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PERSPECTIVE

The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum

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Abstract: A better understanding is needed of how hydrological and biogeochemical processes control dissolved organic carbon (DOC) concentrations and dissolved organic matter (DOM) composition from headwaters downstream to large rivers. We examined a large DOM dataset from the National Water Information System of the US Geological Survey, which represents approximately 100 000 measurements of DOC concentration and DOM composition at many sites along rivers across the United States. Application of quantile regression revealed a tendency towards downstream spatial and temporal homogenization of DOC concentrations and a shift from dominance of aromatic DOM in headwaters to more aliphatic DOM downstream. The DOC concentration–discharge (C-Q) relationships at each site revealed a downstream tendency towards a slope of zero. We propose that despite complexities in river networks that have driven many revisions to the River Continuum Concept, rivers show a tendency towards chemostasis (C-Q slope of zero) because of a downstream shift from a dominance of hydrologic drivers that connect terrestrial DOM sources to streams in the headwaters towards a dominance of instream and near-stream biogeochemical processes that result in preferential losses of aromatic DOM and preferential gains of aliphatic DOM.

Résumé : Une meilleure compréhension de l'influence des processus hydrologiques et biogéochimiques sur les concentrations de carbone organique dissous (COD) et sur la composition des matières organiques dissoutes (MOD) des cours d'eau d'amont jusqu'aux grands fleuves est nécessaire. Nous avons examiné un imposant ensemble de données sur la MOD du Système national d'information sur l'eau de la commission géologique des États-Unis (US Geological Survey), qui représente environ 100 000 mesures de concentration de COD et de composition de MOD en de nombreux endroits le long de rivières à la grandeur des États-Unis. L'application de la régression quantile a révélé une tendance à l'homogénéisation spatiale et temporelle vers l'aval des concentrations de COD et le passage d'une prédominance de MOD aromatiques dans les cours d'eau d'amont à plus de MOD aliphatiques en aval. Les relations concentrations de COD–débit (C-D) à chaque site ont révélé une tendance vers une pente nulle vers l'aval. Nous proposons que, malgré les complexités des réseaux hydrographiques qui ont mené à de nombreuses révisions du concept du continuum fluvial, les rivières tendent vers la chimiostase (pente nulle de la relation C-D) en raison du passage vers l'aval d'une prédominance de facteurs hydrologiques qui relient les sources de MOD terrestres aux cours d'eau d'amont, à une prédominance de processus biogéochimiques dans le cours d'eau ou à proximité qui se traduisent par des pertes préférentielles de MOD aromatiques et des gains préférentiels de MOD aliphatiques. [Traduit par la Rédaction]

Introduction

In most river ecosystems, the downstream transport of dissolved organic matter (DOM) represents the greatest flux of organic carbon (Schlesinger and Melack 1981; Meybeck 1982). DOM can be defined as all organic matter that passes through a filter of specified pore size (Aiken 2014). It serves as a large energy input to aquatic ecosystems that does not accumulate and has a high turnover rate (Fisher and Likens 1973). DOM helps sustain energy flow in river ecosystems through the metabolism of allochthonous (external to river) and autochthonous (internal) sources (Wetzel

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1995). River ecosystems process organic matter inputs from the surrounding catchment and produce new organic matter in dynamic ways that change seasonally and during downstream transport in river networks. Furthermore, DOM is an important, but small and often overlooked, term in the global carbon budget (Cole et al. 2007), and its riverine fluxes are responsive to environmental changes over local to global scales (Bergamaschi et al. 2012).

To evaluate downstream transport by rivers from headwaters to the sea, new approaches to characterize longitudinal succession in river networks are needed. The River Continuum Concept (RCC; Vannote et al. 1980) presented a framework based on perspectives from fluvial geomorphology that conceptualized how organic material from headwater streams influences ecosystem structure and function downstream. The RCC addressed the dissolved component of carbon cycling by hypothesizing that the distribution of the "relative chemical diversity" of soluble organic compounds through the river continuum from headwater seeps to a 12th-order river would decrease abruptly in headwater streams (~order 1 to 2; see figure 2 in Vannote et al. 1980). The expectation was that labile (easily altered) DOM from the catchment would be rapidly removed, while more recalcitrant (less easily altered) DOM would be transported downstream (Fig. 1). The introduction of the RCC catalyzed much research activity, and in the past 30 years, the limitations of this conceptualization of changes in the dissolved component of carbon cycling down river systems has been highlighted, and new conceptualizations that focus on ideas such as serial discontinuity, the role of patchiness, and the importance of floodplain interactions have been introduced (e.g., Poole 2010).

Studies of riverine DOM have expanded greatly in the past decade, employing new analytical approaches and integrating data from local to continental scales (Poole 2010). We now know that riverine DOM is composed of a complex mix of compounds that substantially influences nutrient cycles, microbial food webs, metal and contaminant transport, and drinking water quality through the formation of disinfection by-products (Aiken 2014). Additionally, riverine DOM is the product of many complex processes that produce, consume, and modify organic matter. These processes change over daily to decadal time scales and over space scales ranging from low-order streams to high-order rivers (Mengistu et al. 2013). Unraveling these complex processes is key to improving our understanding of rivers and the many ecosystem services they provide.

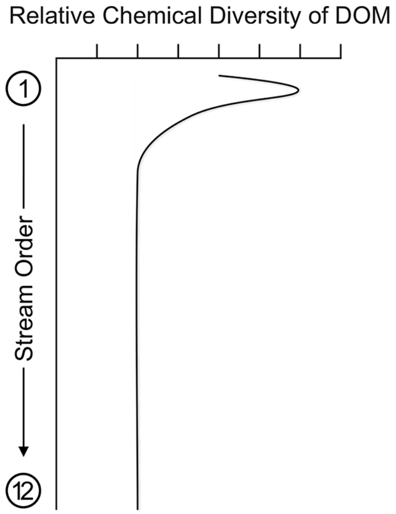
This Perspective explores how the interactions of hydrological and biogeochemical processes result in varying concentration and complexity of DOM in space and time. We compiled three decades of publicly available data from the US Geological Survey (USGS) that span a range from headwater streams to major rivers and that represents perhaps the largest publicly accessible dataset of DOC concentration and DOM composition measurements in rivers and streams. We introduce a conceptual model to explain observed patterns of DOM variability in these river systems. While in our view this new model needs further refinement, we provide a framework around which testable hypotheses may be formed, in an effort to advance our understanding of river biogeochemistry. An improved understanding of controls on the concentration and composition of riverine DOM is needed to predict how river DOM will change in response to climate and land-use or land-cover changes.

Reconceptualizing controls on riverine DOM

Stream order as an organizing principle

There are multiple perspectives on the structure of rivers that could have implications for analyzing DOM dynamics (Poole 2010). Strahler stream order, which was originally developed by geomorphologists to classify position within branching channel networks, remains a useful organizing principle for evaluating processes that occur during downstream DOM transport in rivers (Strahler 1957). Strahler stream order has been shown to be strongly correlated with a variety of metrics, including catchment drainage area (Hughes et al. 2011), stream width (Downing et al. 2012), air–water gas transfer velocities (Raymond et al. 2012), and diatom diversity (Stenger-Kovács et al. 2014). Since a large proportion of the catchment drains directly from first-order streams with decreasing proportions for each successively increasing stream order, Strahler stream order reflects the strength and directness of terrestrial–aquatic linkages. There are limitations to this perspective (e.g., see Hughes et al. 2011); however, studies have shown that Strahler stream order has strong explanatory power for a variety of biological and geochemical properties in flowing waters (Hughes et al. 2011; Downing et al. 2012).

Fig. 1. The River Continuum Concept's (RCC) original depiction of changes in relative chemical "diversity" of dissolved organic matter (DOM) with increasing stream order: in headwater streams ($P/R < 1$, coarse particulate organic matter), DOM is at its highest "diversity"; in minor streams ($P/R > 1$, fine particulate organic matter), DOM is lower in diversity, as labile DOM is rapidly removed leaving behind recalcitrant DOM; and in major streams ($P/R < 1$, fine particulate organic matter), DOM is lowest in diversity, as it is dominated by recalcitrant DOM (see figure 2 in Vannote et al. 1980).

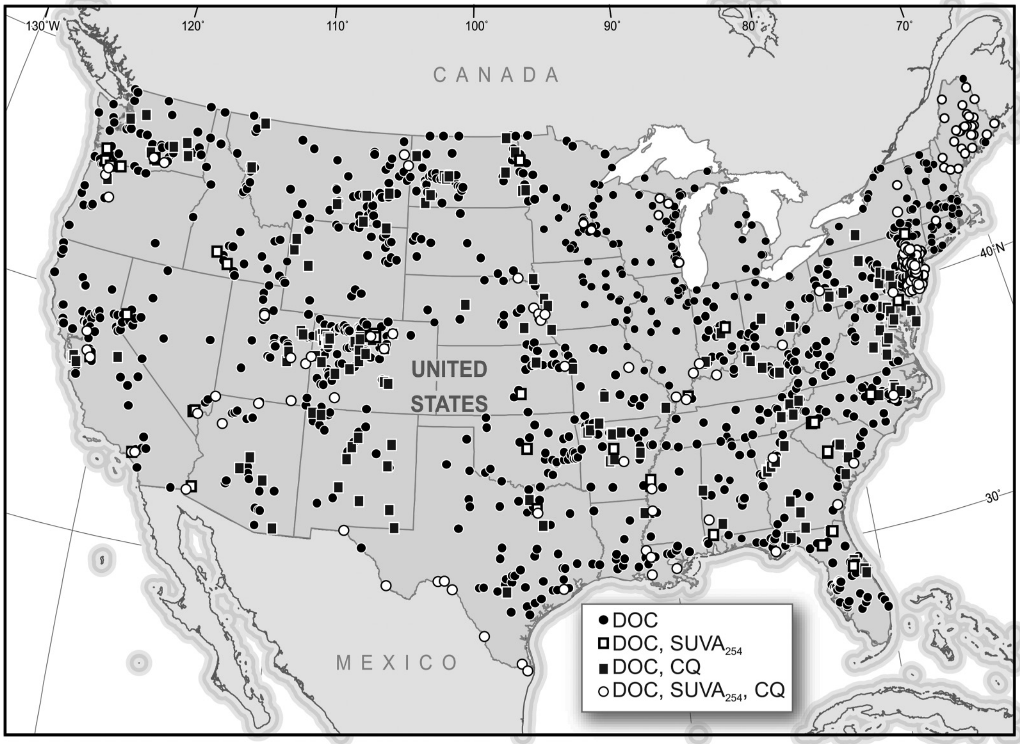


We used Strahler stream order as an organizing principle for our study based on the 1:100 000 scale National Hydrography Data (NHD) digital products (NHDPlus version 2; http://www.horizon-systems.com/NHDPlus/NHDPlusV2_home.php). Stream reach codes were used to associate stream order with stream gages within the NHDPlus dataset (PlusFlowlineVAA). The version of NHDPlus used includes a Strahler calculator to ensure that stream order was not inflated by flow divergence through complex networks (Pierson et al. 2008). Stream orders were subsequently linked to water quality sampling locations by USGS stream gage numbers used by both NHDPlus and NWIS databases.

DOM characterization

Few datasets are available that can be used to analyze the spatial heterogeneity and temporal variability of both DOC concentration and DOM composition across continents. A particular challenge is the lack of data on DOM composition. The optical properties of DOM may be used to estimate functional properties of DOM that are particularly useful for river studies. For example, spectral slope, which can be either the slope of the 275 to 295 nm region or the ratio of the slopes of the 275 to 295 nm and 350 to 400 nm regions, is inversely related to molecular weight (Helms et al. 2008). SUVA_{254} (i.e., specific UV absorbance at 254 nm) is indicative of DOM aromaticity, which in turn is an indicator of

Fig. 2. Map of USGS NWIS sites where dissolved organic carbon (DOC), specific UV absorbance at 254 nm ($SUVA_{254}$), and DOC concentration–discharge (C-Q) data were collected.



reactivity (Weishaar et al. 2003). $SUVA_{254}$ values for riverine aquatic humic substances range from 1.8 L·mg $C^{-1}·m^{-1}$ (microbial sources that are less aromatic) to 4.8 L·mg $C^{-1}·m^{-1}$ (plant litter or soil sources that are more aromatic; Spencer et al. 2012). Fluorescence index is a ratio of the emission intensity of two different wavelengths (450 and 500 nm); values are high (1.8) for systems dominated by materials derived from microbial sources such as algae and bacteria and are lower (1.2) for systems dominated by plant- or soil-derived humic substances (McKnight et al. 2001). These optical quantities, which can serve as proxies for important DOM composition and associated processes, can be accurately measured and compared across diverse aquatic ecosystems.

We used the USGS National Water Information System (NWIS) dataset for rivers (http://waterdata.usgs.gov/nwis; Fig. 2), one of the few publicly available datasets that contain data on both DOC concentrations and $SUVA_{254}$ (composition) among rivers across the United States. DOC concentrations are listed under parameter code 00681 (i.e., organic carbon, water, filtered, milligrams per litre), while the decadal absorbance coefficients (in units of cm^{-1} at 254 nm) are listed under parameter code 50624 (i.e., absorbance, 254 nm, water, filtered, absorbance units per centimetre). $SUVA_{254}$ is calculated as absorbance at 254 nm multiplied by 100 and then divided by the DOC concentration and is reported in units of L·mg $C^{-1}·m^{-1}$. For this study, only samples listed as "surface water" and with greater than 10 surface water measurements were used, with these surface water measurements including all available sampling times for both managed and unmanaged catchment drainages to the streams (see Table 1). The number of DOC samples ranged from 10 to 2031 (median = 30 samples), while the number of $SUVA_{254}$ values per site ranged from 10 to 286 (median = 44 samples). Biological and photolytic effects on optical properties may differ (Moran et al. 2000), but $SUVA_{254}$ is the most readily available and abundant data for inferring DOM composition and associated processes across diverse aquatic ecosystems. This dataset does not allow us to disentangle natural river functions from those affected by anthropogenic processes but does give us an overall impression of how rivers function.

Relationship between stream order and DOM

We examined the spatial heterogeneity (i.e., median for each stream) and temporal variability (i.e., coefficient of dispersion for each stream) of DOC and $SUVA_{254}$ as a function of stream order. The medians estimate the "typical" DOC and $SUVA_{254}$ values for a particular stream, and the coefficients of dispersion give an indication of how much temporal variability there is in these parameters at each stream. We conducted quantile regression analysis in R version 3.0.2 using the "quantreg" package to determine if specific percentiles (5th, 10th, 25th, 50th, 75th, 90th, and 95th) of the frequency distribution of the median and coefficient of dispersion of DOC concentration and DOM composition changed as a function of stream order (Koenker and Hallock 2001). The quantreg package requires a sample size of at least 1000 to calculate P values but can calculate the slope and intercept of regressions with smaller samples sizes. We were able to determine significance for the DOC concentration data ($n = 1429$) but not the $SUVA_{254}$ data ($n = 200$) but report the slope and intercept results to show the general trends. We also investigated nonlinear relationships but could not observe any consistent trends. The relationships between DOC concentration and DOM composition and stream order are likely nonlinear, but the datasets currently available likely have too much noise to be able to detect these relationships reliably.

Quantile regression of median DOC as a function of stream order showed no significant relationship ($P = 0.338$). However, there were a significant negative relationships in the upper percentiles ($P < 0.001$ for 90th and 95th percentiles) and significant positive relationships in the lower percentiles ($P < 0.001$ for 25th, 10th, and 5th percentiles) as a function of stream order (Fig. 3A). Together these findings indicate a convergence of median DOC concentration (i.e., a reduction of both high and low "extreme"

Table 1. Number of DOC, $SUVA_{254}$, and C-Q slope measurements and sites as a function of Strahler stream order obtained from the USGS NWIS database.

Stream order	DOC measurements	DOC sites	$SUVA_{254}$ measurements	$SUVA_{254}$ sites	C-Q measurements	C-Q sites
1	10 464	88	331	7	2 179	17
2	9 537	134	761	16	2 480	27
3	13 098	235	1 824	46	5 580	60
4	12 417	259	1 427	36	6 609	63
5	11 670	274	604	20	3 748	44
6	10 239	246	1 248	23	4 633	48
7	5 636	125	1 088	21	2 888	29
8	2 988	50	1 503	20	2 119	21
9	2 015	18	1 212	11	1 237	9
Total	78 064	1 429	9 998	200	31 473	318

DOC concentrations) downstream. For the coefficients of dispersion of DOC as a function of stream order, there were significant negative relationships for all percentiles ($P < 0.001$) (Fig. 3B). These findings indicate DOC concentrations become less dispersed (more clustered) with increasing stream order.

There was insufficient sample size to calculate the significance of the quantile regressions on the $SUVA_{254}$ data (less than 1000); however, we were able to calculate slopes for the 95th, 90th, 75th, 50th, 25th, 10th, and 5th percentiles, and they were all negative (Fig. 4A). This decrease in $SUVA_{254}$ with increasing stream order indicated more aromatic DOM in low-order streams and less complex aliphatic DOM in higher-order streams. Quantile regression of the coefficients of dispersion of $SUVA_{254}$ as a function of stream order showed negative relationships for the upper percentiles (95th, 90th, 75th, 50th, and 25ths), while the lower percentiles (10th and 5th) had a slightly positive relationship (Fig. 4B). This suggests a slight convergence in the dispersion of $SUVA_{254}$ (i.e., a reduction of both high and low "extreme" $SUVA_{254}$) towards less diversity and complexity downstream.

The importance of integrating both space and time into conceptual models

A major challenge is the development of conceptual models that consider both the spatial and temporal dynamics of DOM in river systems. The RCC made the assumption that DOM in the river system was in steady state and therefore independent of time (Vannote et al. 1980). Research in the intervening decades has repeatedly underscored the importance of considering temporal dynamics in DOM in addition to spatial dynamics and has suggested a relationship between the two (Raymond and Saiers 2010). Changes in discharge alter the DOC concentration and DOM composition across the stream order gradient in different ways and at different time scales (hours to years). At short time scales (e.g., hydrologic events), terrestrial–aquatic transport within a catchment, which is often expressed through hysteretic patterns between runoff and DOC concentrations or DOM composition, can differ dramatically across the longitudinal continuum as a result of differences in source contributions and mixing (Pacific et al. 2010). At longer time scales (e.g., years to decades), DOM export is influenced by climatic cycles (e.g., El Nino–Southern Oscillation) and trends (e.g., warming) (Mengistu et al. 2013).

A conceptual model is needed that explains both the central tendency as well as the spatial and temporal variability observed. In the following section, we advance an updated testable hypothesis and corollaries about DOM in river networks that may explain the DOM patterns observed in this large dataset.

The river as a chemostat

Hypothesis: The interactive effects of riverine biogeochemical processes results in a convergence of DOC concentration and DOM composition with increasing stream order despite hydrological variability

Chemostasis, as applied here, refers to a condition in which the balance of biogeochemical processes, both those that produce and consume DOM, act in concert to diminish variation in concentration and composition. This means that the net balance of biogeochemical processes (e.g., photosynthesis, respiration, photo-oxidation, and adsorption–desorption) is increasingly capable of homogenizing DOC concentration and DOM composition as stream order increases, where hydrological processes (e.g., surface flow, groundwater flow, and evapotranspiration) cause variability in discharge over time. Chemostasis of solute concentrations in rivers has been shown recently, for both conservative (Godsey et al. 2009; Clow and Mast 2010) and nonconservative (Thompson et al. 2011) solutes, across many diverse catchments. Here we use the term to describe the tendency towards increasing chemostasis of DOM as stream order increases across a wide array of streams and rivers in the United States.

We have shown that there is high spatial heterogeneity (median) and temporal variability (coefficient of dispersion) in DOM in headwaters (Figs. 3 and 4). This high site-specific variability is driven by heterogeneity of DOM sources and their ability to "turn on and off" in dynamic fashion, for example, as flow paths rapidly shift from mineral soils to organic-rich soils during storm events. This dynamic behavior is often manifested in the hysteresis behaviour of DOC concentrations commonly observed in headwater streams (Fig. 5). Hysteresis refers to differing relationships between DOC concentration and discharge on the rising and falling limbs of the hydrograph during a runoff event (Evans and Davies 1998). The size, direction, and slope of hysteresis loops can reflect the source and the relative magnitudes and timing of allochthonous inputs of DOM (Butturini et al. 2006). Clockwise directions of change over the course of a hydrologic event suggest that DOM sources are well connected to each other and proximal to the stream, while counterclockwise directions suggest DOM sources are disconnected from each other and distal from the stream. Variable patterns of hysteresis in both concentration and composition during a runoff event and over seasonal and annual time scales are commonly observed in small streams (Pellerin et al. 2012).

Nevertheless, as flows accumulate downstream, we propose this hysteresis behaviour dampens and chemostasis behaviour emerges (Fig. 5). Empirical support for the river as a chemostat would be provided in the relationship between concentration–discharge (C-Q) slopes as a function of stream order and a shift from C-Q > 1 (flushing) to C-Q = 0 (chemostasis). The USGS NWIS

Fig. 3. Quantile regression analysis of (A) median DOC (mg·L−1) and (B) coefficient of dispersion of DOC (mg·L−1) as a function of stream order (*n* = 1429). (Left column) The 95th, 90th, 75th, 50th, 25th, 10th, and 5th percentiles as a function of stream order (solid gray lines), the median fit regression (solid black line), and the least squares regression (red dashed line). Sample estimates of (middle column) intercept and **(**right column**)** slope of the relationship for each percentile, including endpoints of 90% confidence intervals (gray-filled area), the least squares regression estimate of the mean (solid red line), and the standard error of the mean (dashed red lines), are shown. Note that the quantile regression analyses are consistent whether the entire available dataset is used (*N* = 1429) or the subset dataset for which SUVA$_{254}$ exist (*n* = 200). For the coloured version of this figure, refer to the Web site at http://www.nrcresearchpress.com/doi/full/10.1139/cjfas-2014-0400.

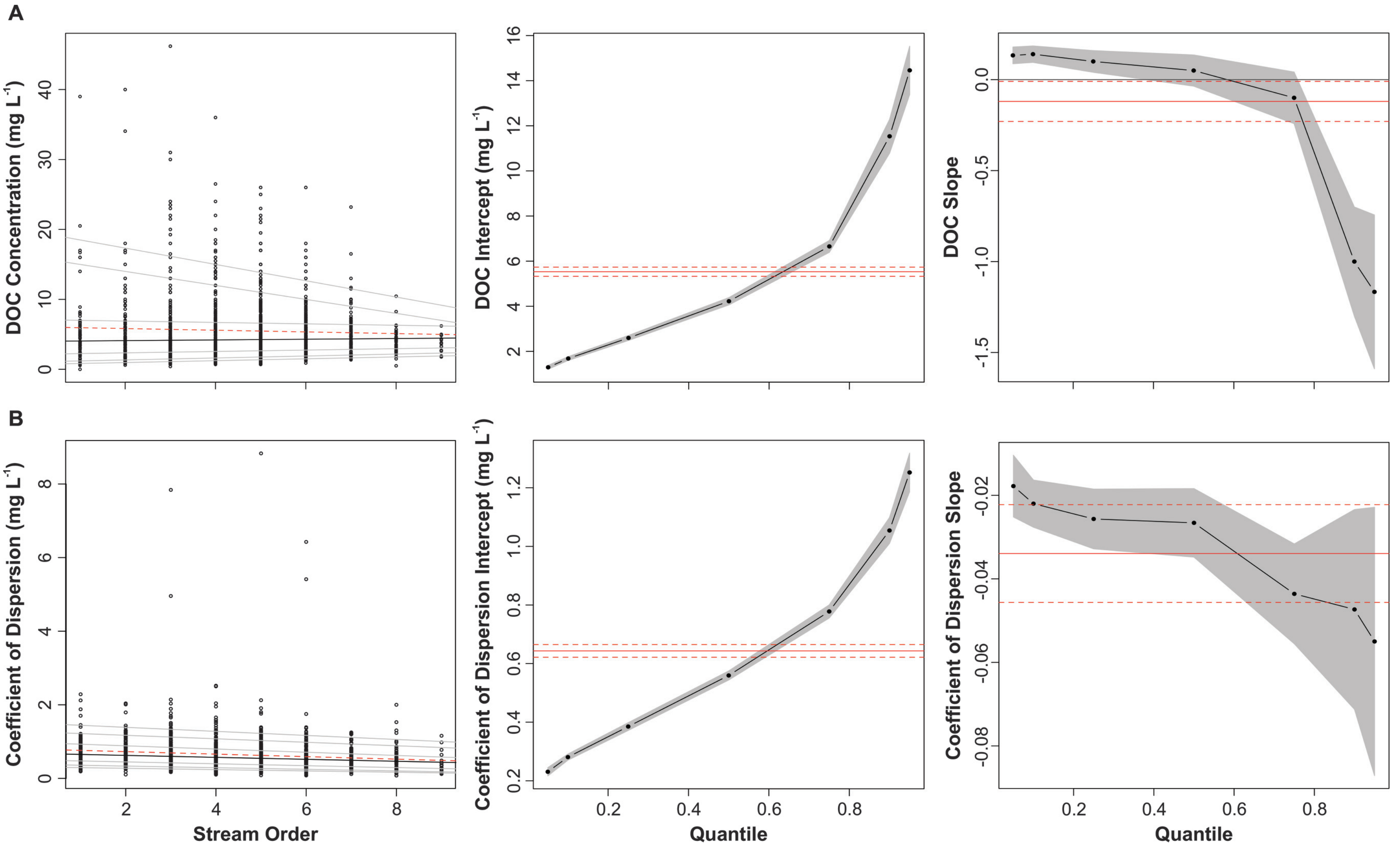


Fig. 4. Quantile regression analysis of (A) median SUVA$_{254}$ (L·mg^{-1}·m^{-1}) and (B) coefficient of dispersion of SUVA$_{254}$ (L·mg^{-1}·m^{-1}) as a function of stream order (*n* = 200). (Left column) The 95th, 90th, 75th, 50th, 25th, 10th, and 5th percentiles as a function of stream order (solid gray lines), the median fit regression (solid black line), and the least squares regression (red dashed line). Sample estimates of (middle column) intercept and (right column) slope of the relationship for each percentile, including endpoints of 90% confidence intervals (gray-filled area), the least squares regression estimate of the mean (solid red line), and the standard error of the mean (dashed red lines), are shown. For the coloured version of this figure, refer to the Web site at http://www.nrcresearchpress.com/doi/full/10.1139/cjfas-2014-0400.

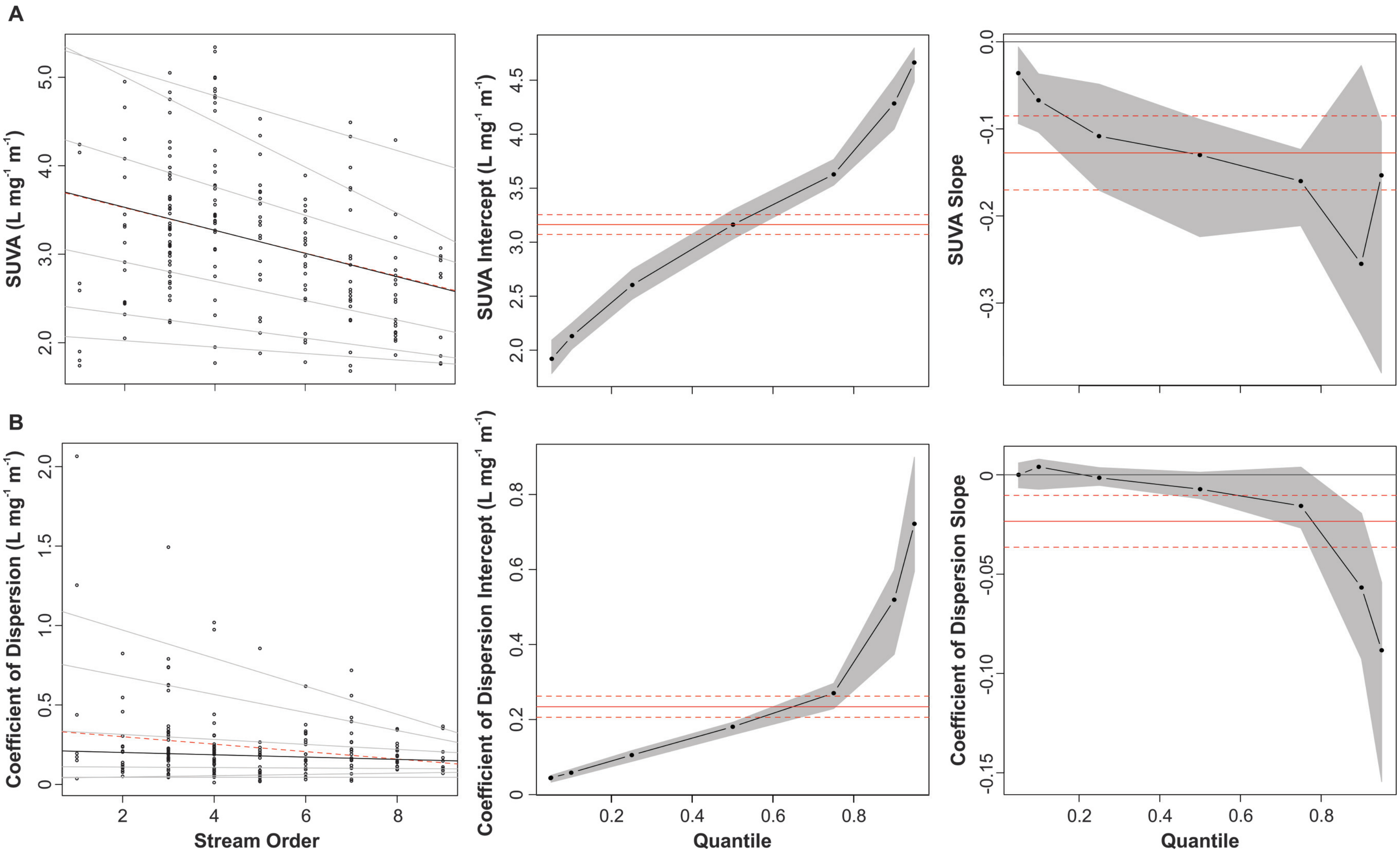
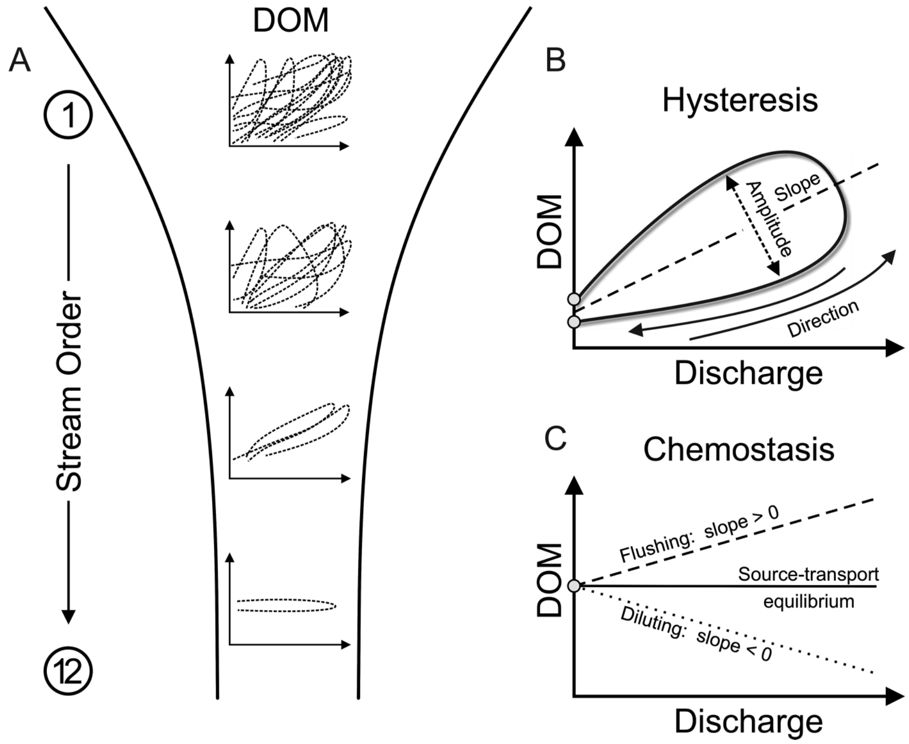


Fig. 5. Stream DOM reflects the nature of coupled terrestrial–aquatic water transport between terrestrial DOM source areas and the stream. (A) Low-order streams exhibit a range of hysteresis behaviours that converge toward chemostatic behaviour as river order increases. (B) The steeper the slope of the hysteresis loop (solid line), the higher the DOM gradient between terrestrial DOM source areas and the stream. A clockwise direction of change over the course of the event indicates that DOM sources are spatially connected to each other and proximal to the stream; a counterclockwise direction indicates DOM sources are spatially disconnected from each other and distal from the stream. The greater the loop amplitude, the greater the hydrological expansion into new terrestrial DOM sources. (C) Chemostasis occurs when DOM remains unchanged despite changes in discharge.



data were used to calculate C-Q slopes. We again performed quantile regression, this time on the C-Q slope data; however, because our sample size was less than 1000, we could not determine which of the relationships were significant. There was a negative relationship in all percentiles, which indicates that all parts of the frequency distribution of C-Q slopes shift downward as a function of stream order (Fig. 6). Again, in contrast with DOC and SUVA$_{254}$, coefficients of dispersion of C-Q slopes were not examined, as the coefficient of dispersion is the inner quartile range divided by median, and streams with slopes close to zero (chemostasis) would have highly positive (or negative) coefficients of dispersion rendering meaningless results. The USGS NWIS data showed that river networks tend to converge on similar chemostatic endpoints, suggesting that common processes may be driving these patterns.

Identifying processes that regulate the downstream transition from DOM hysteresis to chemostasis may provide a means to unravel the complexity of DOC signals in rivers. Why does the temporal variability of river DOC become increasingly stable relative to discharge with increasing stream order? If we conceptualize the catchment as a series of chemostats, DOC should be less variable in both space and time as flow path complexity increases. Generally, this complexity in DOC signals will increase with stream order; thus, we expect that DOC will converge with increasing stream order. The central tendency of the concentration may increase, decrease, or remain the same, depending on the net balance of instream processes or direct discharges, but the variation is expected to decrease.

A hypothetical river network is presented in Fig. 7 that shows how the relative rates of coupled terrestrial–aquatic water transport, *c*, water residence time, *t*, DOM production, *p*, and DOM decay, *k*, may change down the river network in a manner that leads to chemostasis. We propose that catchment processes dominate in low-order streams; *c*, *t*, and *p* are relatively high but *k* is relatively low, leading to a nonchemostatic condition in that concentrations change dramatically with flow. In contrast, we propose that high-order rivers, lakes, and reservoirs behave as chemostats because the contribution of catchment processes become overwhelmed by the influence of instream processes; namely, *c* is relatively low and balanced by export (low *r*), *p*, and *k*, leading to chemostasis. However, other processes may also be important. For example, the influence of groundwater discharge increases downstream (in other words, the dominance of one source over others), and this source of water may serve as a major control on the patterns of DOC concentration and DOM composition (e.g., Burgers et al. 2014). There is also an increasing influence of stored water (i.e., lakes, reservoirs) downstream; these water stores are less dynamic in terms of DOC concentrations and they increasingly dominate river flow as basin area increases and therefore would contribute to the flattening (convergence) of C versus Q (Miller et al. 2014).

We propose that the attenuation of DOM variability down the river network is thus attained by a combination of (*i*) hydrological averaging of diverse terrestrial source area signals through hydrological transport and mixing (i.e., as stream order increases, each additional DOM input has a smaller impact on the total DOM in the river) and (*ii*) biogeochemical cycling of carbon within the river network (with instream production of DOM counteracted by degradation and other removal processes). Hydrological mixing tends to reduce concentration variability, while biogeochemical processing also tends to reduce compositional variability (Montgomery 1999).

Fig. 6. Quantile regression analysis of median C-Q slope as a function of stream order (*n* = 314). (Left column) The 95th, 90th, 75th, 50th, 25th, 10th, and 5th percentiles as a function of stream order (solid gray lines), the median fit regression (solid black line), and the least squares regression (red dashed line). Sample estimates of (middle column) intercept and (right column) slope of the relationship for each percentile, including endpoints of 90% confidence intervals (gray-filled area), the least squares regression estimate of the mean (solid red line), and the standard error of the mean (dashed red lines), are shown. Statistical analyses associated with quantile regression were not possible since there was insufficient C-Q slope data for each bin of stream order tested but indicated a linear, negative relationship for C-Q slope as a function of stream order for all percentiles (95th, 90th, 75th, 50th, 25th, 10th, and 5th). Statistical analyses associated with quantile regression were not possible since there were insufficient C-Q slope data for each bin of stream order tested. For the coloured version of this figure, refer to the Web site at http://www.nrcresearchpress.com/doi/full/10.1139/cjfas-2014-0400.

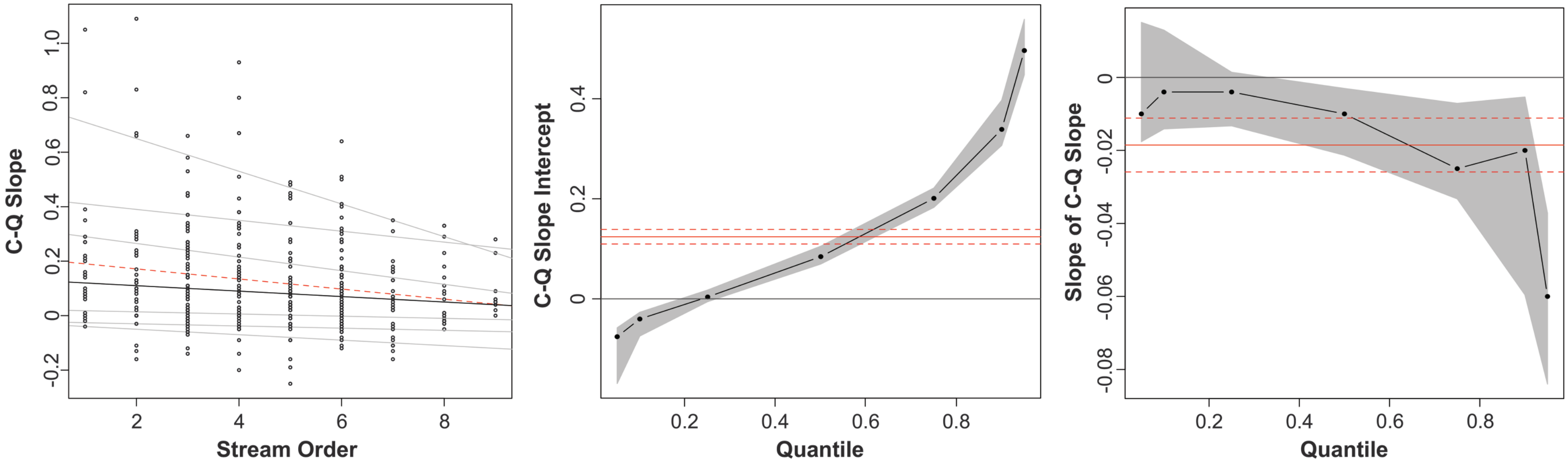
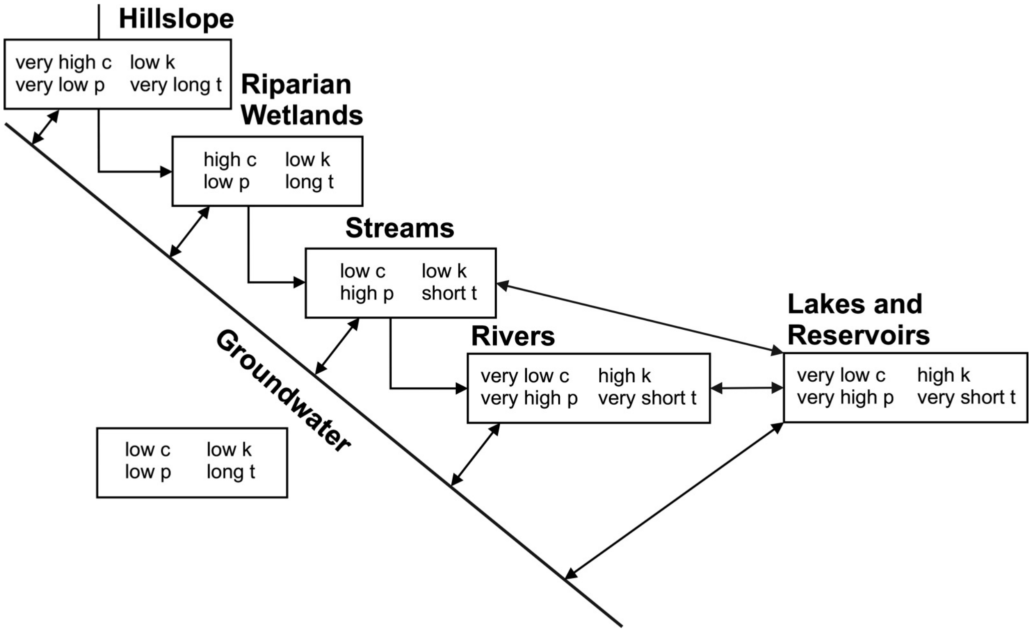


Fig. 7. A simple conceptualization of the river network as a series of chemical reactors. For each chemical reactor, the parameter *c* represents coupled terrestrial–aquatic water transport that delivers terrestrial sources of DOM to the river network, *p* is internal DOM production rate, *k* is DOM decay rate, and *t* is water residence time. As DOM flows downstream, the changing relative roles of *c*, *p*, *k*, and *t* are likely to change DOM variability, ultimately leading to chemostasis. A more accurate conceptualization of the river network would reflect the critical role of geomorphology in generating heterogeneity in form and associated functions and longitudinal and lateral terrestrial–aquatic linkages along the river network.



High DOM variability near terrestrial source areas

Corollary 1: High DOM variability in streams proximal to terrestrial source areas is driven by the dynamic nature of the hydrological connections to the terrestrial ecosystem

For streams close to terrestrial DOM source areas, we predict the effects of coupled terrestrial–aquatic water transport and water contact time on DOM variability are high and effects related to DOM reaction rates are low. Headwater streams are closely connected to their surrounding terrestrial systems, much more so than downstream areas (Freeman et al. 2007), and these connections are critical in establishing the chemical heterogeneity of DOM in river ecosystems. The USGS NWIS data revealed that DOC concentration becomes less dispersed (more clustered) with increasing stream order, supporting a conceptual model that the relative importance of terrestrial loading drivers decreases as a function of stream order over aquatic loading drivers.

Coupled terrestrial–aquatic water transport can be highly variable in terms of timing, magnitude, and organization of water flowing to the stream and altering DOC concentration and DOM composition (e.g., Pellerin et al. 2012). Water flowing above and below the ground contacts differing DOM sources that deliver diverse forms of DOM to headwaters. The preferential sorption and uptake of low molecular weight labile DOM favours downstream export of higher molecular weight, recalcitrant DOM (Aiken 2014). However, the water flow path will influence what sorbing media the water contacts. Water in shallow flow paths can mobilize a large amount of DOM, much of which can be biologically labile, such as that in freshly fallen litter and the forest floor. In contrast, along deeper flow paths that are more dominant at larger basin scales, DOM altered by microbial oxidation and sorption is less labile (McDowell and Likens 1988; Qualls et al. 2002). As a consequence, the downstream export of low molecular weight labile DOM will vary temporally and spatially (Buffam et al. 2001; McLaughlin and Kaplan 2013).

The contact time of water along these flow paths will also influence DOM export characteristics. Short contact times that are common near the stream, in structured soils, steep slopes, and at smaller basin scales can lead to shallow preferential flows that minimize organic matter interaction and DOM mobilization (Schiff et al. 1997). Longer contact times common in flat areas and depressions can lead to greater organic matter interaction and DOM mobilization (Creed et al. 2003). Catchment features such as riparian areas and wetlands have a major influence on DOM export characteristics, despite typically occupying only a small percentage of catchment areas, because they can act as biogeochemical reactors when unsaturated (longer contact time) but are bypassed when saturated (shorter contact time; McGlynn and McDonnell 2003; Pacific et al. 2010).

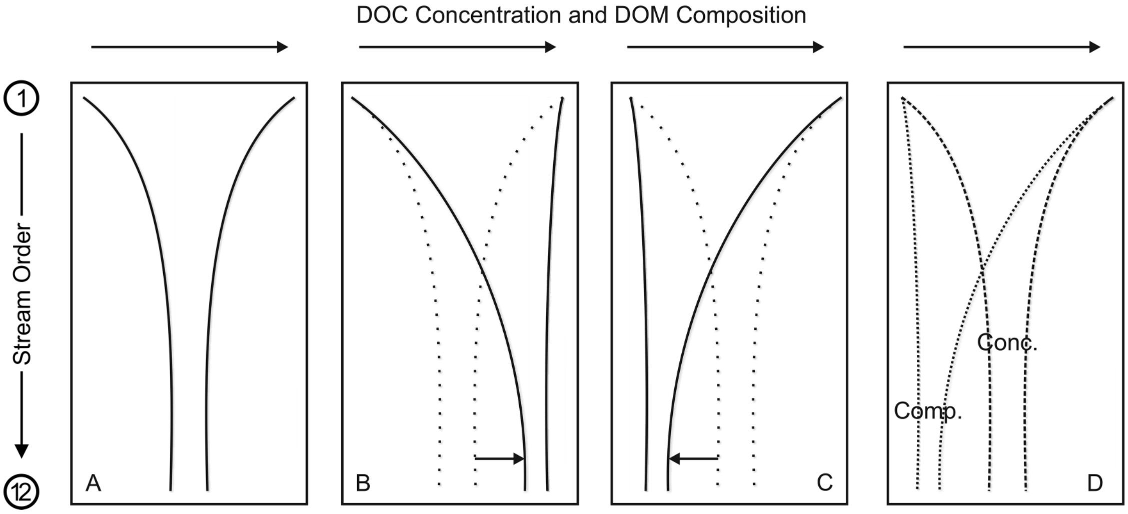
The complexity of coupled terrestrial–aquatic transport in headwaters explains why high variability of DOC concentrations and DOM composition is observed in these low-order streams. Downstream, in higher-order streams, mixing of the upstream waters and an increasing influence of deeper groundwater flow paths dampens DOM variability (Tiwari et al. 2014).

Low DOM variability with increasing disconnection from terrestrial source areas

Corollary 2: Low DOM variability in streams distal from terrestrial source areas is driven by a combination of factors: effective hydrological disconnection from surface water flows from the terrestrial ecosystem; averaging of complex headwater DOM signals by hydrological mixing that contributes to a homogenization of DOM; increasing influence of deeper groundwater flows with longer flow paths and longer residence times that also contributes to a homogenization of DOM; and increasing influence of instream biogeochemical processing

For streams removed in time or space from terrestrial DOM source areas, such as large rivers, we predict few effects of coupled terrestrial–aquatic surface water transport as the nature of these linkages change favouring groundwater transport, but large effects of DOM reaction rates compared with the headwaters. The USGS NWIS $SUVA_{254}$ data shows $SUVA_{254}$ decreasing with increas-

Fig. 8. A convergence of DOM variability to a downstream endpoint of chemostasis may reflect the relative influence of hydrological and biogeochemical processes. Three potential scenarios are as follows: (A) mixing waters from lower stream orders in equal proportions and instream production balanced by instream degradation; (B) greater relative contribution of high concentration DOC from lower stream orders and (or) instream net production of DOM; and (C) greater relative contribution of low concentration DOM from lower stream orders and (or) instream net degradation of DOM. Based on the first scenario in panel A, it is possible there is a change in DOM composition in large rivers despite no change in bulk DOC concentration (D).



ing stream order in all percentiles, indicating a clear shift from aromatic to aliphatic carbon with increasing stream order (Fig. 4). The influence of autochthonous DOC increases with stream order, likely driven by preferential losses of the more aromatic allochthonous DOC and gains of more aliphatic autochthonous DOC, which may be linked through microbial priming (Hotchkiss et al. 2014). The persistence of low SUVA_{254} in higher stream orders may be evidence of lateral connectivity to autochthonous DOM sources in larger rivers (Thorp and Delong 2002).

Inputs of fresh DOM sources are likely partially counterbalanced by processes such as uptake, flocculation, condensation, sorption, photolysis, and degradation that result in convergence of DOC. Many of these processes may be enhanced by hyporheic exchange and interaction with near-stream sediment and soils, which tend to occur over longer path lengths and time frames as stream order increases (Cardenas 2008). Among these processes, sorption of DOM to particle-associated metal complexes or biofilms may be the most rapid (McKnight et al. 2003), with the degree of sorption related to molecule size, aromaticity, and the carboxylic acid content of dissolved organic molecules (McKnight et al. 1992). Photolysis and higher temperatures may lead to enhanced mineralization of DOM to CO_2, the release of smaller organic molecules, and a general "priming" effect for enhanced microbial degradation of DOM in transport (Guenet et al. 2010). Photolysis is high in shallow streams with open canopies and floodplains, clear lakes and reservoirs, and flood plains, but becomes less important as river depth increases and water clarity decreases (Bertilsson and Tranvik 2000). Microbial degradation of DOM during transport occurs not only in the water column but also through continuous hyporheic exchange with water and sediment underlying the stream (e.g., Battin et al. 2008) and is enhanced in previously photolytically altered DOM (Moran et al. 2000). Biodegradation has the opposite effect of photolysis, resulting in increases in DOM aromaticity, potentially dampening the decline in SUVA_{254} with increasing stream order. Water in the channel is continually moving through subsurface zones and returning to the stream, enhancing contact with subsurface microbial communities (e.g., Boulton et al. 1998) and potentially modifying the DOM pool. The microbial loop (Pomeroy 1974) implies that large quantities of carbon pass through a series of microbial consumers, thereby connecting an otherwise unavailable carbon source to higher trophic levels, with substantial CO_2 loss occurring at each step. Flowing waters outgas substantial quantities of CO_2, thus contributing to the downriver convergence in DOC concentration and DOM composition (Battin et al. 2008).

The resulting downstream decline in spatial heterogeneity and temporal variability in DOC concentration and DOM composition occurs gradually. We propose that damping occurs at the stream order where system dominance shifts from hydrological integration to biogeochemical processing, which can vary among river systems, but in general seems to appear in third- or fourth-order streams.

While the USGS NWIS data set, which composites data for all rivers, shows a shift from high to low SUVA_{254} with increasing stream order, there are exceptions to this pattern. For example, the black water rivers examined by Sun et al. 1997 show high SUVA_{254} at high stream order. Therefore, continued testing of the generality of this pattern is needed as new datasets on SUVA_{254} and other DOM compositional measurements become available.

Which processes dampen DOM variability and determine the endpoint of chemostasis?

Corollary 3: DOM chemostatic endpoints are determined by the relative effects of heterogeneous terrestrial contributions versus constant instream mixing, removal, replenishment, and transport processes

We predict that the relative inputs of terrestrial, riparian, floodplain, and groundwater DOM to the river network influence the downriver endpoints of DOM chemostasis (Fig. 8). The endpoint of chemostasis shown in Fig. 8A represents the point where the signal from terrestrial source areas of DOM persists to influence the longitudinal profile (mean and range) of DOC concentration and DOM composition as stream order increases. In this case, instream losses of terrestrial DOM and gains in microbial and planktonic DOM in higher-order streams may not be sufficient to shift the signal away from simple averaging of upstream flows. Furthermore, at higher stream orders (e.g., 10 or greater), inorganic sediments or particulate organic carbon may act as an instream regulator in some cases by attenuating light and thereby limiting photosynthetic production of new microbial DOM and photodegradation of terrestrial and microbial DOM.

Clearly, multiple endpoints of DOM chemostasis are possible. If catchments with relatively high DOM export characterized by high aromaticity represent a large proportion of headwater streams, and the losses of this terrestrial DOM are mitigated by near-stream and instream production of new DOM (e.g., riverine wetland and floodplain contributions throughout the network), then the chemostatic endpoint may exhibit higher concentrations than expected from simple averaging (Fig. 8B). In comparison, if catchments with high DOM export characterized by high aromaticity represent a small proportion of headwater streams, and the losses of this terrestrial DOM are enhanced by high light regimes and (or) the gains of new microbial or planktonic DOM are limited by high sediment load or low nutrient availability, then the river may exhibit lower than expected concentrations (Fig. 8C). DOC concentration and DOM composition may also become uncoupled (e.g., Fig. 8D), particularly in river networks with large contributions from lakes or major impoundments (Miller et al. 2012; Spencer et al. 2012).

Effects of human activities on DOM chemostasis

Corollary 4: Human activities can alter or disrupt the chemostatic endpoint by changing the hydrological and biogeochemical processes that control carbon cycling, inputs, and outputs

We predict that human activities are a major factor that can disrupt natural chemostatic endpoints. Human activities may shift the transition location from hysteresis to chemostasis, or whether a river becomes chemostatic at all. Human activities may also alter natural DOM cycling rates sufficiently to trigger a change from one chemostatic endpoint to another. Such activities include large-scale regional changes in land use – land cover leading to fundamental changes in terrestrial DOM sources; the addition of point and diffuse sources of DOM to the river; extensive modification of river flow (e.g., major diversions or dams, recognizing that dams are a common feature of most river networks and that the DOM signals we are interpreting in the USGS NWIS dataset are partially a manifestation of the effects of these dams) that can change the natural progression with stream order in a river; and alterations in the balance of hydrological and biogeochemical processes, for example, through climate warming.

Humans have caused large changes in catchment structure and function, effectively increasing or decreasing terrestrial DOM sources either directly or indirectly through the addition of other nutrients such as phosphorus and nitrogen that greatly influence the rates of processes that may act as sources or sinks for DOM. These changes are evident as shifts in DOC concentration and DOM composition as streams pass through heavily developed and populated areas. For example, Edmonds and Grimm (2011) found declining DOC concentrations paralleled by increased chemical complexity as a desert river passed through a major urban area. These changes likely result from direct loadings of novel carbon sources and increased opportunity for autotrophic production. Within catchments with human settlement, both point and diffuse sources of DOM impact DOM in river ecosystems. For example, effluents from wastewater treatment plants can be a major source of DOM that differs in composition from natural waters, increasing DOC concentration and DOM composition in streams where effluents are released (Stedmon et al. 2003). Furthermore, human modifications to the river channel disrupt the river continuum with major impacts on DOM transport in rivers (Ward and Stanford 1983). For example, Miller (2012) found that Lakes Powell and Mead (the two largest reservoirs in the United States) lowered DOC concentrations in the Colorado River and changed the composition consistent with degradation of terrestrially derived, aromatic DOM and (or) production of less aromatic, autochthonous DOM in the river network. Poff et al. (2007) report that 84% of dams in the United States are on fourth- to sixth-order streams and argue that dams have a homogenizing effect on river flows, an effect that presumably extends to both water quantity and quality in general and to DOM in particular.

Human-caused climate change is increasing the frequency of extreme weather events, including droughts and floods, which can impact DOM cycling in freshwater ecosystems. Droughts can lead to increased production of refractory DOM in catchments with substantial organic matter accumulation in wetlands, which is subsequently flushed into the river network (Worrall et al. 2003). Floods can lead to increased DOM in rivers, similar to that predicted by the Flood Pulse Concept (Junk et al. 1989; Sedell et al. 1989; Tockner et al. 2000), although more intensely and frequently. These types of climatic shifts will result in complex changes in hydrological and biogeochemical process rates, including changes to DOC concentration and DOM composition that may be directly related to warming (e.g., Hejzlar et al. 2003) or indirectly through catchment changes like fluctuating water tables (e.g., Worrall et al. 2003).

Forging a new course for river DOM research

Our continuously improving ability to probe and map the complex world of organic matter composition and reactivity is an impetus to reconsider fundamental concepts and develop new hypotheses regarding DOM transport, reactivity, and fate. There is still much to be learned using traditional techniques (as evidenced by the analysis presented in this paper); however, new measurement tools provide exciting opportunities for river researchers to fundamentally advance our understanding of DOM in river ecosystems. Data derived from these tools make it possible to develop and test new conceptual models; in particular, where and why riverine DOM variability is greatest, and where and why it is most rapidly damped, needs to be assessed.

We offer the following 10 thoughts to guide researchers in this quest:

- The tendency towards constancy of bulk DOC concentration downstream does not necessarily preclude a river system state of high turnover and high compositional diversity.
- The processes driving DOM variability may be more easily identified by considering concentration and composition simultaneously, which can now be done with relatively simple and inexpensive optical measurements.
- DOM is complex, including thousands of compounds with a range of molecular weights, reactivity, and degradability (Aiken and Leenheer 1993). Techniques are emerging that discriminate among the many compounds that compose DOM, carving the compositional "pie" into previously unknown slices (Table 2) (Aiken 2014). These techniques must be further developed, making them accessible to researchers who can then link chemical characterization to the ecological roles of natural organic matter (Simpson and Simpson 2012).
- DOM is dynamic, varying at spatial scales from soil profiles to entire river networks and at temporal scales ranging from seconds to days. Currently, some of these optical techniques are being transferred to the field, with the continued development of field-deployable fluorometers, including multiwavelength sensors now in development, that provide the ability to link concentration- and composition-related dynamics through high-resolution DOM compositional indices (Carpenter et al. 2013). Deployment of an ensemble of these next generation optical sensors may lead to a more comprehensive understanding of the processes controlling the fate and role of DOM in ecosystem energetics.
- Strategic deployment of distributed networks of these sensors would enable discrimination of source- and process-related signals by indicating whether signals are coherent or unrelated. Data from these distributed networks will set the stage for fundamental discoveries regarding the fate and transport of organic matter from soils to the sea. Future scientists need to

Table 2. Analytical approaches for the chemical characterization of DOM.

Approach	Description	Reference
Isolation and fractionation		
Reverse osmosis	Allows desalting and concentration of most DOM	Koprivnjak et al. 2006
Ultrafiltration	Fractionates DOM by molecular size; larger size fractions retained	Benner et al. 1997
Solid phase extraction	Allows for the fractionation and isolation of chemically distinct fractions of the DOM related to biogenesis and reactivity; commonly used chromatographic resins are XAD resins (also known as DAX), ^{18}C, and PPL	Aiken et al. 1992; Dittmar et al. 2008
Optical analyses		
UV–visible spectroscopy fluorescence	Provides information about chromophores (UV–visible spectroscopy) and fluorophores (fluorescence) in a DOM sample; DOC composition and concentration can be inferred; can be measured in situ	Weishaar et al. 2003; Cory and McKnight 2005; Helms et al. 2008; Spencer et al. 2012
Elemental analyses	Analyzes for elemental content (C, H, O, N, S, P, ash) of organic matter isolates	Huffman and Stuber 1985
Isotopic analyses	Analyzes for ^{13}C, ^{14}C, ^{15}N, and ^{34}S content to provide information about DOM sources, transformation, and age	Butman et al. 2012
Molecular composition analyses		
Nuclear magnetic resonance spectroscopy	Provides structural information about bonding arrangements for C, H, N, and P atoms in DOM	Thorn and Cox 2009; Mazzei and Piccolo 2012
Gas chromatography – mass spectrometry	Provides information about the concentration and presence of individual molecules, such as biomarker compounds (e.g., lignin phenols); recent developments in high-resolution mass spectrometry techniques (e.g., GC-ToF-MS and FTICR-MS) have resulted in the identification of thousands of compounds	Hedges et al. 1994; Hatcher et al. 2001

work towards integrating knowledge once adequate data are available to complement conceptual models.

- Scaling rules must be considered and developed (e.g., other stream organization approaches need to be considered as we explore the generalizability of conceptual models to rivers worldwide).
- Mechanistic studies can be extrapolated to multiple scales in space and time by using these aforementioned measurement techniques, and scaling rules can be applied at multiple scales.
- Integrating measurements into models, where the degree of process simplification can be controlled and varied, can enable the exploration of alternative explanations for the patterns observed in real data.
- A mixture of processes operating over a broad range of temporal and spatial scales can produce chemostatic behaviour. DOM variability and the downriver transition to chemostatic behaviour provide critical information about the shifting dominance of supply, transport, and reactivity controls. Models that capture this chemostatic behaviour may be helpful in anticipating likely responses of these controls to environmental change.
- More detailed examination of river basins where the generalizations outlined here apply as well as those where these patterns are not evident will allow further refinement of the chemostasis hypothesis outlined here, including the role of variation in climate, geomorphology, and human activities.

We stand at the cusp of a new understanding of river DOM sources, production, cycling, and transport. Big ideas, systems thinking, and interdisciplinary collaboration supported by the application of emerging analytical tools and data analyses are needed. We need to connect advances in understanding DOM chemistry to conceptual models that integrate hydrological and biogeochemical processes over different time and space dimensions of river-network DOM dynamics. Conceptual models that consider the complexity of interacting hydrological and biogeochemical processes should help us understand and predict the responses of riverine organic matter to environmental change. These conceptual models of river network DOM dynamics are important because riverine DOC concentration and DOM composition are fundamental to understanding and predicting stream and river ecosystem productivity and function and the role of these ecosystems in local, regional, and global carbon cycling.

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References

Aiken, G.R. 2014. Dissolved organic matter in aquatic systems. *In* Comprehensive water quality and purification. Vol. 1. *Edited by* S. Ahuja. Elsevier Inc., Waltham, Mass. pp. 205–220.

Aiken, G.R., and Leenheer, J. 1993. Isolation and chemical characterization of dissolved and colloidal organic matter. Chem. Ecol. **8**: 135–151. doi:10.1080/02757549308035305.

Aiken, G.R., McKnight, D.M., Thorn, K.A., and Thurman, E.M. 1992. Isolation of hydrophilic organic acids from water using macroporous resins. Org. Geochem. **18**: 567–573. doi:10.1016/0146-6380(92)90119-I.

Battin, T.J., Kaplan, L.A., Findlay, S.E.G., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, J.D., and Sabeter, F. 2008. Biophysical controls on organic carbon fluxes in fluvial networks. Nat. Geosci. **1**: 95–100. doi:10.1038/ngeo101.

Benner, R., Biddanda, B., Black, B., and McCarthy, M. 1997. Abundance, size distribution, and stable carbon and nitrogen isotopic compositions of marine organic matter isolated by tangential-flow ultrafiltration. Mar. Chem. **57**: 243–263. doi:10.1016/S0304-4203(97)00013-3.

Bergamaschi, B.A., Smith, R.A., Sauer, M.J., and Shih, J.-S. 2012. Terrestrial fluxes of sediments and nutrients to Pacific coastal waters and their effects on coastal carbon storage rates. *In* Climate projections used for the assessment of the Western United States. *Edited by* Z. Zhu and B.C. Reed. Professional Paper 1797, US Geological Survey, Reston, Va. pp. 143–158.

Bertilsson, S., and Tranvik, L.J. 2000. Photochemical transformation of dissolved organic matter in lakes. Limnol. Oceanogr. **45**: 753–762. doi:10.4319/lo.2000.45.4.0753.

Boulton, A.J., Findlay, S., Marmonier, P., Stanley, E.H., and Valett, H.M. 1998. The functional significance of the hyporheic zone in streams and rivers. Annu. Rev. Ecol. Syst. **29**: 59–81. doi:10.1146/annurev.ecolsys.29.1.59.

Buffam, I., Galloway, J.N., Blum, L.K., and McGlathery, K.J. 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry, **53**: 269–306. doi:10.1023/A:1010643432253.

Burgers, H.E., Schipper, A.M., and Hendriks, A.J. 2014. Size relationships of water discharge in rivers: scaling of discharge with catchment area, main-stem length and precipitation. Hydrol. Process. **28**: 5769–5775. doi:10.1002/hyp.10087.

Butman, D., Raymond, P.A., Butler, K., and Aiken, G.R. 2012. Relationships between Δ^{14}C and the molecular quality of dissolved organic carbon in rivers draining to the coast from the conterminous United States. Global Biogeochem. Cycles, **26**: GB4014. doi:10.1029/2012GB004361.

Butturini, A., Gallart, F., Latron, J., Vazquez, E., and Sabater, F. 2006. Cross-site comparison of variability of DOC and nitrate *c-q* hysteresis during the autumn-winter period in three Mediterranean headwater streams: a synthetic approach. Biogeochemistry, **77**: 327–349. doi:10.1007/s10533-005-0711-7.

Cardenas, M.B. 2008. Surface water-groundwater interface geomorphology leads to scaling of residence times. Geophys. Res. Lett. **25**: L08402.

Carpenter, K.D., Kraus, T.E.C., Goldman, J.H., Saraceno, J.F., Downing, B.D., Bergamaschi, B.A., McGhee, G., and Triplett, T. 2013. Sources and characteristics of organic matter in the Clackamas River, Oregon, related to the formation of disinfection by-products in treated drinking water. US Geological Survey Scientific Investigations Report 2013–5001.

Clow, D.W., and Mast, M.A. 2010. Mechanisms for chemostatic behavior in catchments: implications for CO_2 consumption by mineral weathering. Chem. Geol. **269**: 40–51. doi:10.1016/j.chemgeo.2009.09.014.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., and Melack, J. 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. Ecosystems, **10**: 171–184. doi:10.1007/s10021-006-9013-8.

Cory, R.M., and McKnight, D.M. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ. Sci. Technol. **39**: 8142–8149. doi:10.1021/es0506962. PMID:16294847.

Creed, I.F., Sanford, D.E., Beall, F.D., Molot, L.A., and Dillon, P.J. 2003. Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes. Hydrol. Process. **17**: 3629–3648. doi:10.1002/hyp.1357.

Dittmar, T., Koch, B., Hertkorn, N., and Kattner, G. 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnol. Oceanogr. Methods, **6**: 230–235. doi:10.4319/lom.2008.6.230.

Downing, J.A., Cole, J.J., Duarte, C.M., Middelburg, J.J., Melack, J.M., Prairie, Y.T., Kortelainen, P., Striegl, R.G., McDowell, W.H., and Tranvik, L.J. 2012. Global abundance and size distribution of streams and rivers. Inland Waters, **2**: 229–236. doi:10.5268/IW-2.4.502.

Edmonds, J.W., and Grimm, N.B. 2011. Abiotic and biotic controls of organic matter cycling in a managed stream. J. Geophys. Res. **116**: G02015. doi:10.1029/2010JG001429.

Evans, C., and Davies, T.D. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. Water Resour. Res. **34**: 129–137. doi:10.1029/97WR01881.

Fisher, S.G., and Likens, G.E. 1973. Energy flow in Bear Brook, New Hampshire: an integrative approach to stream ecosystem metabolism. Ecol. Monogr. **43**: 421–439. doi:10.2307/1942301.

Freeman, M.C., Pringle, C.M., and Jackson, C.R. 2007. Hydrologic connectivity and the contribution of stream headwaters to ecological integrity at regional scales. J. Am. Water Resour. Assoc. **43**: 5–14. doi:10.1111/j.1752-1688.2007.00002.x.

Godsey, S.E., Kirchner, J.W., and Clow, D.W. 2009. Concentration-discharge relationships reflect chemostatic characteristics of US catchments. Hydrol. Process. **23**: 1844–1864. doi:10.1002/hyp.7315.

Guenet, B., Danger, M., Abbadie, L., and Lacroix, G. 2010. Priming effect: bridging the gap between terrestrial and aquatic ecology. Ecology, **91**: 2850–2861. doi:10.1890/09-1968.1. PMID:21058546.

Hatcher, P.G., Dria, K.J., Kim, S., and Frazier, S.W. 2001. Modern analytical studies of humic substances. Soil Sci. **166**: 770–794. doi:10.1097/00010694-200111000-00005.

Hedges, J.I., Cowie, G.L., Richey, J.E., Quay, P.D., Benner, R., Strom, M., and Forsberg, B. 1994. Origins and processing of organic matter in the Amazon River as indicated by carbohydrates and amino acids. Limnol. Oceanogr. **39**: 743–761. doi:10.4319/lo.1994.39.4.0743.

Hejzlar, J., Dubrovský, M., Buchtele, J., and Růžička, M. 2003. The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malše River, South Bohemia). Sci. Total Environ. **310**: 143–152. doi:10.1016/S0048-9697(02)00634-4. PMID:12812738.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., and Mopper, K. 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol. Oceanogr. **53**: 955–969. doi:10.4319/lo.2008.53.3.0955.

Hotchkiss, E.R., Hall, R.O., Baker, M.A., Rosi-Marshall, E.J., and Tank, J.L. 2014. Modeling priming effects on microbial consumption of dissolved organic carbon in rivers. J. Geophys. Res. Biogeosci. **119**: 982–995. doi:10.1002/2013JG002599.

Huffman, E.W.D., and Stuber, H.A. 1985. Analytical methodology for elemental analysis of humic substances. *In* Humic substances in soil, sediment, and water. *Edited by* G.R. Aiken. Wiley-Interscience, New York.

Hughes, R.M., Kaufmann, P.R., and Weber, M.H. 2011. National and regional comparisons between Strahler order and stream size. J. N. Am. Benthol. Soc. **30**(1): 103–121. doi:10.1899/09-174.1.

Junk, W.J., Bayley, P.B., and Sparks, R.E. 1989. The flood-pulse concept in river-floodplain systems. *In* Proceedings of the International Large River Symposium. *Edited by* D.P. Dodge. Can. Spec. Publ. Fish. Aquat. Sci. **106**: 110–127.

Koenker, R., and Hallock, K.F. 2001. Quantile regression. J. Econ. Perspect. **15**: 143–156. doi:10.1257/jep.15.4.143.

Koprivnjak, J.F., Perdue, E.M., and Pfromm, P.H. 2006. Coupling reverse osmosis with electrodialysis to isolate natural organic matter from fresh waters. Water Res. **40**: 3385–3392. doi:10.1016/j.watres.2006.07.019. PMID:16952387.

Mazzei, P., and Piccolo, A. 2012. Quantitative evaluation of noncovalent interactions between glyphosate and dissolved humic substances by NMR spectroscopy. Environ. Sci. Technol. **46**(11): 5939–5946. doi:10.1021/es300265a.

McDowell, W.H., and Likens, G.E. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol. Monogr. **58**: 177–195. doi:10.2307/2937024.

McGlynn, B.L., and McDonnell, J.J. 2003. Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. Water Resour. Res. **39**: WR001525. doi:10.1029/2002WR001525.

McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., and Thorn, K.A. 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environ. Sci. Technol. **26**: 1388–1396. doi:10.1021/es00031a017.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., and Andersen, D.T. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. **46**: 38–48. doi:10.4319/lo.2001.46.1.0038.

McKnight, D.M., Hood, E., and Klapper, L. 2003. Trace organic moieties of dissolved organic material in natural waters. *In* Aquatic ecosystems: interactivity of dissolved organic matter. *Edited by* S.E. Findlay and R.L. Sinsabaugh. Academic Press, San Diego, Calif. pp. 71–96.

McLaughlin, C., and Kaplan, L.A. 2013. Biological lability of dissolved organic carbon in stream water and contributing terrestrial sources. Freshw. Sci. **32**: 1219–1230. doi:10.1899/12-202.1.

Mengistu, S.G., Quick, C.G., and Creed, I.F. 2013. Nutrient export from catchments on forested landscapes reveals complex nonstationary and stationary climate signals. Water Resour. Res. **49**: 3863–3880. doi:10.1002/wrcr.20302.

Meybeck, M. 1982. Carbon, nitrogen and phosphorus transported by world rivers. Am. J. Sci. **282**: 401–450. doi:10.2475/ajs.282.4.401.

Miller, M.P. 2012. The influence of reservoirs, climate, land use and hydrologic conditions on loads and chemical quality of dissolved organic carbon in the Colorado River. Water Resour. Res. **48**: W00M02. doi:10.1029/2012WR012312.

Miller, M.P., Susong, D.D., Shope, C.L., Heilweil, V.M., and Stolp, B.J. 2014. Continuous estimation of baseflow in snowmelt-dominated streams and rivers in the Upper Colorado River Basin: a chemical hydrograph separation approach. Water Resour. Res. **50**: doi:10.1002/2013WR014939.

Montgomery, DR . 1999. Process domains and the river continuum. J. Am. Water Resour. Assoc. **35**: 397–410. doi:10.1111/j.1752-1688.1999.tb03598.x.

Moran, M.A., Sheldon, W.N. Jr., and Zepp, R.G. 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. Limnol. Oceanogr. **45**: 1254–1264. doi:10.4319/lo.2000.45.6.1254.

Pacific, V., Jencso, K., and McGlynn, B.L. 2010. Variable flushing mechanisms and landscape structure control stream DOC export during snowmelt in a set of nested catchments. Biogeochemistry, **99**: 193–211. doi:10.1007/s10533-009-9401-1.

Pellerin, B.A., Saraceno, J.F., Shanley, J.B., Sebestyen, S., Aiken, G.R., Wollheim, W.M., and Bergamaschi, B.A. 2012. Taking the pulse of snowmelt: in situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. Biogeochemistry, **108**: 183–198. doi:10.1007/s10533-011-9589-8.

Pierson, S.M., Rosenbaum, B.J., McKay, L.D., and Dewald, T.G. 2008. Strahler Stream Order and Strahler Calculator Values in NHDPlus [online]. Available from ftp://ftp.horizon-systems.com/nhdplus/NHDPlusV1/NHDPlusExtensions/SOSC/SOSC_technical_paper.pdf.

Poff, N.L., Olden, J.D., Merritt, D.M., and Pepin, D.M. 2007. Homogenization of regional river dynamics by dams and global biodiversity implications. Proc.

Natl. Acad. Sci. U.S.A. **104**: 5732–5737. doi:10.1073/pnas.0609812104. PMID: 17360379.

Pomeroy, L.R. 1974. The ocean's food web: a changing paradigm. Bioscience, **24**: 499–504. doi:10.2307/1296885.

Poole, G.C. 2010. Stream hydrogeomorphology as a physical science basis for advances in stream ecology. J. N. Am. Benthol. Soc. **29**: 12–25. doi:10.1899/08-070.1.

Qualls, R.G., Haines, B.L., Swank, W.T., and Tyler, S.W. 2002. Retention of soluble organic nutrients by a forested ecosystem. Biogeochemistry, **61**: 135–171. doi:10.1023/A:1020239112586.

Raymond, P.A., and Saiers, J.E. 2010. Event controlled DOC export from forested watersheds. Biogeochemistry, **100**: 197–209. doi:10.1007/s10533-010-9416-7.

Raymond, P.A., Zappa, C.J., Butman, D., Bott, T.L., Potter, J., Mulholland, P., Laursen, A.E., McDowell, W.H., and Newbold, D. 2012. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. Limnol. Oceanogr. Fluids Environ. **2**: 41–53. doi:10.1215/21573689-1597669.

Schiff, S.L., Aravena, R., Trumbore, S.E., Hinton, M.J., Elgood, R., and Dillon, P.J. 1997. Export of DOC from forested catchments on the Precambrian shield of central Ontario: clues from 13C and 14C. Biogeochemistry, **36**: 43–65. doi:10.1023/A:1005744131385.

Schlesinger, W.H., and Melack, J.M. 1981. Transport of organic carbon in the world's rivers. Tellus, **33**: 172–187. doi:10.1111/j.2153-3490.1981.tb01742.x.

Sedell, J.R., Richey, J.E., and Swanson, F.J. 1989. The river continuum concept: a basis for the expected ecosystem behaviour of very large rivers? *In* Proceedings of the International Large River Symposium. *Edited by* D.P. Dodge. Can. Spec. Publ. Fish. Aquat. Sci. **106**: 49–55.

Simpson, M.J., and Simpson, A.J. 2012. The chemical ecology of soil organic matter molecular constituents. J. Chem. Ecol. **38**: 768–784. doi:10.1007/s10886-012-0122-x. PMID:22549555.

Spencer, R.G.M., Butler, K.D., and Aiken, G.R. 2012. Dissolved organic matter and chromophoric dissolved organic matter properties of rivers in the U.S.A. J. Geophys. Res. Biogeoci. **117**: G03001. doi:10.1029/2011JG001928.

Stedmon, C.A., Markager, S., and Bro, R. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Mar. Chem. **82**: 239–254. doi:10.1016/S0304-4203(03)00072-0.

Stenger-Kovács, C., Tóth, L., Tóth, F., Hajnal, É., and Padisák, J. 2014. Stream order-dependent diversity metrics of epilithic diatom assemblages. Hydrobiologia, **721**: 67–75. doi:10.1007/s10750-013-1649-8.

Strahler, A.N. 1957. Quantitative analysis of watershed geomorphology. Trans. Am. Geophys. Union, **38**: 913–920. doi:10.1029/TR038i006p00913.

Sun, L., Perdue, E.M., Meyer, J.L., and Weis, J. 1997. Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river. Limnol. Oceanogr. **42**: 714–721. doi:10.4319/lo.1997.42.4.0714.

Thompson, S.E., Basu, N.B., Lascurain, J., Jr., Aubeneau, A., and Rao, P.S.C. 2011. Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. Water Resour. Res. **47**: W00J05. doi:10.1029/2010WR009605.

Thorn, K.A., and Cox, L.G. 2009. N-15 NMR spectra of naturally abundant nitrogen in soil and aquatic natural organic matter samples of the International Humic Substances Society. Org. Geochem. **40**: 484–499. doi:10.1016/j.orggeochem.2009.01.007.

Thorp, J.H., and Delong, M.D. 2002. Dominance of autochthonous autotrophic carbon in food webs of heterotrophic rivers. Oikos, **96**: 543–550. doi:10.1034/j.1600-0706.2002.960315.x.

Tiwari, T., Laudon, H., Beven, K., and Ågren, A.M. 2014. Downstream changes in DOC: inferring contributions in the face of model uncertainties. Water Resour. Res. **50**: 514–525. doi:10.1002/2013WR014275.

Tockner, K., Malard, F., and Ward, J.V. 2000. An extension of the flood pulse concept. Hydrol. Process. **14**: 2861–2883. doi:10.1002/1099-1085(200011/12)14:16/17<2861::AID-HYP124>3.0.CO;2-F.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R., and Cushing, C.E. 1980. The river continuum concept. Can. J. Fish. Aquat. Sci. **37**(1): 130–137. doi:10.1139/f80-017.

Ward, J.V., and Stanford, J.A. 1983. The serial discontinuity concept of lotic ecosystems. J. N. Am. Benthol. Soc. **8**: 2–8.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. **37**: 4702–4708. doi:10.1021/es030360x. PMID:14594381.

Wetzel, R.G. 1995. Death, detritus and energy flow in aquatic ecosystems. Freshw. Biol. **33**: 83–89. doi:10.1111/j.1365-2427.1995.tb00388.x.

Worrall, F., Burt, T., and Shedden, R. 2003. Long term records of riverine dissolved organic matter. Biogeochemistry, **64**: 165–178. doi:10.1023/A:1024924216148.