region 3	P*		P*					P*								0.62
Region 4																NA
Region 5	P*															0.32
Region 6					P*	P*										0.58
Region 7														N*		0.32
Region 8		P*					P*				N*		N*			0.66
Region 9																0.54
Region 10		P*								P*						0.34
Region 11									P*				N*		N*	0.40
Region 12																NA
Region 13																0.51
Region 14																NA
Region 15				P*												0.17
Region 16																NA
Region 17	P*		P*													0.75
Region 18					P*		N**					N*				0.59

Om: soil organic matter; Wet: wetland area; T: temperature; R: runoff; Area: drainage area for each station; Barr: percentage of barren land; Urban: percentage of urban area; Shrub: percentage of shrub area; Crop: percentage of cropland; Clay: percentage of soil clay; Sw: soil water content; Sd soil bulk density; Slop: average slope of the drainage area; 1st: percentage of first order watersheds; Tn: total nitrogen in waters; Tp: total phosphorus in waters; Damd: dam density. N: negative correlations; P: positive correlations; Ad-R²: adjusted coefficient of determination; *: $P < 0.05$; **: $P < 0.01$.

Table 3. Impacts of multiple environmental variables on POC concentration over different river orders

	Tp	Damd	Sd	Wet	Sw	Om	Clay	R	Ad-R ²
Order 1-3		P*	P*						0.37
Order 4	P*			P*	P*				0.31
Order 5	P*								0.32
Order 6 and higher	p**					P*	N*	N*	0.50

Om: soil organic matter; Wet: wetland area; R: runoff; Clay: percentage of soil clay; Sw: soil water content; Sd soil bulk density; Tp: total phosphorus in waters; Damd: dam density; N: negative correlations; P: positive correlations; Ad- R²: adjusted coefficient of determination; *: $P < 0.05$; **: $P < 0.01$.

Figures

Figure 1. POC concentration at the 1145 U.S. Geological Survey gauge stations

Figure 2. POC concentration in the 18 U.S. water resource regions (Region 1: Pacific Northwest; Region 2: Missouri; Region 3: New England; Region 4: Souris-Red-Rainy; Region 5: Great Lakes; Region 6: Upper Mississippi; Region 7: Mid-Atlantic; Region 8: California; Region 9: Great Basin; Region 10: Upper Colorado; Region 11: Ohio; Region 12: Lower Colorado; Region 13: Arkansas-White-Red; Region 14: Rio Grande; Region 15: South Atlantic-Gulf; Region 16: Tennessee; Region 17: Lower Mississippi; Region 18: Texas-Gulf)

(A)

(B)

Figure 3. Linear regression between POC and suspended sediment (A) and between POC and chlorophyll-a (B).

Figure 4. Factors with significant impacts on POC over the entire U.S. and the 18 water

resource regions (Om: soil organic matter; Wet: wetland area; T: temperature; R: runoff; Area:

drainage area for each station; Barr: percentage of barren land; Urban: percentage of urban area;

Shrub: percentage of shrub area; Crop: percentage of cropland; Clay: percentage of soil clay; Sw:

soil water content; Sd soil bulk density; Slop: average slop of the drainage area; 1st: percentage

of first order watersheds; Tn: total nitrogen in waters; Tp: total phosphorus in waters; Damd:

dam density)

Figure 5. POC concentration by river orders