CONCEPTS & SYNTHESIS

EMPHASIZING NEW IDEAS TO STIMULATE RESEARCH IN ECOLOGY

Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept

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Abstract. Hydrological precipitation and snowmelt events trigger large "pulse" releases of terrestrial dissolved organic matter (DOM) into drainage networks due to an increase in DOM concentration with discharge. Thus, low-frequency large events, which are predicted to increase with climate change, are responsible for a significant percentage of annual terrestrial DOM input to drainage networks. These same events are accompanied by marked and rapid increases in headwater stream velocity; thus they also "shunt" a large proportion of the pulsed DOM to downstream, higher-order rivers and aquatic ecosystems geographically removed from the DOM source of origin. Here we merge these ideas into the "pulse-shunt concept" (PSC) to explain and quantify how infrequent, yet major hydrologic events may drive the timing, flux, geographical dispersion, and regional metabolism of terrestrial DOM. The PSC also helps reconcile long-standing discrepancies in C cycling theory and provides a robust framework for better quantifying its highly dynamic role in the global C cycle. The PSC adds a critical temporal dimension to linear organic matter removal dynamics postulated by the river continuum concept. It also can be represented mathematically through a model that is based on stream scaling approaches suitable for quantifying the important role of streams and rivers in the global C cycle. Initial hypotheses generated by the PSC include: (1) Infrequent large storms and snowmelt events account for a large and underappreciated percentage of the terrestrial DOM flux to drainage networks at annual and decadal time scales and therefore event statistics are equally important to total discharge when determining terrestrial fluxes. (2) Episodic hydrologic events result in DOM bypassing headwater streams and being metabolized in large rivers and exported to coastal systems. We propose that the PSC provides a framework for watershed biogeochemical modeling and predictions and discuss implications to ecological processes.

Key words: climate; DOM; New England; nutrients; pulse event; scaling; snowmelt event; USA; watershed.

INTRODUCTION

Dissolved organic matter (DOM) is central to the ecology and chemistry of inland waters as an energy and nutrient source, transporter of heavy metals and pollutants, and control on light attenuation. DOM biogeochemistry has been studied intensively for decades, yet continues to receive attention due to fundamental uncertainties (Tank et al. 2010). Key research foci involving DOM include the controls on its movement from the terrestrial landscape, modification of DOM during its transit through streams and rivers

and toward the ocean, the effects of DOM composition on ecosystem function, and its role in watershed and global C cycling. Here we present a new conceptual theory, the pulse-shunt concept (PSC), that links these foci under the macrosystems framework, which attempts to link drainage network structure and function to temporal variation in hydrological and biogeochemical drivers across spatial scales (Heffernan et al. 2014).

There are numerous conceptual models for DOM dynamics in drainage networks. The river continuum concept (RCC), which utilizes drainage network scaling, has been a central tenet in stream and watershed biogeochemistry for decades. According to the RCC, downstream communities are adapted to capitalize on organic matter inefficiencies of upstream communities (Vannote et al. 1980),

and the diversity of DOM compounds decreases with stream order due to the uptake of DOM in low-order streams. The RCC received further attention with respect to organic carbon in context of the spiraling concept that provided a reach-scale mechanistic model for DOM removal in sediment biofilms (Newbold et al. 1982). Thorp et al. (2006) also utilized drainage network scaling coupled with patch dynamics for the riverine ecosystem synthesis (RES), which has recently been expanded upon in the macrosystems framework (McCluney et al. 2014). The RES extends previous efforts by incorporating functional units such as floodplains (Junk et al. 1989, Ward and Stanford 1995) into the linear dynamics of the RCC to constrain drainage network function.

The importance of hydrologic variation and disturbance for river ecology has also been recognized for decades (Poff et al. 1997, Fisher et al. 1998, Stanley et al. 2010), yet has not been fully incorporated into watershed biogeochemical modeling. The PSC attempts to integrate and extend these various concepts and incorporate a more quantitative approach for evaluating watershed hydrology and discharge variations within the river network. The basic premise behind the PSC is straightforward. Labile DOM is pulsed off of the landscape via surface and subsurface pathways during high-discharge events that are associated with rainfall or snowmelt. The terrestrially derived DOM is shunted rapidly downstream due to increases in stream water velocities that occur during the events. The reduction in residence time perturbs the downstream gradient in DOM lability and compositional diversity established during base-flow conditions, leading to greater export of DOM from the riverine network that is biochemically reactive and has retained its terrestrial signature.

Here we argue that hydrologic events are a dominant driver of DOM dynamics at the large watershed scale. We introduce and review scaling and hydraulic laws that can be used to demonstrate and model the PSC. We also discuss how the PSC can account for patch dynamics and variation in watershed connectivity in order to determine how watershed hotspots and variation in form impacts DOM dynamics.

The pulse: hydrological events mobilize DOM.—The pulse component of the PSC is well documented. Early studies reported that DOM concentrations in stream water increased with discharge during snowmelt events (Hornberger et al. 1994, Boyer et al. 2000). Over the ensuing decades, research has confirmed the importance of precipitation and snowmelt events to total annual DOM export across a range of watersheds and seasons (Ciaio and McDiffett 1990, Brown et al. 1997, Hinton et al. 1998, Volk et al. 2002, Even et al. 2004, Wellington and Driscoll 2004, Inamdar et al. 2006, Saunders et al. 2006, Dhillon and Inamdar 2014, Jung et al. 2014, Lambert et al. 2014). Analyzing 5000 United States Geological Survey (USGS) measurements of DOM concentration (dissolved organic carbon, DOC) for 31 small forested watersheds in the east-

ern United States, Raymond and Saiers (2010) demonstrated that 86% of annual forested DOC export occurs during hydrologic events and that 60% of this event-associated export occurs during large events that make up only 5% of days of the year. Furthermore, a few recent studies show that the increase in DOM concentrations with discharge holds for tropical storms and hurricanes, and the export of DOM during these events approach the mean annual DOM export during non-hurricane years (Yoon and Raymond 2012, Caverly et al. 2013, Dhillon and Inamdar 2013, Brown et al. 2014, Jung et al. 2014).

Empirical observations also have repeatedly shown that the chemical composition and reactivity of soil water and stream water DOM changes markedly during rainfall and snowmelt (Easthouse et al. 1992, Hagedorn et al. 2000, Buffam et al. 2001, Kaushal and Lewis 2003, Volk et al. 2005, Hood et al. 2006, Dalzell et al. 2007, Vidon et al. 2008, Sanderman et al. 2009, Jung et al. 2014). For example, elevated lignin phenol concentrations during an event have been attributed to enhanced leaching of surface vegetation and organic-rich upper soil layers and the bypassing of lower soil profiles with a strong affinity for DOM (Hernes et al. 2008). Similarly, ^{13}C and ^{14}C of DOC measured with changing discharge indicate the flushing of less processed (more enriched ^{13}C), younger (higher ^{14}C) DOC with increased flow (Schiff et al. 1997, Neff et al. 2006, Raymond et al. 2007, Sanderman et al. 2009). Events also tend to export DOM with a higher degree of aromaticity and humic content (Hood et al. 2006, Vidon et al. 2008, Fellman et al. 2009). Recent work in Harvard Forest demonstrates the importance of events to the export of bacterially labile DOM. Similar to bulk DOM, the percentage and flux of labile DOM increases with hydrologic events (Wilson et al. 2013). Other studies have documented an increase in the lability and photo-reactivity of stream water DOM with events (Buffam et al. 2001, Fellman et al. 2008, 2009, Holmes et al. 2008, Pellerin et al. 2012, Singh et al. 2014).

Based on these findings, we infer that event-based delivery of DOM from terrestrial sources to streams occurs ubiquitously, particularly in temperate watersheds, and that these punctuated deliveries comprise a major fraction of terrestrial DOM subsidies to streams and rivers. Although the pulsed nature of DOM movement from the landscape is well recognized, the phenomenon is poorly integrated into DOM theory and modeling.

The shunt: rapid downstream transport.—The characteristics of the shunt reflect increases in stream water velocities and corresponding decreases in solute residence times that are associated with high-discharge events. The PSC postulates a relationship between the size of the hydrologic event and the distance DOM travels before it is removed or modified due to microbial or photochemical reactions. This characteristic length scale is governed by properties that affect DOM reaction rates (e.g., temperature, stream water composition, DOM lability) and by the geomorphology of the drainage network, which governs the distribution in stream water residence times.
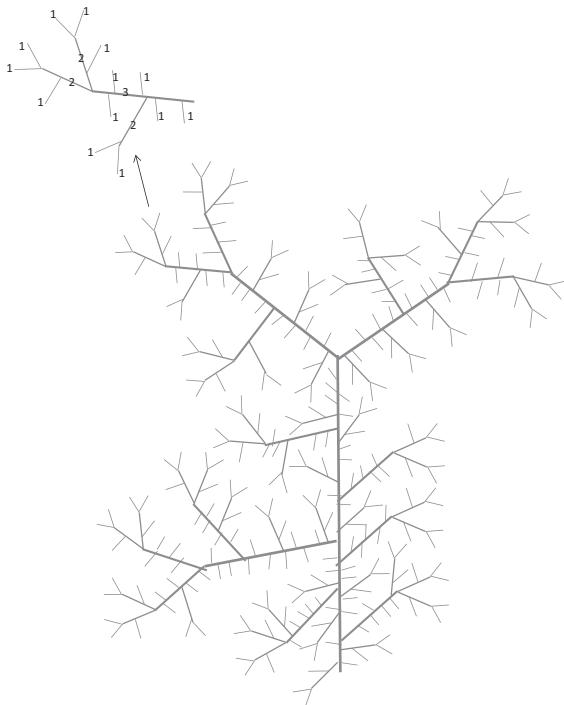
FIG. 1. A visual representation of the first five orders of the representative eighth-order New England (USA) watershed used in the model.

The basic idea of the shunt has recently been explored in the context of nutrient spiraling for nitrogen and phosphorus. These studies use different mathematical approaches to evaluate the relative importance of the reaction rate and residence time. Wollheim et al. (2006) presented a scaling approach to quantify the uptake velocity for nutrients and concluded that large rivers "potentially exert considerable influence over nutrient exports." Ensign and Doyle (2006) performed a metadata analysis of 404 spiraling experiments and concluded that cumulative NO_3 and PO_4 uptake increase with stream order, thereby illuminating the importance of large rivers to nutrient processing. Finally, Hall et al. (2013) employed hydraulic-scaling laws to investigate the relationships among nutrient reaction rates, stream size, and residence times, and argued for a stronger role of large streams in regulating nutrient transport. These studies reach qualitatively similar conclusions on the responses of nutrient spiraling to reactions rates and residence times; however, they do not address the coupling of spiraling with the pulse of terrestrial materials into the surface water network.

Conceptual and Quantitative Framework

The PSC is intended to explain, in a general sense, the manner in which discharge variation influences the terrestrial supply of DOM to headwater streams and the utilization of DOM along the drainage network. To evaluate the hypothesized relationships among flow and DOM supply and utilization, we performed a suite of calculations on surface water and DOM routing through a model drainage network over a mean annual range of flow conditions. For clarity and simplicity, we present the basic quantitative framework of the PSC using a hypothetical watershed and drainage network using these explicit assumptions: (1) 200 000 km² temperate forest watershed, and (2) dendritic eighth-order drainage network characterized by a main-stem length of 500 km; see Fig. 1 and Table 1.

In the following sections, we combine principles and mathematical elements from several classical hydrology, geomorphology, and biogeochemistry models to form the base framework of the PSC. The logic behind the PSC's quantitative framework is the sequential addition of mathematical equations describing the following properties: (1) drainage network connectivity and geomorphology, (2) hydraulic geometry and scaling, (3) DOM concentration and discharge relationships, (4) DOM bioreactivity, and (5) reach-level DOM transfers and downstream subsidies. En masse, these routing calculations describe the change in DOM concentrations along the drainage network in response to discharge variation, mixing with other waters, and rate-limited decomposition.

Using scaling laws to approximate watershed morphology.—The connectivity and hierarchical nature of drainage basins have long been studied by hydrologists (Horton 1945, Strahler 1957). Horton and Strahler derived a branching-tree classification in which headwater streams have a Strahler stream order of 1 that increases with each confluence of two streams of the same order (Fig. 1 inset). Horton (1945) presented a framework for determining the number and length of stream orders within a basin. These "Horton ratios," which recognize the self-similar fractal nature of drainage basin networks, describe the ratio of length (R_L), area (R_a), or number (R_n) of streams of order o to the next higher stream order $o + 1$ (Dodds and Rothman 1999):

$$R_L = L_{o+1}/L_o \qquad (1)$$

$$R_a = a_{o+1}/a_o \qquad (2)$$

$$R_n = n_{o+1}/n_o \qquad (3)$$

where L is mean stream length, a is watershed area, and n is the number of streams, respectively. We performed a scaling-law analysis of New England (the northeastern portion of the United States) using NHDplus to estimate values of R_L and R_a of 1.9 and 4.6, respectively (NHDplus data set *available online*).[4] Through further analysis of the self-similarity

[4] http://www.horizon-systems.com/nhdplus/

TABLE 1. River network attributes for a hypothetical eighth-order forested New England watershed.

Order	No. stream segments	Mean length (km)	Mean basin area (km²)	Velocity (m/s) for $Q = 0.83$	Residence time (d) for $Q = 0.83$	Velocity (m/s) for $Q = 0.1$	Residence time (d) for $Q = 0.1$
1	25 581	5.6	8	0.26	0.25	0.17	0.36
2	5561	10.6	21	0.31	0.40	0.21	0.58
3	1209	20.2	97	0.41	0.57	0.28	0.85
4	263	38.4	447	0.55	0.80	0.37	1.21
5	57	72.9	2055	0.76	1.10	0.49	1.71
6	12	138.5	9452	1.07	1.50	0.68	2.37
7	3	263.2	43 478	1.51	2.01	0.93	3.24
8	1	500.0	200 000	2.18	2.65	1.32	4.37

Notes: Stream number, length, and basin area approximate data from NHDplus Hydrosheds (http://www.horizon-systems.com/nhdplus/). Also provided are the velocity and residence time for stream orders for discharge (Q; cm/d) at the effective discharge for dissolved organic carbon (DOC) assuming annual discharge data from three forested headwater streams in New England (Fig. 2) and a nominal discharge of 0.1 cm/d.

of basins, Dodds and Rothman (1999) demonstrated that $R_a \sim R_n$.

Tokunaga (1966) developed scaling laws that express patterns of stream connectivity in watersheds. In particular, Tokunaga's law predicts the number of lower-order streams (T_v) draining into a higher-order stream

$$T_v = T_1 (R_t)^{0-1} \qquad (4)$$

where T_1 is Tokunaga's constant and R_t is the Tokunaga ratio. Eq. 4 can be used, for example, to determine the number of first-order streams ($v = 1$) that feed a fourth-order stream ($o = 4$), and, more generally, to generate a Tokunaga table that quantifies connectivity among all streams of all orders of a basin. Recent work demonstrates a climate dependence of Tokunaga parameters (Zanardo et al. 2013), although research on physical (e.g., geologic) controls on these parameters are lacking.

Using Eqs 1–4 and assuming an eighth-order basin area of 200 000 km² yields a drainage network composed of more than 30 000 stream segments (Table 1). Stream lengths range from 5.6 km for first-order streams to 263.2 km for seventh-order rivers, while watershed areas scale from 8 km² for headwater catchments to 43 000 km² for watersheds drained by seventh-order streams. Inspection of the corresponding Tokunaga table illustrates an approximate doubling of the number of connections for each unit increase in the difference between stream orders (Table 2). These estimates of connectivity were made by setting R_t equal to R_l, as prescribed by Dodds and Rothman (1999), and adjusting estimates of T_1 such that values of T_v computed with Eq. 4 matched those reported in NHDplus for the New England region. This optimization yielded a best-fit T_1 value of 2.7.

Water and DOM routing through the model drainage network.—Surface water runoff within the hypothetical

basin was assumed to be generated from first-order watersheds, which cover the entire area of the 200 000 km² basin and were considered to be the sole source of DOM to the drainage system. We represented discharge variability of first-order streams by averaging flow-frequency curves quantified from discharge data collected from three headwater streams located at latitudes that span the New England region (Fig. 2). The flow-frequency curve was estimated by grouping discharge into 15 bins. The highest bin was for discharges greater than 12 cm/d, and the bounds on each lower bin were determined by dividing the proceeding bound in half (e.g., 12, 6, 3…). A flow-frequency curve quantifies the likelihood ($f(Q)$) that discharge (Q) will equal a given value. In the headwater streams evaluated here, daily discharges of ∼0.15 cm/d occur most frequently (Fig. 2).

Concentrations of DOM exported from headwater catchments co-vary with stream discharge (Hinton et al. 1998, Boyer et al. 2000, Buffam et al. 2001, Kaplan et al. 2006, Raymond and Saiers 2010). Based on the findings of Raymond and Saiers (2010), we assumed the concentration of DOM exported from the terrestrial reservoir to first-order streams (C_1^{in}) increases approximately as a power-law function of discharge:

$$C_1^{in} = g Q_1^h \qquad (5)$$

where the subscript 1 denotes first-order streams, Q is volumetric discharge per watershed area, and g and h are empirical constants, which, according to the analysis of Raymond and Saiers (2010), equal 1.02 and 0.345, respectively.

Stream water DOM is susceptible to rate-limited decomposition and thus DOM concentrations exiting the mouths of first-order streams are lowered by an amount that depends on the stream-reach residence time and a decomposition rate constant. Provided that a linear kinetics reaction governs DOM decomposition, stream water DOM concentration at the outlets of
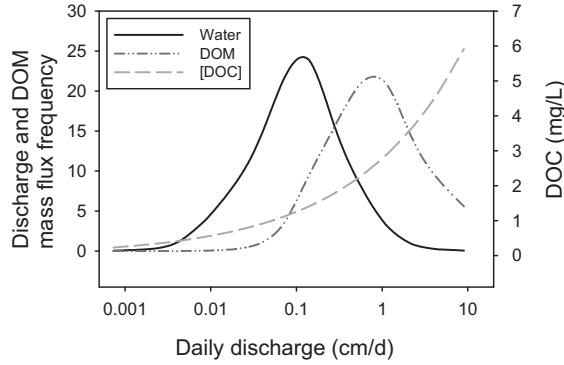
Fig. 2. Discharge frequency and the contribution of events to dissolved organic carbon (DOC) export for a representative first-order New England watershed. The discharge frequency (shown on a log scale) was calculated for 15 discharge bins from three small United States Geological Survey (USGS) watersheds (USGS sites 01093800, 01105600, 0106400) spanning the latitude of New England. The figure depicts a smoothed curve of these bins. DOC concentration was estimated from these discharge data using equations from Raymond and Saiers (2010) to calculate DOC according to Eqs 10–12, and is shown as the dashed line. According to this figure, the peak in daily discharge frequency of dissolved organic matter (DOM) is at a daily discharge of ~0.15 cm/d. The DOC flux frequency peaks at a discharge closer to 0.8 cm/d, or where the DOC concentration curve crosses the flow-frequency curve. This is known as the effective discharge for DOC.

first-order watersheds (C_1^{out}) can be described as function of C_1^{in} and residence time

$$C_1^{out} = C_1^{in} e^{-kT_1} \qquad (6)$$

where T_1 is the DOM residence time within first-order reaches and k is the rate constant that quantifies DOM decomposition within these reaches.

The mass flux of DOM from a first-order watershed can be obtained by integrating the product of Eq. 6 and the flow frequency ($f(Q)$) described previously:

$$F_1^{out} = A_1 \int_{Q_{1a}}^{Q_{1b}} f(Q_1) C_1^{out} dQ_1 \qquad (7)$$

where A_1 is the mean area of the first-order watersheds and Q_{1a} and Q_{1b} refer to the discharge interval of the flow-frequency curve over which the DOM flux is calculated.

The flux of DOM from first-order streams (F_1^{out}) was apportioned to higher-order streams according to estimates of drainage-network connectivity (Table 2). Second- through seventh-order streams similarly contribute water and DOM to higher-order streams of the drainage network. The total input flux of DOM to a stream of order o (F_o^{in}) can be expressed as

$$F_1^{out} = A_1 \int_{Q_{1a}}^{Q_{1b}} f(Q_1) C_1^{out} dQ_1 \text{ for } o = 2 \text{ to } 8 \qquad (8)$$

where the subscript i denotes the order of contributing streams and m_{ilo} is the number of ith-order streams that drain to the oth-order stream (see Table 2).

The difference between input and output fluxes of DOM for a particular stream order depends on the kinetics of biogeochemical processes that remove DOM from the water column. Assuming decay rates vary linearly with stream water DOM concentrations, the relationship between input and output fluxes for a stream of order o is

$$F_o^{out} = F_o^{in} e^{-k_o T_o} \text{ for } o = 2 \text{ to } 8 \qquad (9)$$

where k_o is a rate constant for DOM decomposition within oth-order streams. We based our initial analysis on the simplifying assumption that k is independent of stream order and set $k_1, k_2, \ldots, k_8$ equal to 0.22 d^{-1}, which is consistent with values estimated

TABLE 2. A Tokunaga (1966) table depicting the relative connectivity among stream orders for the hypothetical eighth-order river drainage network used in the pulse shunt concept (PSC) model example.

Stream order	1	2	3	4	5	6	7	8
1		2.7	5.1	9.7	18.5	35.2	66.9	127.0
2			2.7	5.1	9.7	18.5	35.2	66.9
3				2.7	5.1	9.7	18.5	35.2
4					2.7	5.1	9.7	18.5
5						2.7	5.1	9.7
6							2.7	5.1
7								2.7

Notes: Values are the number of streams of an order (rows) that drain into a higher stream order (columns; no streams drain into first-order streams). The table was determined by using assumptions in order to approximate the stream numbers reported in NHDplus for this region.

from stream-release experiments with DOM (Kaplan et al. 2006).

Specification of the DOM output fluxes for each stream order of the drainage network relies on estimates of residence time. Residence time in stream order o (T_o) equals the ratio of stream length (L_o) to mean stream water velocity (V_o). We calculated L_o for each stream order with Eq. 1 and estimated V_o from discharge through application of published scaling relationships:

$$V_o = aQ_o^b \text{ for } o = 1 \text{ to } 8 \qquad (10)$$

where a and b are empirical constants (Leopold and Maddock 1953, Raymond et al. 2012). Similarly to Raymond et al. (2013), we used the mean of two compilations for a and b, or −1.35 and 0.20, respectively.

Summary of DOM routing model.—This model, then, estimates the export of DOM from first-order watersheds (Eqs 5–7) and describes how the mean DOM input fluxes (Eq. 8) and DOM output fluxes (Eqs 9, 10) change with increasing stream order owing to mixing of waters from upstream reaches and time-dependent DOM decomposition. The amount of DOM utilized within a particular stream order can be readily quantified as the difference between F_o^{in} and F_o^{out}. The DOM fluxes can be calculated for any discharge interval of the flow-frequency curve (Fig. 2) to evaluate the surface water transport of DOM for a narrow range of discharge events or, alternatively, for the full range of flows observed during an annual period.

PSC Model Reveals Emergent Macrosystem Watershed Properties

Consideration of the PSC in the context of a simplified, hypothetical watershed provides insights into the role of interactions between transport and biogeochemistry in the fate of DOM within river basins. This exercise also illuminates emergent properties of DOM cycling in large watersheds that can be classified as macrosystems (Heffernan et al. 2014). The first emergent property is related to DOM subsidies along large-river continua with hierarchical drainage networks. According to our model, upstream subsidies to a given stream order are largely restricted to DOM contributions from the next three smaller stream orders (Fig. 3). In particular, our calculations reveal that streams of order o receive ~50% of their DOM subsidy from the preceding stream order ($o−1$), ~25% of their DOM from streams of order $o−2$, and 12% from streams of order $o−3$. This trend largely reflects the insignificant contribution of discharge from orders $<o−3$. Thus, more than 85% of the DOM subsidy to an eighth-order stream is supplied by fifth-, sixth-, and
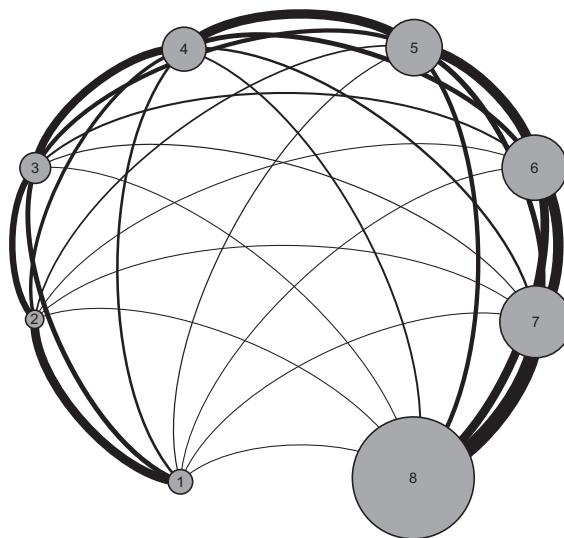
FIG. 3. A network graph for predicted annual uptake of terrestrial DOC among stream orders for a hypothetical large forested watershed using the pulse-shunt concept (PSC) modeling framework and assumptions outlined in this study. The amount of utilized DOC in each stream order is depicted by the size of the circle. The amount of this utilized DOC that was added from each preceding stream order is depicted by the size of the connected lines. In this example, the PSC predicts an annual DOC input from the terrestrial landscape of 1.8 g·m⁻²·yr⁻¹, and total drainage network uptake (the sum of all lines) of 1.3 g·m⁻²·yr⁻¹. For stream order 8, 46% of the utilized organic carbon was from stream order 7 (SO_7), 27% from SO_6, 14% from SO_5, 7% from SO_4, 3.3% from SO_3, 1.5% from SO_2, and 1.2% from SO_1.

seventh-order streams. It predicts a small importance for first-order streams at fifth order and higher. This relationship for upstream DOM subsidies can be generally expressed as

$$R_s = \frac{F_{o+1}}{F_o} \qquad (11)$$

where R_s is the ratio of stream subsidy, and F_o is the flux of a constituent from stream order o (the contribution of stream order n to stream order $n + 1$). For this test watershed, our simple model predicts $R_s \approx 2$, which approximates the values of R_L and R_t in Eqs 1 and 4, respectively.

Application of the PSC additionally illuminates the importance of hydrologic event intensity in regulating DOM fluxes through large river networks. Our model results demonstrate that relatively few days with higher discharge are responsible for a surprisingly large proportion of the annual DOM flux from the landscape and the amount of reactive DOM in the drainage network. The most frequent daily discharge (i.e., peak of the stream flow-frequency curve ($f(Q)$), is 0.15 cm/d; however, stream water DOM concentrations (C) increase monotonically with Q, and hence, the product $f(Q)·C$ peaks at a stream flow of ~0.8 cm/d (Fig. 2). This peak in the $f(Q)·C$

curve is known as the effective discharge for DOM, or the discharge where the most work is done in exporting DOM (Doyle et al. 2005). The effective discharge in the DOM-uptake flux (DOM consumption rate) similarly occurs at a stream flow of ~0.8 cm/d (data not shown). Hence, the uptake of DOM in the drainage basin is highest during low-frequency, high-discharge days when the flux of DOM from the landscape is high.

The uptake of DOM during low-frequency, high-flux days is greatest in larger streams because the majority of DOM is shunted through low-order streams. We estimate that, for an average hydrologic year, the total uptake of DOM increases as stream order increases (Fig. 3). Although DOM uptake increases in a consistent fashion between second- and seventh-order streams, uptake jumps substantially in the eighth-order, main-stem river, owing to the long residence time and the high loading of DOM from the entire drainage network. On average, the model predicts a ~1.6% increase in the fraction of total uptake with each increase in stream order, while the cumulative annual DOM uptake is 22% for stream orders 1–3 and 54% for stream orders 6–8.

Another way to explore the importance of hydrologic event intensity is to compare 2 year with identical overall water yield, but a different frequency of events. Mean annual stream yield for the eastern United States is 100 cm (Raymond and Saiers 2010). If the 100 cm is delivered over 100 1-cm/d discharge events, the flux of terrestrial DOM to the drainage network is ~2.8 g·m^{-2}·yr^{-1}, with ~0.45 g·m^{-2}·yr^{-1} (25%) making it to the ocean (Table 3). On the other hand, if the 100 cm is delivered as 20 5-cm/d events, the flux from the landscape is 4.8 g·m^{-2}·yr^{-1}, with 1.9 g·m^{-2}·yr^{-1} (40%) making it to the ocean (Table 3). Thus, under these two different scenarios, the change in event magnitude increases the transfer of terrestrial DOM to the drainage network by a factor of 1.7. Moreover, the export of DOM to the coast increases by a factor of 2.7 because the fraction of DOM consumed during transit through the drainage network decreases with increasing event size (Table 3). Finally, even though the percentage of DOM removed during the less

frequent larger storm scenario decreases, the total DOM consumed in the drainage network during these events increases from ~2.1 to 3.0 g·m^{-2}·yr^{-1} due to the larger transport of terrestrial DOM into the drainage network.

The impact of variation in event size on DOM dynamics can also be explored with data from a USGS gauging station. Station 01093800 utilized in the model (Fig. 2) has a 40-year record with a mean (±SD) discharge of 68.4 ± 19.3 cm/yr. The total water yields were similarly high in 1975 (80.0 cm) and 1984 (82.3 cm), but the frequency distribution in daily discharge differed between the 2 yr. Although the annual water yield differed by only ~3%, the DOM fluxes from the landscape were 1.96 vs. 2.31 g·m^{-2}·yr^{-1} for 1975 and 1984, respectively, a difference of 18%. The frequency of high-discharge events was greater in 1984 than in 1975, with 81% of carbon being exported in 1984 on days when discharges >0.75 cm/d compared to only 63% in 1975. Furthermore, a smaller fraction of terrestrially derived DOM was utilized within the stream network during 1984, when high-discharge events occurred with greater frequency, and hence the mass of DOM exported to the coast was 1.5-fold greater in 1984 (0.63 g/m^2) than in 1975 (0.42 g/m^2).

We can also explore how seasonality in both DOC delivery and uptake impact the PSC. According to the Q_{10} law, bacterial respiration and production are affected by temperature (Bott and Kaplan 1985, Sander and Kalff 1993, Fischer et al. 2002, Peierls and Paerl 2010), with the rates of these processes generally increasing by a factor of 2–3 for every 10°C rise in temperature. In fact, a Q_{10} of 2 for the bacterial uptake of riverine DOM has been demonstrated in the lab (Raymond and Bauer 2000). We can approximate the temperature effect on DOM processing within the drainage network by assuming a Q_{10} value of 2 and that the value of the decay coefficient ($k = 0.22$ d^{-1}) used in our previous analysis applies at 20°C. Invoking these assumptions for a large discharge event (2.25 cm/d) that leads to a terrestrial DOM pulse of 82.5 mg·m^{-2}·d^{-1} results in 2.3 times greater DOM uptake within the channel network during the summertime

Table 3. The impact of discharge event size on fluxes of DOC off the landscape and to the ocean.

Size of event (cm/d)	Annual number of events	Terrestrial DOC input (g·m^{-2}·yr^{-1})	Removal (%)	Export to ocean (g·m^{-2}·yr^{-1})
0.2	500	1.59	85	0.23
0.5	200	2.12	79	0.45
1	100	2.77	74	0.71
5	20	4.83	61	1.87
10	10	6.14	56	2.73

Note: To arrive at these estimates, the model was run five different times with simplified hydrograms that had a single event size but a total discharge of 100 cm/yr.

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(25°C) than wintertime (5°C). During winter months, ~70% of the DOM escapes processing, while in summer months only 20% escapes uptake in the drainage network. Thus, seasonal changes in temperature play a potentially important role in riverine DOM uptake and export.

The delivery of DOM to drainage networks is also correlated to temperature. Numerous studies using high temporal resolution data sets from temperate watersheds have now reported the concentration of DOM during a summer discharge event is higher than for the same discharge during colder months (Raymond and Saiers 2010, Wilson et al. 2013). With respect to fluxes out of a watershed, an increase in terrestrial DOM loading to drainage networks at higher temperatures could provide a compensating effect to the increase in uptake due to higher k's for warmer months. We can adjust concentrations for temperature using results from the literature (Raymond and Saiers 2010) so that

$$C_1^{in} = gQ_1^h + (W_t - 15) \times 0.15 \qquad (12)$$

where W_t is the water temperature (°C). Effectively, Eq. 12 assumes that the concentration calculated using Eq. 5 was for a standard temperature of 15°C and that a 1°C change in water temperature increases the concentration by 0.15 mg/L for water temperatures higher than 15°C and decreases the concentration by 0.15 mg/L for water temperatures lower than 15°C. The 0.15 in Eq. 12 was approximated from the relationship between temperature and DOC found in Raymond and Saiers (2010), and is conservative compared to a recent study (Wilson et al. 2013). Comparing winter with summer, Eq. 12 estimates a ~2.4 times increase in DOC concentration in the summer and therefore flux of terrestrial DOC into the drainage network with a 2.25-cm/d discharge event (Table 4). However, because the decomposition constant increases by a factor of 4 with a 20°C increase in temperature and the flux of terrestrial DOC into the drainage network is higher, the summer uptake of terrestrial DOC increases by a factor of 5.7 (Table 4). These simple calculations highlight the potential importance of warm weather events for subsidizing the allochthony of drainage networks.

Caveats, Watershed Complexity, Sensitivity, and Future Research Needs

For explanatory purposes, this preliminary version of the PSC does not yet account for functional landscape units (e.g., river ecosystem synthesis concept; Thorp et al. 2006) other than uplands. There are various landscape units that could be integrated into our modeling approach. In particular, functional units that regulate addition of DOM to drainage networks

TABLE 4. Results from an analysis where both the concentration of DOC and the decomposition constant (k) were allowed to vary as a function of temperature.

Flux	5°C	15°C	25°C
Terrestrial DOC input (mg·m⁻²·d⁻¹)	48.8	82.5	116.3
Terrestrial DOC uptake (mg·m⁻²·d⁻¹)	16.3	45.7	92.3
Terrestrial DOC export (mg·m⁻²·d⁻¹)	32.5	36.8	24
DOC (mg/L)	2.2	3.7	5.2
Uptake (%)	33	55	79

Notes: Shown here is the variation in terrestrial DOC input to the drainage network, uptake within the drainage network, and export out of the drainage network by varying concentration and k. The same discharge frequency statistics as the main example were utilized.

and alter the decomposition constant and residence time should be considered (Fig. 4). Fringing wetlands and riparian zones, for example, contribute DOM to streams along the continuum, and new studies should determine the relationship between these functional units and stream order and discharge events (Battin et al. 2008, Stanley et al. 2012). The spatial location of reservoirs, hyporheic zones, and floodplains are also potentially important functional units (McCluney et al. 2014, Fig. 4). The relative importance of these could vary with stream order and respond predictably to events and can be incorporated into the PSC. Hyporheic zones, for instance, are likely important in regulating residence times in low-order systems, while reservoirs are generally more important in larger rivers. It is also possible that these functional units could be included in a modeling framework as coefficients that alter input or removal rates.

In addition to functional units, other abiotic and biotic factors should be considered in light of the PSC. DOM decomposition rates are also sensitive to the composition of DOM and the community of microbes present. Photo-oxidation, and hence the level of irradiance, may also be important in regulating DOM concentrations, particularly in coastal zones, where there is little canopy shading and concentrations of suspended sediments are low (Spencer et al. 2009). Photo-oxidation in rivers can also be limited by suspended sediments, which will also respond to events. While more complex treatments of DOM reaction within the pulse-shunt framework are theoretically tractable, new field-based measurements will be necessary to constrain their parameterization.

It is important to note that although it is argued here that DOM uptake is lower in small streams at annual and decadal time scales, the uptake in headwater streams is still critically important to the biogeochemistry, stability, and ecology of upland, forested watersheds. Furthermore, the PSC, as currently described, focuses on the transport of terrestrial
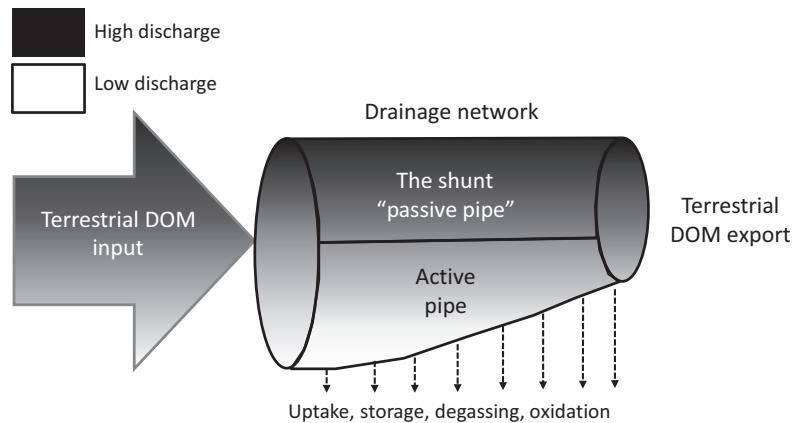
Fɪɢ. 4. A conceptual figure of the PSC modified from Cole et al. (2007). According to this figure, terrestrial DOC input is dominated by high-discharge events, encapsulating the high effective discharge for DOC export from headwater streams. Much of the DOC from these high-discharge events enters a passive pipe and is transported conservatively, or shunted through the drainage network and exported. DOC that enters the watershed at lower to moderate discharge events enters the active pipe, where it may be processed and is not exported.

DOM from land to the ocean and doesn't explicitly capture the role of autochthonous DOM. The riverine productivity model stresses the potential importance of this source of organic matter to rivers (Thorp and Delong 1994). The PSC can be adapted to incorporate autochthonous DOM inputs (e.g., Hotchkiss and Hall 2015). The input and incorporation of autochthonous DOM in many networks is limited to periods of long residence times and autochthonous DOM inputs and transport may occur predominantly during low-flow events (Roach 2013). Incorporation of new and highly variable autochthonous inputs presents a challenge due to the paucity of existing empirical data on autochthonous production during high Q events and key environmental controls such as turbidity. New probes and organic geochemical approaches, including high throughput and intense characterization techniques (e.g., FT-ICRMS), will aid in distinguishing the autochthonous from terrestrial sources of riverine DOM (Fellman et al. 2010, Stubbins et al. 2010, Sobczak and Raymond 2015).

Relevance of Pulse Shunt

The PSC contributes to the new macrosystems sub-discipline and attempts to provide predictive power to the large drainage network scale using new technological and methodological advances (Heffernan et al. 2014). The success of future field studies aimed at testing the PSC will require embracing cross-scale interactions, thus mandating the study of both headwater watersheds and large regional river responses (Soranno et al. 2014). The PSC stresses studying how functional units in watersheds respond to hydrologic events within a scaling framework.

The PSC also builds off of the recent "active pipe" model proposed by Cole et al. (2007). The PSC postulates that drainage networks switch between active and passive pipes depending on factors which influence residence time and decomposition kinetics (Fig. 4). According to the scenarios discussed previously, watersheds are more passive when discharge is high, water temperatures are cold, and watersheds are small. Conversely, watersheds are more active when discharge is low, water temperatures are warm, and watersheds are large. Furthermore, event statistics and watershed form will interact to determine the relative importance of passive vs. active moments, and initial modeling argues for a larger role of passive transport, particularly in upper reaches of watersheds. We reiterate some of the main components of the PSC:

(1) The PSC accounts for the connectivity of watersheds (Fig. 1). The utilization of the Tokunaga connectivity concept was not included in previous conceptual studies on nutrient spiraling, but is requisite when considering large drainage networks and is amenable to natural and human drivers that alter connectivity patterns. Future research on the controls of connectivity and how different landscape functional units (e.g., reservoirs, wetlands) impact connectivity are needed.

(2) The PSC highlights the importance of large rivers for the processing of terrestrial DOM. Due to the increase in concentration and decrease in residence time with events, both the pulse and the shunt are accentuated by events, compounding the importance of big rivers for the removal of terrestrial DOM at annual time scales.

(3) The PSC predicts that the annual frequency of large precipitation events is arguably equally

important to overall annual rainfall magnitude when determining fluxes from drainage networks. Future measurements and modeling approaches need to account for rainfall frequency when estimating and monitoring DOM export, particularly when targeting the response of export to climate change.

(4) The PSC can be extended to incorporate multiple landscape functional units. There is a need to understand how different landscape functional units interact with storm frequency to determine fluxes from the landscape and residence times. Here we focused on the upland landscape, but there is a need to understand how functional units such as wetlands and floodplains respond to events in order to predict the integrative response.

(5) The PSC, like other conceptual models before it, underscores the power of integrating scaling laws into biogeochemical research. Recent and future advances in GIS and remote sensing products will greatly accelerate and strengthen our ability to integrate landscape scaling into drainage network biogeochemistry. Examples include understanding the controls on Horton ratios, Tokunaga ratios, hydraulic exponents and constants, and determining if landscape functional units follow scaling laws.

(6) The PSC reinforces the need for a better understanding of decomposition constants and residence times. Both of these parameters are highly dynamic yet poorly resolved, thus highlighting critical frontier research areas in the hydrological and biogeochemical sciences.

(7) The PSC improves how we conceptualize and quantify the role of stream and river networks at annual and decadal time scales, thereby providing a more accurate depiction of the important role of large watersheds in the global C cycle.

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