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Effects of climate and land-surface processes on terrestrial dissolved organic carbon export to major U.S. coastal rivers

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ABSTRACT

This study aims to understand the influences of climate change and land surface processes on the variation of in-stream DOC concentrations in coastal rivers crossing different climate zones. Monthly observations spanning multiple years in seven major rivers in four different climate zones within the U.S. were analyzed for correlations between dissolved organic carbon (DOC) concentration and surface air temperature, precipitation, land cover and discharge. The major watersheds were the Altamaha River (GA), the Apilachicola River (FL), the Columbia River (OR), the Delaware River (NJ), the Sacramento and San Joaquin Rivers (CA) and the Susquehanna River (MD). One minor watershed, the Neponset River (MA) was also analyzed. Results indicate that temperature is the most important variable for DOC export when the variation of annual mean temperatures is large (e.g., >5 °C) with sufficient precipitation levels. Land-surface characteristics and discharges are better correlated to DOC concentrations when the variations of annual mean temperatures are small (e.g. <2 °C). However, results from the small watershed (Neponset) showed that land surface processes can vary annual DOC concentrations about ±1.65 mg/L from mean value. This study is the first to examine DOC relationships in watersheds in multiple climate zones, and it was determined that weak correlations between temperature and DOC found in previous studies may be attributable to the fact that those studies examined small watersheds contained within a single climate zone. DOC flux per square meter was calculated based on incremental temperature increases. The results indicate that an increase of 1 °C would result in a 0.476 mg/L increase of in-stream DOC in large watersheds. Climate warming would have a greater impact on riverine DOC yields in cooler climate zones (up to 26% per °C) than on those in warmer climate zones (up to 6% per °C).

1. Introduction

By the year 2100, global mean surface air temperatures are projected to increase by between 1.4 and 5.8 °C (Frumhoff et al., 2008; IPCC, 2007). The higher gross primary productivity, warmer soil and increased precipitation attendant to climate change (Clair et al., 1999; Correll et al., 2001; Striegl et al., 2005; Kardjilov et al., 2006; Kirshen et al., 2008) may accelerate terrestrial dissolved organic carbon export from rivers to coastal waters (Harrison et al., 2008). Evans et al. (2012) reviewed evidence for increasing DOC concentrations in surface waters. DOC has increased across much of the Northern hemisphere (e.g. Europe and North America). Butman and Raymond (2011) also reported that U.S. rivers and streams are increasingly saturated with carbon. The reported increase of terrestrial carbon balance has the potential for profound impacts on aquatic ecosystem functioning, water treatment costs and human health. Furthermore, the widespread and pervasive increase of DOC suggests the possibility of a universal driver of this trend. DOC of terrestrial origin plays an important role in surface water acidification, metal binding and transport, carbon turnover processes and marine/freshwater ecology (Khan and Schnitzer, 1972; Buffle, 1984; Hope et al., 1994; Stedmon et al., 2006; Holmes et al., 2008). A significant component of DOC flux is a result of terrestrial processing of organic matter in soils, vegetation and wetlands, and is thus directly impacted by climate. Streams transport labile carbon through watersheds to oceans or lakes, and an increased DOC yield in these streams could potentially have major impacts on coastal ecosystems (Duarte and Prairie, 2005; IPCC, 1990).

The effects of climate change on the dynamics of terrestrial DOC are through complex biological, chemical and physical processes including microbial metabolism, root exudation and leaching/erosion of soil organic matter (Kaiser and Keller, 2001;

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Jones et al., 2009). For example, live vegetation contributes significant amounts of DOC to terrestrial stream water through leaf litter and the subsequent leaching of that litter as well as of the vegetation itself (France et al., 1996; Mcdowell and Fisher, 1976). This is an example of the DOC contribution of a well-understood, primary land surface process. What is not well understood, however, is how climate conditions alter the origin, function and fate of DOC in coastal watersheds. In light of these climate change questions, it is also important to understand what temporal and spatial scales are appropriate to study climate impacts on biochemical cycling (Haei et al., 2010), i.e., carbon export.

Current efforts to study the impacts of climate change on terrestrial DOC dynamics have been largely based on watershed systems within single climate zones (Correll et al., 2001). Huang and Chen (2009) and Tian et al. (2012) analyzed two years' worth of monthly field data collected from a small urban watershed in the northeastern U.S. They reported that climate-related factors (temperature and precipitation) control DOC end-members in salt marsh, forest, agricultural industrial and residential lands. These work concluded that annual variation in temperature is the major driver of carbon export, along with precipitation. In their studies, Clair et al. (1994) and Correll et al. (2001) concluded that precipitation alone is the major driver of carbon export.

In contrast, Hruska et al. (2009) suggested that climate has played no role in observed DOC changes over a 14-year period (1993–2007), in the two catchments they studied. Chow et al. (2006) reported that a significant amount of DOC was produced in the surface soil under constantly flooded hydrological conditions (as opposed to being directly impacted by climate factors). One inference that can be made from these contrasting studies is that understanding the impacts of climate change on DOC export to a single watershed requires field measurements over decades, even if that watershed is in a single-landscape system, e.g., homogenous land cover.

Some efforts have examined multiple adjacent watersheds from different landscape systems in order to study the impact of climate on DOC. Raymond and Oh (2007) examined climate controls on riverine carbon export from three major river watersheds. These watersheds were of differing landscape systems within one climate zone type, Continental Humid. They reported that temperature was not as significant as land surface processes (in this case, interannual stream discharge) to DOC export. Raymond and Oh (2007) concluded that physical processes are more significant than biological processes, since water redistributes DOC from terrestrial to riverine systems. However, other workers (Ciais et al., 1995; Schaeffer et al., 2011; Miller and Zepp, 1995) reported that surface temperature is a key factor for controlling biological processes in terms of primary productivity.

The conflicting nature of the results of prior work indicate that considerable uncertainties exist regarding the processes controlling DOC delivery to streams, particularly under differing climatic and land surface process conditions. Arguably, the focus of prior work has been too localized in terms of watershed characteristics and climate zones to produce a more holistic picture of carbon export. Further, the temporal requirements for data collection in carbon-export studies are uncertain. For some watersheds, decadal-scale datasets may be appropriate; multi-watershed comparisons may require finer (or coarser) resolutions.

The objective of this study is to understand the impacts on carbon export not only of climate factors, but also land cover and stream discharge across different climate zones. We took advantages of field observations from several major river watersheds of different climate regions, and explored the relationship between climate factors (surface temperatures and precipitations), and terrestrial DOC export to rivers. We further studied the observed riverine carbon-export processes in small watersheds over 24 months and explored if climate factors maintain the important controls compared to land surface variables (hydrological properties and land use) within a single climate region. The study confirms that the effect of climate factors (surface air temperature, precipitation) on in-stream DOC concentrations in a small watershed requires observations of a larger number of years. Therefore, longitudinal observations in major rivers crossing multiple climate zones are excellent for exploring the effects of climate on riverine DOC dynamics. The observations of small numbers of years in small rivers located in a single climate zone are good to study land surface effects. Ultimately, addressing these issues and questions will be particularly beneficial for understanding the land-water biogeochemical dynamics that are influenced by climate change.

2. Methods

2.1. Study and sampling sites

We selected seven major (>33,000 km^2) watersheds along the U.S. west and east coasts. Four of the seven major river watersheds selected are in the east coast: the Delaware in New Jersey (NJ), the Susquehanna in Maryland (MD), the Altamaha in Georgia (GA), and the Apalachicola in Florida (FL). The other three major river watersheds are in the west coast: the Columbia in Oregon (OR) and the Sacramento and San Joaquin, both in California (CA). The entire drainage areas of these rivers cover four dominant climate zones: Hot Humid Continental (NJ, and MD), Subtropical Humid (GA and FLA), Warm Summer Mediterranean (OR), and Hot Summer Mediterranean (CA). The rivers located cross four climatic zones have necessary environments for studying the impacts of climate change on soil DOC leaching ecology. Fig. 1a shows their locations, and Table 1 lists the abbreviations used for the rivers hereafter used in this article.

We obtained climate data (mean precipitation and temperature) from the National Climatic Data Center (NCDC, 2011). Data were from 1996 to 2010 and at different temporal scales. These data were averaged at multiple NCDC stations within each watershed in the U.S. It should be noted that the COL watershed lies within both the U.S. and Canada. However, the Canadian portion is ~15% of the total basin area, and precipitation decreases significantly from the northwestern part of the basin. We argue therefore that the error associated with this unsampled Canadian portion is minimal.

The surface air temperatures at individual watersheds generally rise from south to north with increasing latitude. Annual mean temperatures of all watershed sites (Fig. 7) ranged from 6 to 23 °C (43–73 °F). Annual mean precipitation (Fig. 3) varies significantly among these watersheds. Drainage areas ranged between 33,152 km^2 (DEL) and 670,000 km^2 (COL) (Table 2). The proportions of land cover types are similar among the watersheds (Table 2). We utilized the 2001 National Land Cover Data (NCLD) (EPA, 2001) from the U.S. Environmental Protection Agency. Our study areas contained thirteen NLCD land cover/land use types, which we merged into four major land cover classes (Table 3). The percentages of each reclassified land cover type are listed in Table 2.

DOC concentrations and associated stream discharges were monitored at gauge stations maintained by the USGS National Stream Quality Network (NASQAN) program (Hooper et al., 2001; Jones et al., 2003). Gauge station data are listed in Table 4. Monthly DOC concentration measurements were available for a range of 2–14 years depending on the watershed. We collected a total of 453 samples; Table 4 lists the distribution of samples by watershed. The seven selected NASQAN gauge stations also reported discharge data, with the exception of that for the Altamaha River (NASQAN

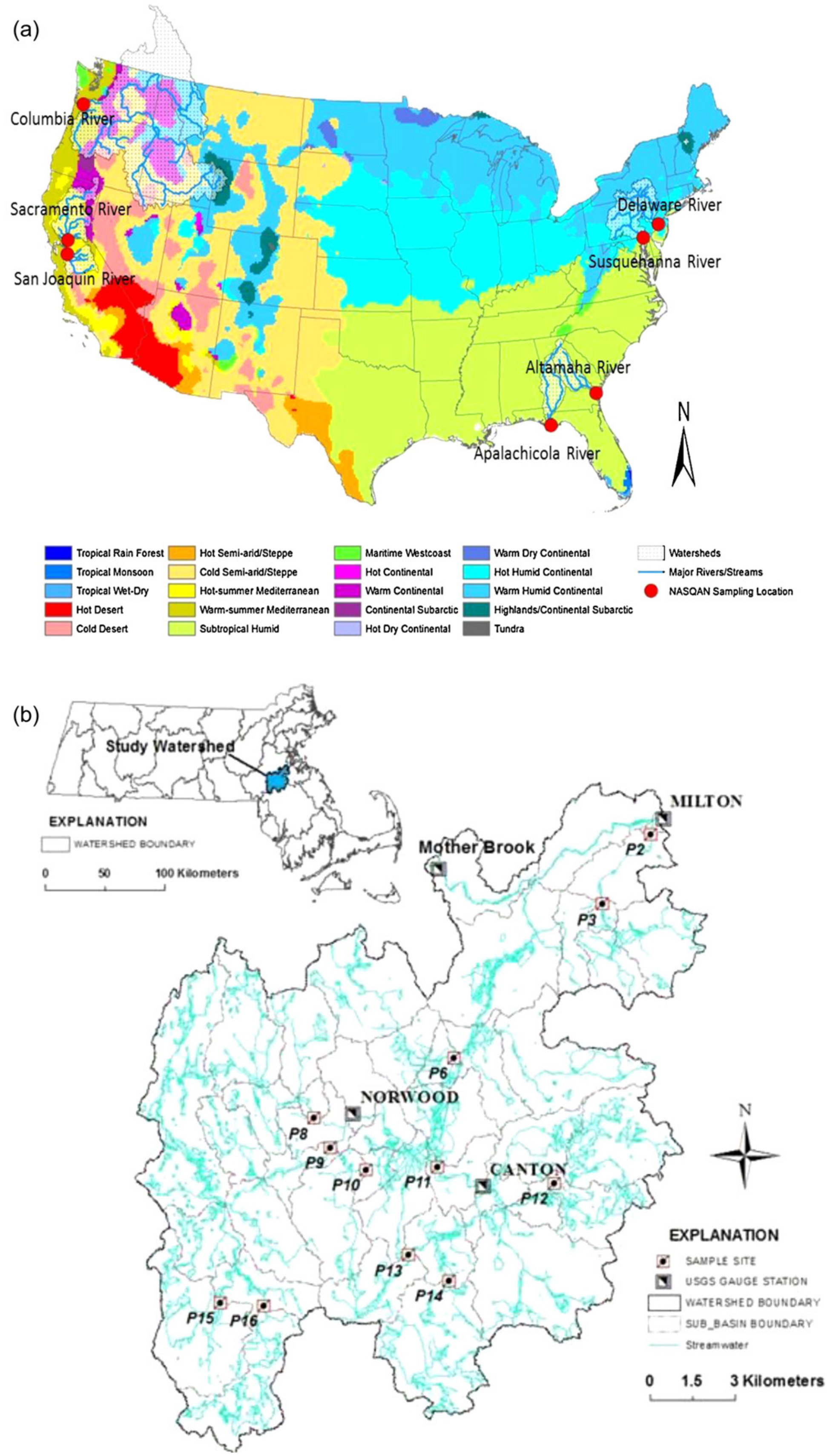

Fig. 1. (a) Climate zones in U.S. and sampling stations at the seven major coastal rivers in USGS NASQAN program. The associated watersheds of each outlet are shaded polygons. The river networks are shown as dark-blue polylines. (b) The Neponset River watershed south of Boston. Drainage area is ~370 km^2.

Table 1
River names, abbreviations used in this study and climate zones. States in which a majority of each watershed is located are also listed. This study categorizes watersheds as either major or minor.

River name	Abbreviation	State	Climate zone	Category
Altamaha	ALT	Georgia	Subtropical Humid	Major
Apilachicola	API	Florida	Subtropical Humid	Major
Columbia	COL	Oregon	Warm Summer Mediterranean	Major
Delaware	DEL	New Jersey	Hot Humid Continental	Major
Neponset	NEP	Massachusetts	Hot Humid Continental	Minor
Sacramento	SAC	California	Hot Summer Mediterranean	Major
San Joaquin	SJQ	California	Hot Summer Mediterranean	Major
Susquehanna	SUS	Maryland	Hot Humid Continental	Major

Table 2
Land cover data for watersheds and climate zone distributions (CZD) in this study. For CZD, watersheds either cover multiple climate zones (M) or are contained within single climate zones (S). Data are from the time period 1997 to 2010. For the Neponset River, see Fig. 10b.

	ALT	API	COL	DEL	NEP	SAC	SJQ	SUS
% Wetland	13.06	14.64	2.06	5.72	11.57	2.76	3.26	2.38
% Forest	50.48	50.2	73.57	67.06	51.77	45.06	62.42	62.45
% Agriculture	26.37	25.77	20.94	16.99	0.85	43.62	29.14	27.43
% Developed	10.08	9.4	3.29	10.23	35.82	8.53	5.17	7.74
Drainage area (km^2)	35,224	49,728	670,000	33,152	370	59,570	35,058	70,189
CZD	S	S	M	S	S	S	S	S

Table 3
NLCD land use/land cover types of the watersheds and the merged reclassifications used in this study.

NLCD land use/land cover type	Reclassification used in this study
Developed-Open Space	Developed
Developed-Low Intensity	Developed
Developed-Medium Intensity	Developed
Barren Land	Forest
Deciduous Forest	Forest
Evergreen Forest	Forest
Mixed Forest	Forest
Pasture/Hay	Agriculture
Cultivated Crops	Agriculture
Palustrine Forested Wetland	Wetland
Palustrine Scrub/Shrub Wetland	Wetland
Open Water	Wetland

I.D. 02226160). Instead, we used the discharge data collected at a nearby USGS water gauge station (I.D. 02226000). The difference in drainage areas between these two stations is <0.03%.

This study includes an additional minor river watershed, the Neponset River watershed (370 km^2, ~2 m^3/s discharge). This is an urban estuary located south of Boston, MA. We collected 480 samples over four years within 12 sub-basins of the Neponset River watershed southeast of Boston, MA (Fig. 1b). DOC concentrations at selected outlets were measured monthly from March 2006 to October 2010. However, due to instrument malfunctions in our laboratory, samples from 2008 were stored frozen for longer than 12 months. For this reason we eliminated all 2008 samples from our dataset and use only those from 2006, 2007, 2009 and 2010. Further details concerning the Neponset River sites and laboratory procedures are described in Huang and Chen (2009) and Tian et al. (2012). We include NEP samples in this study to examine whether and how DOC responses to climate change in small watersheds differ from those in larger watersheds. NEP data were collected separately from those data for other rivers, and may be considered a nested case study within our larger study.

2.2. Statistical analyses

We conducted linear regression analysis using SPSS statistical software to identify significant variables associated with variation in DOC concentrations. Variables were deemed significant when the P value was less than 0.05. We used the coefficient of multiple determinations R^2 to measure how well the environmental variables of temperature, precipitation and land use explained observed DOC variations.

3. Results

3.1. Temperature comparisons

Surface air temperatures were very different across the seven major watersheds. Fig. 2 shows the averaged variations of monthly temperatures over the study period of the seven major watersheds. API has the highest annual mean temperature of ~20.7 °C. Annual mean temperatures in the other five watersheds ranged from 9.2 to 16.4 °C. The mean monthly temperatures of the SAC and SJQ watersheds in the summer season (June, July, August) show little differences from those of the DEL and SUS. However, winter (December, January, February) temperatures differences are larger between U.S. east and west coasts. ALT and API display similar seasonal temperature variations with a fairly consistent 3 °C

Table 4
USGS gauge station and drainage data pertaining to collected samples (453 samples total).

River and gauge info	Site ID	Latitude	Longitude	Drainage (mi^2)	# Samples	Start year	End year
Altamaha R. near Everett City, GA	02226160	31°39′16″	−81°49′41″	14,000	27	2007	2010
Apilachicola R. near Sumatra, FL	02359170	29°56′57″	−85°00′56″	19,200	22	2008	2010
Columbia near Beaver Army Terminal, OR	14246900	46°10′55″	−123°10′50″	256,900	131	1995	2010
Delaware R. at Trenton, NJ	01463500	40°13′18″	−74°46′41″	6780	69	1998	2010
Sacramento R. at Freeport, CA	11447650	38°27′22″	−121°30′01″	23,000	97	1996	2010
San Joaquin R. near Vernalis, CA	11303500	37°40′34″	−121°15′55″	13,536	77	1997	2010
Susquehanna R. at Conowingo, MD	01578310	39°39′28.1″	−76°10′28.2″	27,100	30	2004	2010

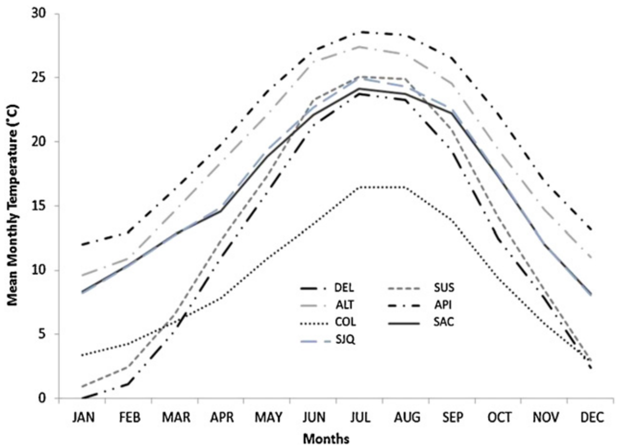

Fig. 2. Mean monthly surface temperature averaged over the period 1996–2010 and over each of the seven major coastal river watersheds.

difference. Western watersheds (COL, SAC, SJQ) share similar seasonal temperature patterns, with a maximum difference of ~6.7 °C throughout the year.

3.2. Precipitation and discharge relationships

Fig. 3a shows annual mean precipitation data for the seven major watersheds, and Fig. 3b shows average monthly precipitation data for these watersheds. Annual precipitation patterns do not correlate well with annual mean surface temperatures, which is unsurprising given that the watersheds are located in four different climate zones. API and COL received annual precipitation amounts of 132 and 135 cm, respectively. DEL, ALT and SUS annual averages were comparable at ~117 cm. SAC and SJQ are located in the Hot Summer Mediterranean climate zone, and thus receive

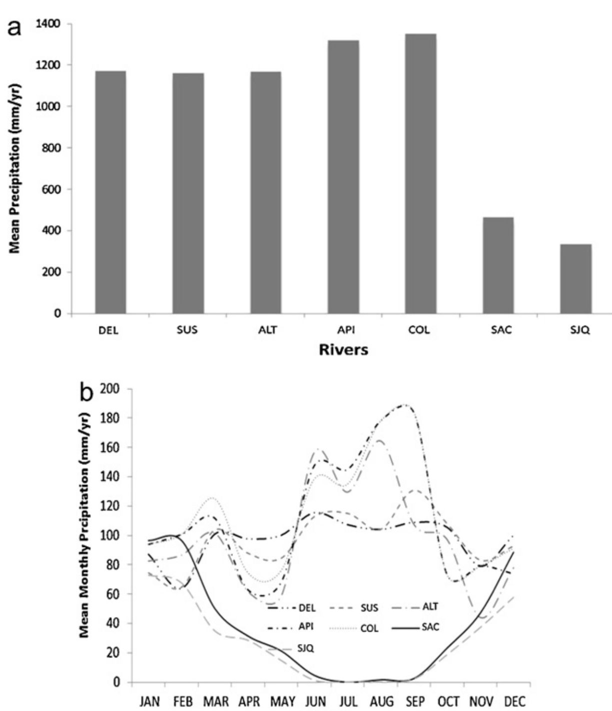

Fig. 3. (a) Annual mean precipitation averaged over the period 1996–2010 for each watershed. (b) Monthly precipitation averaged over past the period 1996–2010 in each watershed.

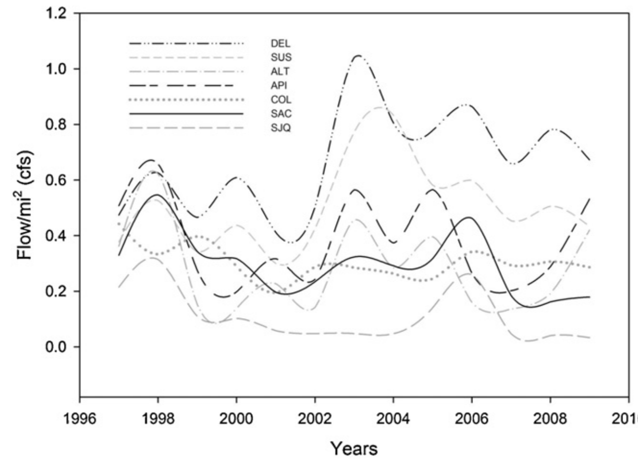

Fig. 4. Annual mean river flows, normalized by drainage area of corresponding river watershed (m^3/m^2/year).

much lower levels of precipitation (Fig. 3a). Averaging the monthly precipitation data (Fig. 3b) divides the seven major watersheds into seasonal groups. The dry summer group has low precipitation values June–September and includes the watersheds SAC and SJQ. The remaining watersheds are in the wet summer group, which has high precipitation values June–September.

Discharge rates for the seven major watersheds are shown in Fig. 4. Watersheds with high levels of annual precipitation did not necessarily have a high annual average streamflow per unit drainage area (m^3/m^2/year). We attribute this to infiltration and evaporation. For instance, API receives the highest annual precipitation of the four east coast watersheds. However, its streamflow (m^3) per m^2 was the lowest. This may be due in part to the presence of wetlands in the catchment, and their ability to retain water. Furthermore, despite receiving the same annual precipitation, ALT, DEL and SUS (east coast) all have very different streamflows per m^2 over the study period (Fig. 4). ALT had higher surface temperature, and its annual streamflow per m^2 is lower than that of both DEL and SUS. Similar results were obtained for west coast watersheds (Figs. 3a and 4). Correlations between precipitation and river flow in multiple-climate-zone watersheds remain controversial, unlike the positive relationship in watersheds contained within a single climate zone (Raymond and Oh, 2007). It should be noted that

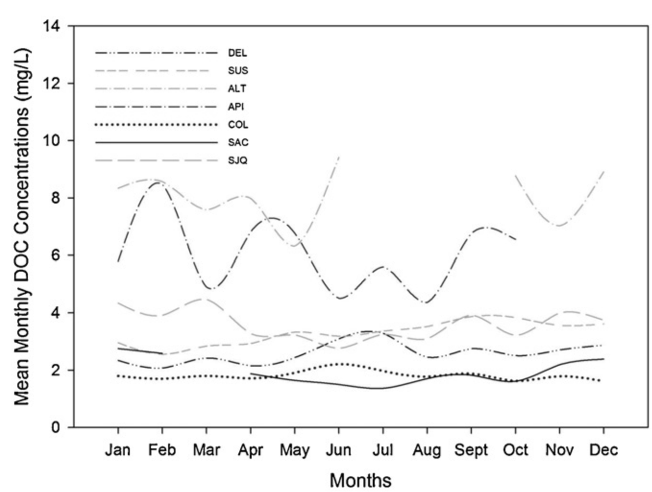

Fig. 5. Monthly DOC concentrations averaged over periods ranging from 2 to 14 years in each of the seven major watersheds (no data were available for ALT from July to September, nor for API from November to December nor for SAC in March).

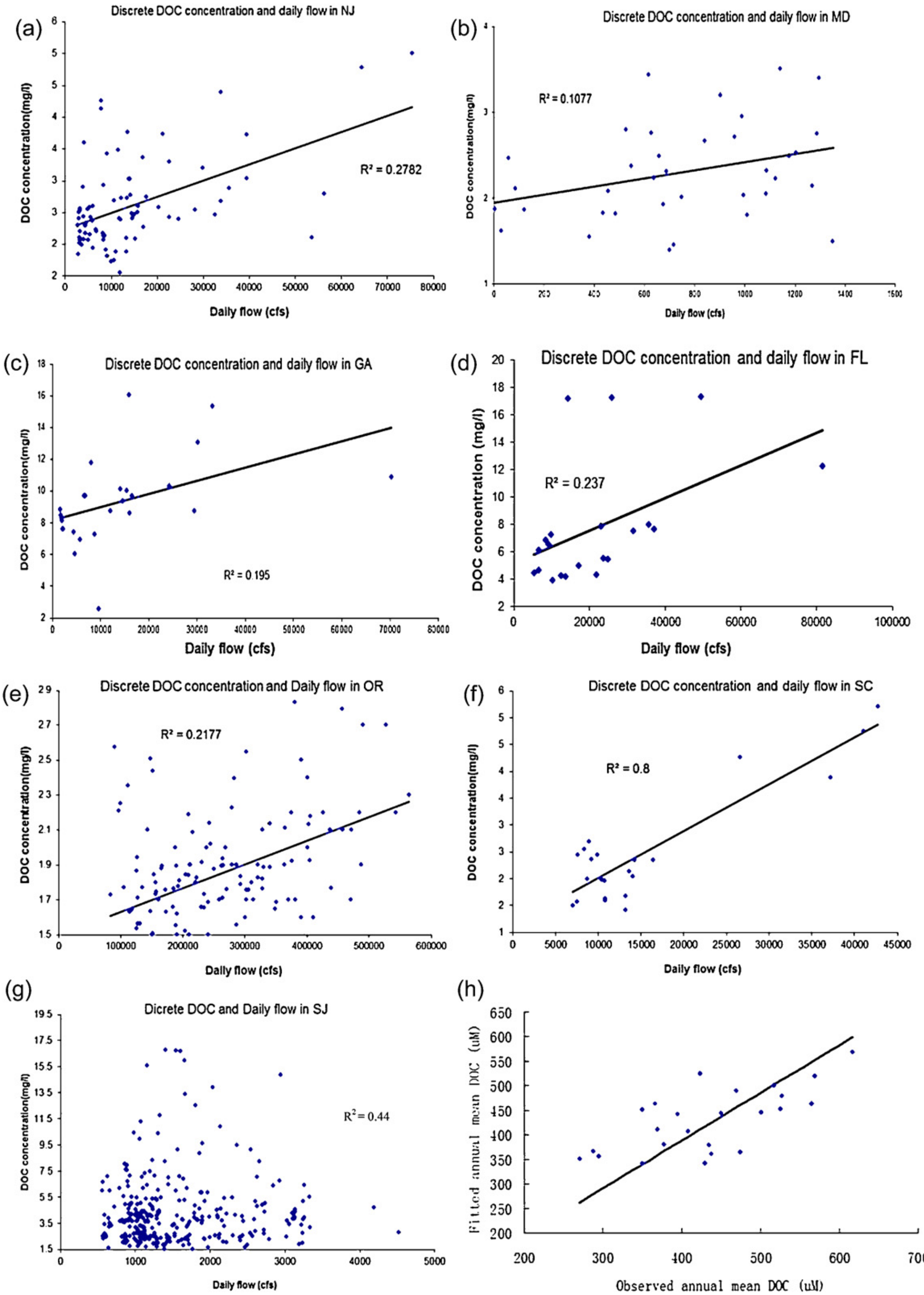

Fig. 6. Correlations between river discharges and DOC concentrations in the seven major rivers. (a) DEL, (b) SUS, (c) ALT, (d) API, (e) COL, (f) SAC and (g) SJQ. DOC samples in the SAC and API were collected only during either high or low flow ends. The lack of sampling during medium flow periods left a gap in the scatter plots (Fig. 5d and f). The discharges at the sub-basin level of a small watershed explained about 44% of in-stream DOC concentrations in a linear regression model (5 h).

in this study, inter-annual discharge appears strongly related to inter-annual precipitation within each watershed.

3.3. DOC concentrations and correlations to discharge

Fig. 5 shows monthly DOC concentrations in the seven major rivers, averaged over periods ranging from 2 to 14 years. The largest variations in monthly DOC concentrations were in API and ALT. COL, SAC and SUS show the lowest DOC variations. DOC concentrations show similar seasonal trends for watersheds in the same climate zone. Fig. 6a–f displays correlations between DOC and discharge for the seven major rivers. A positive correlation between mean DOC concentration and annual discharge exists in all rivers except SJQ. The flow of this river is altered significantly by agricultural irrigation. For SAC, discharge explains ~80% of in-stream DOC ($R^2 = 0.8$). However, for other rivers this correlation is much lower, with R^2 ranging between 0.1 and 0.3. Our results (see below) suggest that relationships between DOC and discharge are dependent upon other factors such as precipitation, temperature and watershed drainage area.

3.4. Seasonal variation and DOC

The strong seasonal patterns of mean surface temperature (Fig. 2) did not match well with riverine DOC concentrations for individual watersheds (Fig. 5). However, seasonal DOC concentration trends are similar for watersheds in the same climate zone (Fig. 5). For example, DEL and SUS are in the Hot Humid Continental climate zone and have a similar pattern throughout the year. These rivers have their lowest concentrations in January, which then increase to their highest concentrations in December. For these two rivers, DOC concentration patterns did not vary in the same way temperature patterns did. For both Warm Summer and Hot Summer Mediterranean climate zones, hot temperatures and low precipitation rates in summer were accompanied by decreased DOC concentrations for COL, SAC and SJQ. ALT and API in the Subtropical Humid climate zone have similar seasonal DOC patterns to those of the Mediterranean climates, with minor differences in the magnitudes of DOC concentrations. Overall, temperature patterns did not match DOC seasonal variations in the Subtropical and Mediterranean climate zones. As a result, we infer that measurement and analysis of the impacts of climate on in-stream DOC should be at an annual scale, and not a seasonal scale.

3.5. Temperature and DOC

Fig. 7 shows regression analysis of mean surface temperatures against mean riverine DOC concentrations. In the collective analysis of all seven major watersheds (in different climate zones), mean surface temperatures are highly correlated with DOC ($R^2 > 0.64$, $p < 0.01$). The mean annual surface temperatures ranged from 8.9 to 21.1 °C, with a range in latitude of 29–46° north. Mean annual DOC concentrations range from 1 to 7.5 mg/L. For most rivers, DOC variations are below 2 mg/L, except for ALT and API, which are ~3 mg/L. Annual mean DOC concentrations generally increase in a linear fashion with annual mean surface temperatures. Temperature explains ~89% of the observed DOC concentrations in five watersheds (ALT, API, COL, DEL and SUS). This group does not include watersheds in the Hot Summer Mediterranean climate zones (Fig. 7). Our results indicate that the magnitude of terrestrial DOC yields is more strongly controlled by temperature than other factors such as discharge latitude and seasonal precipitation.

For each of the seven major watersheds, we determined mean annual DOC flux in terms of mg/m^2 and increments of flux per degree C (Fig. 8). The two components of flux calculation are annual

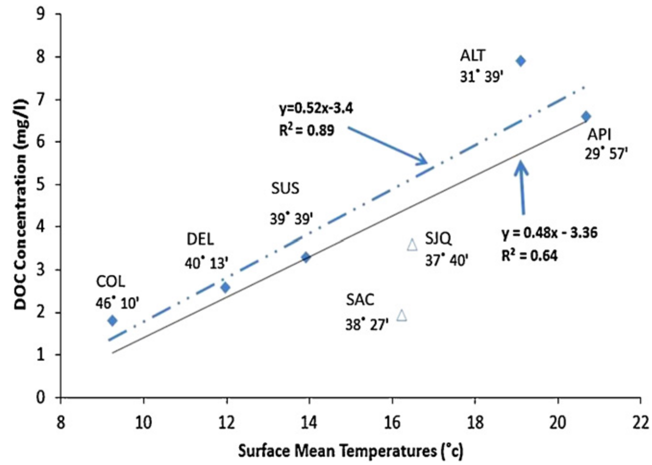

Fig. 7. Mean annual DOC concentrations versus mean surface air temperatures in the seven major rivers. The dashed line regression describes climates that are not Warm Summer Mediterranean (SAC and SJQ). The solid regression line describes samples from all seven rivers including SAC and SJQ.

mean DOC concentration and annual discharge (flow, shown in Fig. 4). Our calculations show that ALT and API have the highest annual DOC fluxes of the seven major watersheds (Fig. 8). SJQ had the lowest DOC yields per unit area. The linear relationship between annual temperature and in-stream DOC concentrations (Fig. 7) demonstrates that a 1 °C rise of average annual surface temperatures would increase annual mean in-stream DOC concentrations in the seven studied rivers by 0.476 mg/L. This increase in DOC concentration would lead to a subsequent increase in DOC export in the range of 0.135–0.327 g of carbon per square meter per year in the seven study watersheds. The percentages of DOC flux increments in response to a 1 °C temperature increase ranged from 6 to 26% (Fig. 8). Temperature increases impact the DOC yields in northern U.S. rivers more so than in southern U.S. rivers; 26% for COL versus 6% for ALT and 7% for API. The increment percentages decrease from north to south for all rivers except SAC.

3.6. Neponset River trends

Annual mean DOC concentrations within NEP (the additional watershed) show a relatively weaker correlation to annual mean

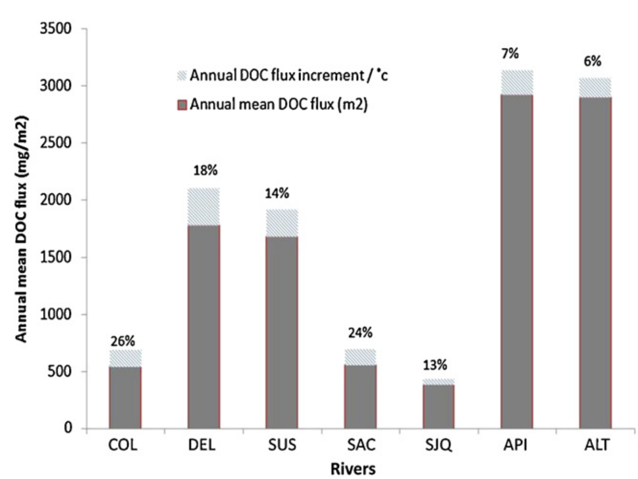

Fig. 8. Mean annual DOC flux m^{-2} (solid bars) and increment m^{-2} year^{-1} (patterned bars on top) in response to 1 °C increase of mean annual surface temperature. Labels denote increment by percentage.

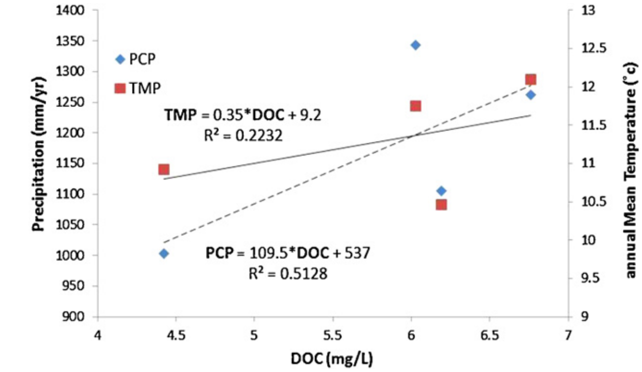

Fig. 9. Correlations of annual mean in-stream DOC concentrations to annual precipitation, as well as to annual mean temperatures over four years in the Neponset River watershed, PCP = precipitation and TMP = temperature.

surface temperature than to annual mean precipitation (Fig. 9). Inter-annual temperature variation over four years was less than 2 °C (right *Y* axis in Fig. 9). The DOC in this small urban watershed yielded a stronger correlation to annual mean precipitation than it did to temperature (left *Y* axis in Fig. 9). Fig. 10a shows the range of variation of DOC concentrations (∼±1.65 mg/L from the mean). This minor watershed in a local climate zone contains diverse land uses in each sub-basin. Fig. 10b shows land use for the sampled sub-basins, which average ∼30 km^2 in area. In a previous study, Tian et al. (2012) reported that vegetation types, drainage

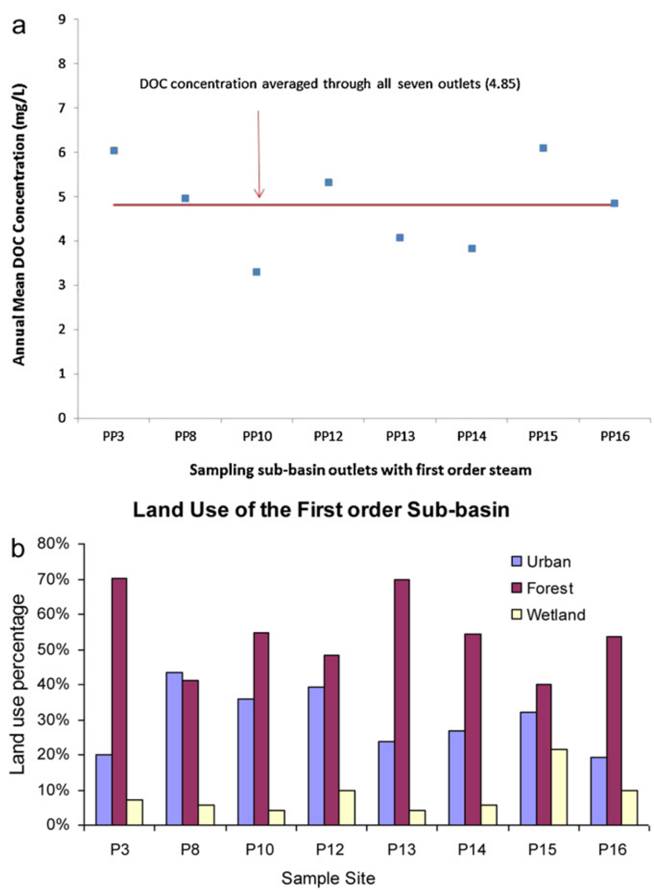

Fig. 10. (a) Variation of annual mean DOC concentrations in each of the first order sub-basins in the Neponset River watershed. The mean is 4.85 mg/L and the maximum difference is ±1.65 mg/L. (b) Distribution of land use types in each of the first order sub-basins in the Neponset River watershed.

area, discharge, and seasons were strong predictors to in-stream DOC concentrations in this minor watershed (R^2 = 0.76 and 0.64 at seasonal and annual scales respectively).

4. Discussion

The significant variations of mean annual DOC concentrations (Fig. 7) between catchments from different climate zones are driven primarily by climate conditions (temperature and precipitation). Land surface processes (land-use type and density, hydrology and soil properties) are secondary factors. However, in the case of watersheds located within a single climate zone, land surface processes are the primary factors controlling riverine DOC concentrations, especially where the inter-annual mean temperature variation is small (less than 2 °C).

4.1. The importance of temperature on DOC

Two things that we learned from this study are that surface temperature is a more important control on riverine DOC flux than land surface processes, and that it is appropriate to apply an annual temporal scale to quantify DOC–temperature relationships. DOC dynamics in rivers were correlated better with watershed surface temperatures in three climate zones (R^2 = 0.89) without including Hot Summer Mediterranean, which has low precipitation during summers. This suggests that the effects of temperature and precipitation are major drivers of DOC flux. The low precipitation in the Hot Summer Mediterranean climate zone explains the weaker temperature–DOC linear relationship (R^2 < 0.64) when SAC and SJQ are included in the analysis (Fig. 7). Temperature and water are the essential conditions, together with Photosynthetically Active Radiation – PAR, for gross primary productivity (Guo et al., 2007), and precipitation levels (or hydrological properties) determine a soil's water availability (Curtin et al., 2011; Winterdahl et al., 2011). It follows that biological processes have a greater effect on DOC yields than physical processes do when elevated surface temperature is combined with sufficient water availability in soil. Furthermore, higher annual surface temperature is usually associated with longer growing degree days (Hinchliffe et al., 2011). Given sufficient precipitation, growing degree days contribute to enhanced gross primary productivity, which ultimately is the source of DOC yields in rivers (Dierig and Crafts-Brandner, 2011).

4.2. Land cover and DOC

Our monthly measurements in the Neponset River watershed demonstrated land use are very important to terrestrial DOC dynamics. Especially, they are the dominant factors when the variations of annual mean temperatures are small (e.g. <2 °C). Andersson & Nyberg (2008) reported that a small percentage of wetlands in the catchment can contribute large amounts of DOC to rivers. Laudon et al. (2011) quantitatively described that as much of 50% of DOC in a catchment can originate from wetlands even when they occupy just 10% of the catchment area. In our study, ALT and API had the highest DOC export and also the highest percentage of wetlands (Fig. 7 and Table 2). However, the differences of the annual mean riverine DOC concentrations between the seven major rivers are more likely driven by climate factors instead of land use, since the percentages of each land use (i.e., forest, agriculture, wetland and urban area) among the seven major watersheds are very similar. Therefore, impacts of land uses on DOC concentrations should not be significantly different between these watersheds. At the least, impacts of land use on annual riverine DOC concentrations are unlikely to be linear along the latitudinal temperature gradient. For example, DEL has the highest latitude of the eastern rivers, but the percentage of its watershed that is wetland is 5.75%, which is the median of wetland percentage of the eastern rivers. The percentage of forested cover of the seven watersheds was between 45% and 73.6%, with no direct linear relationship between latitude (temperature gradient) and forested cover. SAC has the highest percentage of agricultural land, but its annual DOC concentration is close to the average of the seven major rivers. The random nature of land cover distribution (wetland, forest, developed, agricultural) would act to weaken the linear temperature–DOC relationship (Fig. 7). Therefore the correlation coefficient between annual surface temperature and mean in-stream DOC concentration should be even stronger without the interfering effects of land cover.

4.3. Land cover, temperature and DOC in NEP

In the NEP, precipitation varied from 1000 to 1350 mm/year over four years (2006–2007 and 2009–2010). In this watershed, precipitation variation is well-correlated with DOC and explains ~51% of the DOC variation at an annual scale (Fig. 9). Since precipitation drives land surface characteristics (i.e., discharge) in small watersheds within particular climate zones, surface characteristics such as land cover are more important than temperature in NEP, versus the other watersheds.

For the seven major watersheds at annual time scales, temperature and precipitation are strongly correlated to riverine DOC, and it is clear that temperature was the key factor driving the large variations in DOC when the variation of temperature is significant. However, in the NEP (Fig. 9), results for the relationships between DOC, temperature and surface processes indicate that at seasonal and annual scales, flow, drainage area and land cover are more important variables than temperature ($R^2 = 0.22$). Temperature is important for large watersheds that cross multiple climate zones, but the NEP temperature variation is small, with a maximum annual temperature variation of 1.61 °C over five years (Fig. 9). This type of low temperature variation would be expected for watersheds in a single climate zone. Further, this small range in temperature is difficult to examine statistically for relationships to DOC concentration. We therefore conclude that temperature is not as significant a control on DOC in small watersheds as it is in large watersheds. This may explain the lack of correlation between temperature and DOC in past studies, e.g., Chow et al. (2006) and Hruska et al. (2009).

4.4. DOC, stream discharge and land cover

In the seven major watersheds, discharges per unit area are weakly correlated to temperature and annual precipitation (Figs. 3b and 4). Our analysis demonstrated that in the case of ALT and API in the Subtropical Humid climate zone, precipitation does not necessarily lead to high flow. In these settings, evapotranspiration and infiltration affected by temperature, vegetation and soil properties alter discharge rates as precipitation takes place. However, in extra-tropical climates acceleration of terrestrial DOC export will be attendant to acceleration of the hydrologic cycle, and thus highly sensitive to discharge or precipitation, as in NEP. Therefore, the correlations between in-stream DOC and riverine discharges or land cover are appropriate to study at sub-basin levels instead of at basin levels of small river watersheds.

4.5. Temporal scales for capturing DOC biological processes

The quantitative relationships between riverine DOC and surface temperatures were strongest at the annual scale. This was true for both the seven major watersheds and the NEP samples. Our annual-scale results strongly support the notion that the response of riverine DOC to climate variables is a biological process. Temperature and water determine primary productivity, which is the major source of riverine DOC flux. Rising temperature may also increase decomposition of soil organic matter (SOM), which may then increase DOC released to freshwaters. However, the plant decay/decomposition process, and thus the DOC transport from land to rivers, could take longer than one year, since these involve plant growth and conversion of accumulated organic matter to DOC (Hansson et al., 2010). Therefore, we have integrated the long-term effect of temperature on DOC yield with data averages of multiple years.

4.6. Spatial distribution of climate impacts on DOC

It is important to understand where climate change would have greater impacts on annual increments in DOC flux, since high annual increments in DOC flux are expected to have a significant impact on aquatic ecosystems. Our results indicate that climate change (i.e. increased temperature) would cause higher increases in riverine DOC flux in low temperature areas than in high temperature areas (Fig. 8). For COL (Fig. 8), an increase of 1 °C would result in a rise of 26% of DOC flux, the highest of the seven major rivers. COL also is in the coolest climate zone. The lowest increment of DOC flux in response to every 1 °C raise is 6% in the ALT (Fig. 8), which has the highest measured DOC concentration of the seven rivers and is in the hottest climate zone. The inverse relationship between incremental DOC flux and climate zone/DOC concentration suggests that warming would have greater impacts on watersheds in high latitudes/cooler climate zones.

A large component of DOC in freshwaters eventually ends up as CO_2 in the atmosphere (Butman and Raymond, 2011). A significant amount of carbon contained in land, which first is absorbed by plants through the air, leaks into streams and rivers and is then released into the atmosphere before reaching coastal waterways. This process is a source of carbon dioxide. The evidence of increasing in-stream DOC flux at large scales explains why rivers and streams in the United States are releasing substantially more carbon dioxide into the atmosphere than previously thought (Butman and Raymond, 2011). As the climate warms there will be more rain and snow in some areas. This increase in precipitation will result in even more terrestrial carbon flowing into rivers and streams, and thus being released into the atmosphere. Therefore, more predictive and precise models of carbon uptake versus carbon released at global scales must include the carbon in streams and rivers.

5. Conclusion

This study is the first to examine the impacts of temperature on terrestrial DOC exports using study sites across multiple climate zones. Our results yielded a strong linear relationship between mean surface temperatures and mean in-stream DOC concentrations at the annual scale for seven major watersheds. The results confirmed that climate change (temperature) is the primary factor driving terrestrial DOC flux. We conducted our analysis using monthly field observations in multiple years. Furthermore, our study yields evidence that landscape factors are secondary variables controlling terrestrial DOC exports when annual mean temperature variation is sufficiently large, i.e., >5 °C. Therefore, climate change may have significant impacts on riverine DOC dynamics in areas where annual surface temperature is high and that have sufficient precipitation.

It is important to understand that a 1 °C warming would increase annual mean DOC concentrations in large rivers by 0.476 mg/L.

An increase in global mean surface air temperature between 1.4 and 5.8 °C by the year 2100 as projected by Frumhoff et al. (2008) would result in a 0.67–2.76 mg/L rise of riverine DOC concentration. The impacts of climate warming on terrestrial DOC export would be greater in watersheds in high latitudes than those in lower latitudes. An increase of 1 °C could lead to a DOC export of up to 26% per square meter per year from watersheds in the northern U.S., and an increase of up to 6% per square meter per year in the southern U.S. The percent-increment of annual DOC flux per square meter is mainly controlled by the variation of temperature as well as land surface processes such as discharge. Precipitation increases terrestrial DOC sources through increased gross primary productivity, and provides energy to drive DOC from the landscape to rivers via surface runoff and groundwater movement.

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