

REVIEW

10.1002/2015JG003204

Key Points:

- Better understanding of DOC processing in river networks is needed
- Reach-scale DOC uptake velocity is faster for simple compounds than leachates
- Reach-scale DOC uptake velocities are implausibly fast at the network scale

Supporting Information:

- Supporting Information S1

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Citation:

Mineau, M. M., W. M. Wollheim, I. Buffam, S. E. G. Findlay, R. O. Hall Jr., E. R. Hotchkiss, L. E. Koenig, W. H. McDowell, and T. B. Parr (2016), Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements, *J. Geophys. Res. Biogeosci.*, 121, 2019–2029, doi:10.1002/2015JG003204.

Received 1 SEP 2015

Accepted 2 AUG 2016

Accepted article online 6 AUG 2016

Published online 28 AUG 2016

Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements

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Abstract Quantifying the role that freshwater ecosystems play in the global carbon cycle requires accurate measurement and scaling of dissolved organic carbon (DOC) removal in river networks. We reviewed reach-scale measurements of DOC uptake from experimental additions of simple organic compounds or leachates to inform development of aquatic DOC models that operate at the river network, regional, or continental scale. Median DOC uptake velocity (v_f) across all measurements was 2.28 mm min^{-1} . Measurements using simple compound additions resulted in faster v_f (2.94 mm min^{-1}) than additions of leachates (1.11 mm min^{-1}). We also reviewed published data of DOC bioavailability for ambient stream water and leaf leachate DOC from laboratory experiments. We used these data to calculate and apply a correction factor to leaf leachate uptake velocity to estimate ambient stream water DOC uptake rates at the reach scale. Using this approach, we estimated a median ambient stream DOC v_f of 0.26 mm min^{-1} . Applying these DOC v_f values (0.26 , 1.11 , 2.28 , and 2.94 mm min^{-1}) in a river network inverse model in seven watersheds revealed that our estimated ambient DOC v_f value is plausible at the network scale and 27 to 45% of DOC input was removed. Applying the median measured simple compound or leachate v_f in whole river networks would require unjustifiably high terrestrial DOC inputs to match observed DOC concentrations at the basin mouth. To improve the understanding and importance of DOC uptake in fluvial systems, we recommend using a multiscale approach coupling laboratory assays, with reach-scale measurements, and modeling.

1. Introduction

A large fraction of terrestrial net ecosystem production can be exported as dissolved organic carbon (DOC) to inland water bodies [Cole and Caraco, 2001; Fahey et al., 2005; Luysaert et al., 2007], but the amount of DOC removed as it travels through river networks is not known. In global carbon (C) budgets, the role of inland waters had been largely overlooked [e.g., Schlesinger, 1997] but there is increasing awareness that C is transformed, mineralized, stored, and produced in freshwater ecosystems. The potential importance of lakes and fluvial networks in global C budgets has been underscored by Cole et al. [2007], Battin et al. [2009], and Tranvik et al. [2009], but much uncertainty remains regarding DOC processing rates in streams and rivers [Battin et al., 2008]. The processing of DOC in streams and rivers resulting in the removal of DOC from the fluvial networks is primarily due to microbial mineralization, but abiotic processes, such as adsorption, flocculation, and photooxidation, can also play a role. Meaningful progress in quantifying the contribution of inland waters to C fluxes and transformations necessitates knowing in situ rates of ambient DOC processing at the reach scale that can be scaled up to fluvial networks.

Streams have the potential to mineralize significant quantities of terrestrial DOC [Battin et al., 2008], and most terrestrial runoff first enters surface hydrologic networks through small streams [Alexander et al., 2007]. However, the degree to which streams and rivers contribute to DOC processing is poorly known due to the lack of robust estimates of whole-ecosystem DOC transformations [Cole et al., 2007]. Unlike nitrogen (N) and phosphorus (P), where hundreds of reach-scale uptake measurements of inorganic N and P inform knowledge of nutrient demand and processing in river networks [Ensign and Doyle, 2006], in situ measurements of ambient DOC processing are far fewer. The reason is simple: N and P have only a few mineral forms that are easy to experimentally add to streams at environmentally relevant concentrations. DOC, on the other

hand, is a complex mixture of compounds, and the mineralization and transformation rate of an individual compound in this pool varies widely and can depend, in part, on its interactions with other compounds in the pool [Kuznyakov *et al.*, 2000]. Therefore, it is difficult at best to experimentally add a compound or suite of compounds that represents the ambient DOC found in inland waters.

The most commonly used techniques to estimate DOC uptake in freshwater ecosystems—laboratory incubations and whole reach enrichments—pose methodological problems that limit the use of DOC uptake rates estimated by these experiments. Bottle incubations or bioassays have been used to extrapolate DOC uptake to whole watersheds [e.g., Moody *et al.*, 2013; Cory *et al.*, 2014]. However, this approach is limited in that bottle incubations fundamentally represent water column processing and exclude potentially more important benthic and hyporheic processes, thereby inadequately representing whole-ecosystem in situ conditions. Even if an attempt is made to include sediment processes in a microcosm experiment, the rate of DOC uptake depends highly on experimental conditions, including the water to sediment ratio [McDowell, 1985], which is experimentally difficult to replicate values that represent those of natural ecosystems. Furthermore, such approaches may underestimate DOC processing because sample manipulation and long incubation times would exclude production and respiration of super labile DOC which occurs on timescales of minutes [Pollard, 2013].

The other commonly used technique to measure DOC processing at the reach scale consists of steady state or pulsed additions of relatively labile and traceable DOC either as simple compounds (e.g., labile model compounds like acetate, glucose, and arabinose) or fresh leachates of leaves, soil, or other organic material [e.g., Newbold *et al.*, 2006; Bernhardt and McDowell, 2008] and measuring the decline of added DOC downstream relative to a nonreactive tracer. Although this method is useful to compare uptake rates among streams, the processing of compounds or leachates does not represent uptake rates for the ambient DOC pool because the ambient pool is typically much more diverse in its constituent DOC molecules than either leachates or specific compounds.

Estimates of ambient stream water DOC uptake have been made by scaling laboratory measurements to field estimates or using a mixing model of O₂ concentrations at depths in the streambed to estimate carbon demand. Using the latter approach, Battin *et al.* [2003] estimated that DOC supported 39% of hyporheic respiration. Kaplan *et al.* [2008] paired lab bioreactor measurements of ambient stream water DOC and isotopically labeled leaf leachate with in situ uptake measurements of the leachate to derive a conversion factor between bioreactor uptake and ambient stream water DOC uptake in situ. This approach estimated that DOC could fuel 70% of community respiration in this stream [Kaplan *et al.*, 2008]. Using a hyporheic mesocosm, Sobczak and Findlay [2002] estimated that incoming DOC accounted for 52% of sediment respiration. If DOC fuels most benthic respiration, as is suggested by these studies, and respiration in streams is substantial, then C processing in streams may remove a considerable proportion of DOC as it is transported through river networks.

As published measurements of reach-scale DOC uptake become more common, there is a need to summarize and evaluate these data to inform our understanding of in-stream DOC removal. We present a comprehensive review of reach-scale DOC uptake measurements in streams to evaluate the range of current estimates, compare approaches, and assess potential controls of DOC uptake among streams. We also compare the bioavailability of leaf leachates relative to ambient DOC from published bioassays to calculate a scaling factor to estimate ambient DOC processing from reach-scale leaf leachate additions. Finally, we evaluate the degree to which reach-scale measurements of DOC uptake may represent river network-scale DOC uptake by using a river network inverse model to calculate the terrestrial DOC inputs necessary to generate observed river DOC concentrations given the range of DOC uptake reported in the literature.

2. Methods

2.1. Literature Review

We conducted a literature review using the Google Scholar and Web of Science™ search engines to identify as many publications as possible published through August 2014 reporting DOC uptake in streams from reach-scale additions of DOC as simple compounds or organic matter leachates (supporting information Table S1). Data for DOC uptake velocity (v_r) were extracted from publications, and all units were converted

to mm min^{-1} . DOC v_f is the mass transfer velocity of DOC in the water column to the benthos and is calculated as Qk/w , where Q is discharge, k is the distance-specific decay rate, and w is the stream mean wetted width [Tank *et al.*, 2006]. In some cases DOC v_f was not reported but could be calculated from data provided in the publication. We also collected metadata for each experimental stream such as location, discharge and ambient nitrate (NO_3), soluble reactive phosphorus (SRP), and DOC concentration. We also noted latitude, mean annual temperature, and mean annual precipitation of the study site when reported and gathered these values from additional sources (e.g., NOAA climate data; the Long Term Ecological Research Network database) when necessary. When additions lasted multiple consecutive days and uptake was measured on several occasions, we used the v_f value from the first day of addition because it is most comparable to short-term (a few hours) additions, which was the most commonly used approach. We treated each stream in a study as a data point. Therefore, in the few instances where more than one discrete uptake measurement in a given stream was reported (multiple reaches or nonconsecutive dates) we used the average v_f value for each stream (supporting information Table S1).

To compare the bioavailability of ambient stream water and leaf leachate DOC, we also reviewed the literature as described above to find studies reporting bioassays (laboratory bottle and bioreactor experiments) conducted on both ambient stream water DOC and leaf leachate DOC. Using reported percent DOC consumed and duration of the experiment, we calculated first-order decay coefficients, k (day^{-1}), and the ratio of k for ambient DOC (k_{amb}) and leaf leachate (k_{LL}) DOC in bioassays. We assumed that this median ratio from bioassays is also representative of differences in DOC bioavailability in streams, although we recognize that the amount of DOC removed may vary substantially depending on setting (bottle versus bioreactor versus in stream). We then used this ratio as a scaling factor applied to median DOC v_f from reach-scale leaf leachate additions (v_{fLL}) to generate a single estimate of reach-scale v_f value for ambient DOC using the following calculation:

$$\text{Ambient DOC } v_f = v_{\text{fLL}} \times \left(\frac{k_{\text{amb}}}{k_{\text{LL}}} \right) \quad (1)$$

To test if v_f values significantly differed for experiments using compounds and leachates, we conducted a Mann-Whitney U test using R [R Development Core Team, 2011]. To investigate potential correlates of DOC demand, we first binned data by study to ensure independence and regressed reach-scale DOC v_f against ambient nutrient concentrations (NO_3 , NH_4 , and SRP), ambient DOC concentration, mean annual temperature, and mean annual precipitation at the study site (results in the supporting information Figure S1). We log transformed DOC v_f and NO_3 , NH_4 , SRP, and DOC concentrations to meet the assumption of normally distributed residuals and fit ordinary least squares regressions in R. Transformation improved normality of residuals, but if residuals remained nonnormally distributed, we assumed that the regression was nonetheless robust. Similar to the approach used by Hall *et al.* [2013], we used the standardized major axis regression (SMA) [Warton *et al.*, 2006] package (SMART in R to calculate slopes and their 95% confidence intervals to test if log DOC uptake length (S_w) scaled allometrically with log-specific discharge (discharge/mean width, Q/w ; $\text{m}^2 \text{min}^{-1}$). We used S_w , which is calculated as k^{-1} , rather than v_f in this case because Q and w are used to calculate v_f .

2.2. Scaling and Modeling

We used an inverse modeling approach to calculate the terrestrial DOC inputs needed to match the measured annual mean concentration near the watershed outlet when values of DOC v_f from this review were applied to an entire river network. Our goal was to assess whether our synthesis of reach-scale DOC v_f is representative of DOC demand at river network scales, as determined by whether inputs of DOC from terrestrial landscapes to meet demand are reasonable. For this analysis, we assume that DOC v_f is uniform throughout the river network, which we acknowledge is unlikely. However, studies of nutrient v_f have found little evidence of systematic changes with river size [Ensign and Doyle, 2006; Tank *et al.*, 2008], making this a reasonable first approximation. Further, this approach is meant to assess the validity of the mean results using different approaches for DOC v_f if applied at network scales.

We conducted the inverse modeling across a range of watershed size and river DOC concentrations under average flow conditions. We used mean annual DOC concentrations and area-weighted discharge (runoff)

Table 1. DOC Uptake Velocity (v_f) From Reach-Scale Additions of Compounds and Leachates^a

DOC-Type Added	<i>n</i>	Median v_f (mm min ⁻¹)	v_f Range (mm min ⁻¹)
Acetate	30	4.80	0.40–28.67
¹³ C acetate	7	3.84	0.36–13.68
Glucose	12	2.91	2.04–6.66
Arabinose	13	1.08	0.60–2.46
Sucrose	8	2.25	0.30–8.76
Urea	1	1.65	
Glutamic acid	1	1.39	
Urea + acetate	6	3.59	1.22–8.90
Acetate + formate	1	0.18	
All simple compounds	79	2.94	0.18–28.67
Leaf leachate	12	1.29	0.002–7.08
¹³ C leaf leachate	2	0.64	0.07–1.22
Soil leachate	4	1.17	0.60–3.78
Manure leachate	3	0.31	0.08–0.98
Fish carcass leachate	1	3.78	
All leachates	22	1.11	0.002–7.08
All DOC types	101	2.28	0.002–28.67

^a*n* indicates the number of measurements. v_f range is not reported when a single value was found.

model accounts for the location of terrestrial runoff relative to river network location (i.e., includes direct runoff to small versus large rivers). The model used cumulative runoff routing to calculate discharge. In separate model runs, we applied four levels of DOC v_f from our review uniformly across each network: (1) median value for all simple compound additions (2.94 mm min⁻¹), (2) median value for all reach-scale additions (2.28 mm min⁻¹), (3) median value for all leachate additions (1.11 mm min⁻¹), and (4) the bioavailability-scaled estimate (0.26 mm min⁻¹) uniformly across each river network. Assuming that benthic processes dominate, serial DOC removal in the model is simulated according to equation (2).

$$R = 1.0 - e^{(-v_f/HL)} \quad (2)$$

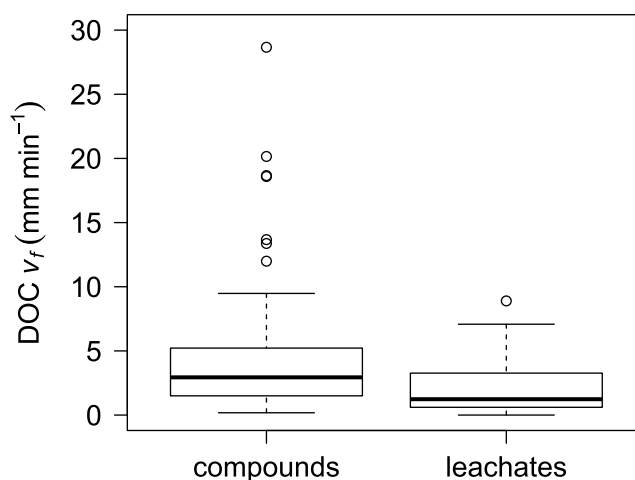


Figure 1. Boxplot of DOC v_f indicating the interquartile range (box), median value (line), $1.5 \times$ interquartile (whiskers), and outliers (points) for uptake measurements using simple organic compound and leachate additions. $n = 79$ for compounds and $n = 22$ for leachates. v_f for compounds is significantly faster than v_f for leachates ($W = 1410$, $P = 0.003$).

values reported for seven rivers: Penobscot, Kennebec, Androscoggin, Susquehanna, and Potomac by Hanley *et al.* [2013] in addition to previously unpublished data for mean DOC concentration (over 10 years) and runoff in two rivers draining smaller watersheds (400–475 km²), the Ipswich (MA, USA) and Lamprey (NH, USA) (watershed characteristics in supporting information Table S2). We performed simulations using the Framework for Aquatic Modeling in the Earth System (FrAMES), a river network hydrology and biogeochemical model [Wollheim *et al.*, 2008, 2015]. We set uniform runoff over each watershed equivalent to the annual mean. We used a simulated topological river network at a resolution of 3 min for the five large watersheds and 15 s for the two smaller watersheds. The spatially distributed

where hydraulic load (HL) is equal to discharge/(width \times length). Simulated discharge (m³ s⁻¹), width (m), and length (m) for each grid cell are estimated by FrAMES and are described in Stewart *et al.* [2013]. For each level of DOC v_f , we varied DOC concentration in terrestrial runoff until the predicted DOC concentration was within 0.1 mg L⁻¹ of observed annual mean DOC concentration at the basin mouth (supporting information Table S2). We report modeled DOC concentration in terrestrial runoff (i.e., soil + groundwaters reaching the fluvial network) for each v_f scenario and compare these to published values for stream and soil water DOC and terrestrial C budgets to determine if v_f values are plausible or realistic at the network scale.

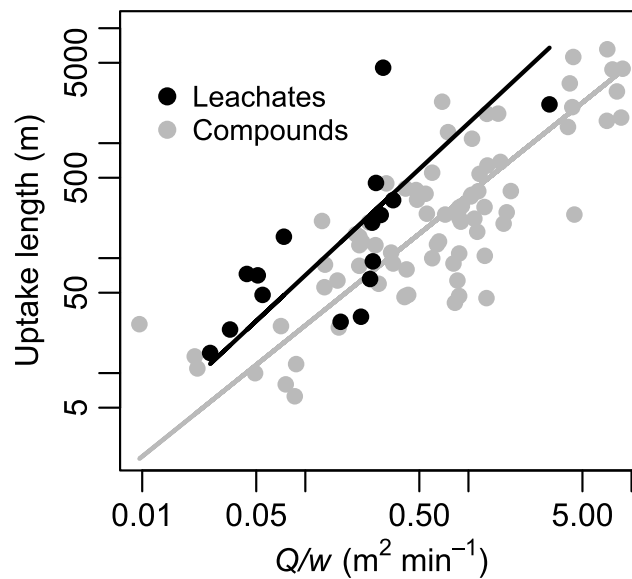


Figure 2. Standardized major axis regression of DOC uptake length with specific discharge (discharge/mean width) for leachates (black symbols) and compounds (grey symbols). Slope for leachates is 1.32 with 95% confidence interval of 0.895–1.951. Slope for compounds is 1.14 with 95% confidence interval of 0.995–1.306. The higher elevation of the leachate regression relative to the compounds indicates that for a given specific discharge leachate DOC typically has a longer uptake length than compound DOC.

3. Results

Median DOC v_f for all reach-scale measurements ($n = 101$) was 2.28 mm min^{-1} (Table 1 and supporting information Table S1). On average, experiments that used leachates had lower DOC v_f values than those using specific compounds (Table 1 and Figure 1, $W = 1410$, $P = 0.003$) suggesting slower processing of leachate DOC relative to simple organic compounds. As is common for whole stream nutrient additions, most DOC uptake measurements were conducted in small streams. Median discharge reported in these studies was $0.014 \text{ m}^3 \text{ s}^{-1}$ with the highest discharge being $3.083 \text{ m}^3 \text{ s}^{-1}$. SMA slope of uptake length versus specific discharge was 1.14 (95% confidence interval: 0.995–1.306) for compounds and 1.32 (0.895–1.951) for leachates (Figure 2). This analysis indicates that uptake length for both forms of

added DOC scaled isometrically with specific discharge as slope confidence intervals include 1. Therefore, discharge is more variable than uptake velocity across sites, suggesting that v_f does not systematically change across the range of stream sizes studied to date.

In bottle/bioreactor incubations, leaf leachate DOC was more bioavailable than ambient DOC (Table 2). The median ratio of bioassay ambient stream water DOC k_{amb} to bioassay leaf leachate k_{LL} was 0.234 (range 0.106–0.556; Table 2). By applying this scaling factor to median reach-scale leaf leachate v_f as described in equation (1), we obtained an estimated reach-scale ambient DOC v_f of 0.26 mm min^{-1} .

Applying the range of median DOC v_f values from the literature review ($0.26\text{--}2.94 \text{ mm min}^{-1}$) to whole river networks revealed that runoff concentrations between 4.3 and 360 mg L^{-1} (Figure 3) and terrestrial DOC export fluxes of 23 to $1818 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (supporting information Table S2) would be necessary to offset

net in-stream removal and produce the mean annual concentrations observed at the mouth of the seven river networks we considered for this modeling exercise. Estimated DOC concentrations in terrestrial runoff using the bioavailability-corrected leachate v_f (0.26 mm min^{-1}) were slightly above typical headwater stream DOC concentrations (4.3 to 14.8 mg L^{-1} , Figure 3). Application of median leachate v_f (1.11 mm min^{-1}) throughout the network resulted in DOC concentrations in terrestrial runoff that were between typical DOC concentrations in stream water and soil water ($24\text{--}105 \text{ mg L}^{-1}$, Figure 3

Table 2. Decay Rate ($k \text{ d}^{-1}$) for Ambient DOC and Leaf Leachate DOC in Bioassays

Ambient DOC ($k \text{ d}^{-1}$)	Leaf Leachate DOC ($k \text{ d}^{-1}$)	Ambient k : Leachate (k)	Reference
0.011	0.086	0.128	Qualls and Haines [1992]
0.009	0.085	0.106	Sobczak et al. [2003]
0.104	0.363	0.287	Meyer et al. [1987]
0.010	0.018	0.556	Trulleyova and Rulik [2004] ^a
0.013	0.033	0.394	Trulleyova and Rulik [2004] ^a
0.014	0.026	0.538	Trulleyova and Rulik [2004] ^a
0.229	0.978	0.234	Lock and Hynes [1976]
7.698	62.807	0.123	Kaplan et al. [2008]
0.051	0.245	0.208	Wiegner and Tubal [2010]
		0.234	Median

^aThe three bioassays reported by Trulleyova and Rulik [2004] used different inoculum treatments added to the same ambient DOC and leaf leachate.

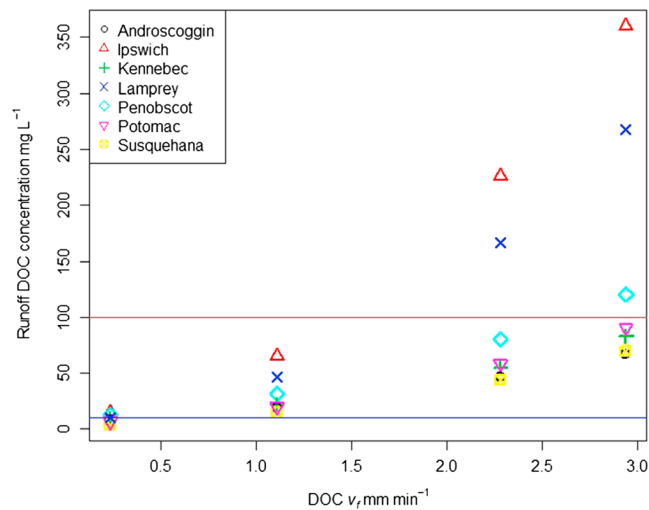


Figure 3. Runoff DOC concentration needed to generate mean annual DOC concentration in the mainstem river near the watershed outlet when DOC v_f values from the literature review ($0.26\text{--}2.94\text{ mm min}^{-1}$) are applied throughout the river network in seven northeast U.S. watersheds. A blue reference line at 4.3 mg L^{-1} indicates the upper bound of forested headwater stream average DOC concentration in this region [Raymond and Saiers, 2010]. Brown reference lines at 105 mg L^{-1} indicates the upper bound of soil water DOC concentration across a wide range of soil carbon to nitrogen ratio [Aitkenhead and McDowell, 2000]. We consider plausible DOC runoff concentrations representative of watershed average to be between stream water and soil water concentrations.

approach focused on benthic processing over water column DOC removal and that water column removal may be increasingly important in larger rivers. However, whole river v_f measured via the organic C spiraling technique ($0.03\text{--}0.47\text{ mm min}^{-1}$) [Hall et al., 2016] was still substantially higher than DOC v_f estimated from river water column incubations during the same sampling campaigns ($0.001\text{--}0.02\text{ mm min}^{-1}$) [Hotchkiss et al., 2014], suggesting that benthic demand represents a substantial portion of carbon uptake, even in larger rivers. Our application of reach-scale uptake rates throughout whole river networks shows that only some of the lowest reach-scale estimates of DOC v_f are realistic because of the substantial input of terrestrial C that would be necessary to explain watershed exports if higher estimates of DOC v_f are assumed (Figure 3). DOC removal in river networks may be substantial even when lower DOC uptake rates are assumed. In the modeling exercise we present, even the lowest estimate of reach-scale DOC v_f (0.26 mm min^{-1}) results in 27 to 45% of water column DOC removed by in-stream processing during transport through the seven northeast U.S. watersheds.

DOC v_f from reach-scale additions of labile DOC were comparable to those reported for NH_4 , NO_3 , and PO_4 uptake. Median v_f of 5, 1, and 2 mm min^{-1} has been reported for NH_4 , NO_3 , and PO_4 , respectively [Ensign and Doyle, 2006]. At 2.28 mm min^{-1} , median reach-scale DOC v_f derived from the addition of simple compounds and leachates is most similar to PO_4 v_f . However, our watershed-scale model results suggest that realistic ambient reach-scale DOC v_f are likely 10 times slower than addition experiments suggest. We note that the median DOC v_f we report does not account for several instances where investigators attempted to measure DOC uptake but no significant uptake was detected. For example, Bechtold et al. [2012] found no significant net DOC uptake in 7 out of 13 streams and Blaen et al. [2013] found no significant net DOC uptake in 9 out of 12 streams, both using acetate additions. There can be many reasons that significant uptake is not detected during a reach-scale measurement. First, uptake may, in fact, be minimal due to biotic (e.g., low activity or biomass of microbial heterotrophs) and abiotic factors (e.g., limited hydrologic exchange with the benthos due to substrate consistency). Alternatively, experimental error (e.g., the experimental reach is too short, too few samples, or low analytical precision) may yield no detectable uptake when the true rates are low or moderate. Therefore, we cannot account for these nonsignificant uptake measurements because

[Aitkenhead and McDowell, 2000]). Application of overall median DOC v_f (2.28 mm min^{-1}) and simple compound median v_f (2.94 mm min^{-1}) also resulted in predicted terrestrial DOC concentrations within the range of organic soil water DOC concentrations (Figure 3), although some river systems with higher export DOC concentrations exceeded these values (Ipswich and Lamprey).

4. Discussion

4.1. DOC Removal From Reach to Network Scale

We found that reach-scale DOC uptake measurements suggest that streams can retain or remove a substantial amount of terrestrial-derived DOC as it is transported downstream through river networks. Similarly, multiple studies estimate that DOC fuels much of the respiration in stream sediments [Sobczak and Findlay, 2002; Kaplan et al., 2008]. We acknowledge that our v_f modeling

the cause for the lack of observable uptake is uncertain. If these potentially very slow DOC v_f measurements were to be included in our review, the median estimate would drop and thus be somewhat closer to a plausible river network DOC uptake value. We compared runoff DOC concentration to headwater stream and soil water DOC concentrations; however, we can also convert runoff DOC concentrations to areal terrestrial DOC export to compare with such estimates. For example, *Canham et al.* [2004] estimated that upland forests export about $40 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and wetlands export approximately $200 \text{ kg ha}^{-1} \text{ yr}^{-1}$ as DOC in the Adirondack region of NY. Furthermore, the C budget for the Hubbard Brook experimental forest estimates that forest floor leaching DOC flux is $256 \text{ kg ha}^{-1} \text{ yr}^{-1}$ [*Fahey et al.*, 2005]. Considering these benchmarks, we found that when applied to whole river networks, only the bioavailability-corrected DOC v_f estimate (0.26 mm min^{-1}) required realistic average terrestrial DOC export ($23\text{--}112 \text{ kg ha}^{-1} \text{ yr}^{-1}$). This further supports that the bioavailability-corrected DOC v_f estimate is the more plausible approximation of average river network terrestrial DOC removal. Other whole network analyses linking measurements in headwater streams with flux throughout the Ipswich river network suggested that DOC v_f of terrestrial organic matter was even lower, at 0.03 mm min^{-1} [*Wollheim et al.*, 2015].

Most DOC delivered to coasts by rivers is of terrestrial origin [*Cole and Caraco*, 2001], but aquatic primary production can also input labile DOC from algal exudates within streams and rivers [*Kaplan and Bott*, 1982; *Hotchkiss et al.*, 2014; *Hotchkiss and Hall*, 2015]. This additional DOC, some of which would be rapidly consumed, is not accounted for in our model. A DOC v_f of 0.26 mm min^{-1} may approximate ambient terrestrial DOC removal under average conditions; however, total DOC removal accounting for allochthonous and autochthonous DOC sources is presumably higher. It is also likely that DOC removal is highly variable in space and time, and DOC removal rates in streams and rivers depend on the lability of DOC inputs in addition to environmental conditions that regulate microbial activity [*Raymond et al.*, 2016]. Nonetheless, our modeling exercise allows us to identify a plausible value of DOC uptake at the river network scale, which suggests that a substantial portion of terrestrial DOC inputs can potentially be removed in-transit through fluvial ecosystems.

4.2. Effects of Discharge on DOC Uptake

We found little relationship between stream size and uptake rate. This was evidenced by an isometric scaling relationship between DOC uptake length and specific discharge for both simple compounds and leachates (Figure 2). This suggests that similar to nutrients [*Wollheim et al.*, 2001; *Tank et al.*, 2008; *Hall et al.*, 2013], v_f is relatively uniform compared to variations in discharge. However, 15 out of the 16 measurements at discharge $>0.2 \text{ m}^3 \text{ s}^{-1}$ were from a single study conducted in the Catskill region of NY [*Newbold et al.*, 2006]. High flow events caused by precipitation or snowmelt may play an important role in exporting large quantities of DOC from headwaters [*Raymond and Saiers*, 2010; *Raymond et al.*, 2016]. Additional measurements of DOC uptake in larger streams and rivers and during high flow events, though challenging, would be useful to evaluate the effect of discharge and river size on DOC processing. Compound additions could use the same approach as has been done for NO_3 in large rivers [*Tank et al.*, 2008], but leachate additions would be much more difficult because of the amount of leachate needed to enrich the DOC pool or fluorometric character of a large volume of river water.

4.3. Factors Controlling DOC Demand

Investigators have had little success relating factors controlling DOC demand to reach-scale DOC uptake measurements to factors controlling DOC demand. For example, *Johnson et al.* [2009] report that DOC (as acetate) v_f had no relationship with land use, season, and N or P availability in the stream. *Newbold et al.* [2006] did find that DOC (as glucose and arabinose) v_f was positively correlated with both gross primary production and community respiration. Several studies, including this review (Figure S1), found no relationship between N and P availability and DOC uptake. However, *Mineau et al.* [2013] did stimulate DOC uptake using experimentally elevated N and P availability during leaf leachate additions. Factors likely to affect DOC processing capacity in streams, such as exchange with and size of the hyporheic storage zone and the source or composition of ambient DOC, are not typically measured and reported along with DOC uptake measurements. Investigation of factors controlling DOC processing in streams and rivers requires further targeted research and manipulation experiments that include diverse environments spanning climatic and chemical gradients.

4.4. DOC Quality and Composition

DOC quality and composition present a critical challenge to our understanding and modeling of C spiraling in inland water. In contrast to estimating rates of nitrate, ammonium, or phosphate uptake which are molecule specific, DOC uptake estimates are the average of a distribution of uptake rates spanning DOC compositions with very slow to very fast uptake rates. When that distribution is estimated using a single molecule with high or low lability, the estimate of that distribution may not necessarily represent the average. Existing research has largely used high quality or highly bioavailable DOC compounds (i.e., acetate or monosaccharides) to estimate DOC uptake. These simple compounds reported faster DOC v_f relative to measurements using leachate additions. Individual compounds were likely processed more readily due to their simple and small molecular structure that can pass through microbial cell membranes more quickly relative to the more complex mixtures of C compounds found in leachates. Using biodegradation assays, several researchers have described DOC utilization as a continuum of biological reactivity from highly labile to nonlabile [Cory and Kaplan, 2012; Koehler *et al.*, 2012], which suggests that in streams, DOC uptake may be just as variable and strongly affected by the composition of the DOC present.

4.5. Priming

Some studies measured reach-scale uptake as change in concentration of the specific compound added with distance downstream [e.g., Newbold *et al.*, 2006], but others add compounds and measure changes in total DOC concentration [e.g., Johnson *et al.*, 2009]. When using the latter approach, a priming effect may influence DOC uptake estimates. The phenomenon of priming has been the focus of much study in soil ecosystems [Kuzyakov *et al.*, 2000] but is just recently attracting broader consideration in aquatic ecosystems [Guenet *et al.*, 2010; Bianchi, 2011; Hotchkiss *et al.*, 2014; Guenet *et al.*, 2014] (but see de Haan [1977] for early work on this topic). A priming effect is defined as a short-term change in the turnover time of organic matter caused by treatments, usually addition of relatively labile organic C [Kuzyakov *et al.*, 2000]. In bioassays and microcosms, the addition of glucose sometimes stimulates ambient C mineralization above measured background rates; recent bioassay studies estimated a priming effect of 12% for soil organic matter in lake water [Guenet *et al.*, 2014] and 35% for soil exudates and ambient dissolved organic matter in rivers [Hotchkiss *et al.*, 2014], while no priming effect was detected in experimental hyporheic zone microcosms with mixed DOC sources [Bengtsson *et al.*, 2014]. Though positive priming of DOC mineralization has not been definitively measured in situ at the reach scale [but see Thouin *et al.*, 2009], it is likely that the addition of labile DOC could stimulate mineralization of ambient DOC. If priming occurs, the DOC v_f derived from addition of highly labile DOC sources may be too high and not representative of typical river network scale DOC uptake. However, a negative priming effect may also be created by the addition of labile C to streams. For example, Lutz *et al.* [2012] found that the addition of large amounts of labile C resulted in microbial demand shifting from the ambient DOC pool to the added labile DOC, resulting in increased export of ambient DOC. In either case, priming may affect DOC uptake measurements when labile DOC is added to a stream.

4.6. Alternative Approaches to Reach-Scale DOC Additions

Moving forward, we highlight additional approaches to estimate DOC processing at the reach scale and network scale without logistical limitations of experimentally adding labile DOC, especially in larger streams and rivers. One promising method is the C spiraling approach, which can be used to compare the retentiveness and processing efficiency of organic C across streams and rivers [Newbold *et al.*, 1982; Thomas *et al.*, 2005; Griffiths *et al.*, 2012; Hall *et al.*, 2016]. The C spiraling approach uses estimates of organic C pools (benthic and in transport) and heterotrophic respiration to calculate whole-ecosystem spiraling metrics, including v_f [Newbold *et al.*, 1982]. Synoptic surveys, detailed mass balances, and network-scale modeling could also inform the net removal of terrestrial DOC in fluvial networks [Lauerwald *et al.*, 2012; Kaushal *et al.*, 2014; Wollheim *et al.*, 2015; Raymond *et al.*, 2016]; however, rapid removal of labile C (short time between inputs and immediate use) cannot be detected using measurements of water chemistry alone. Further use of these and other methods to detect network-scale OC removal will be greatly advanced by a better quantitative understanding of DOC loading from landscapes to inland waters. Achieving the understanding necessary to quantify and scale the role of river networks in regional to global C budgets will require explicit measurements, from streams to large rivers, of in situ rates of DOC production, mineralization, and spiraling; terrestrial DOC inputs; and the role of in-stream mineralization in regulating the quantity and quality of DOC exported from river networks.

Current commonly used approaches for quantifying DOC uptake rates in stream and river ecosystems do not produce representative estimates that can be applied to fluvial network or global scales. To better understand the role of freshwaters in the global C budget and the role of DOC in aquatic ecosystem function, it is critical to quantify ambient rates of DOC uptake. DOC is used by stream bacteria to sustain their respiration and growth [Kaplan and Bott, 1983; Bott et al., 1984], and the associated respiration contributes to the CO₂ flux from freshwater ecosystems [Hotchkiss et al., 2015]. However, DOC removal and mineralization in river networks are poorly understood at broad spatial scales. Considering differences documented in bioassays of leaf leachates and ambient DOC (Table 2) as well as the estimated terrestrial DOC input necessary to sustain DOC uptake (Figure 3), the in situ uptake rate of ambient DOC is certainly lower than that which is estimated by reach-scale rates of leachates or simple compound removal. However, the bioavailability of ambient DOC varies among streams [Meyer, 1994], flow conditions [Buffam et al., 2001; Holmes et al., 2008; Wilson et al., 2013], and seasons [Fellman et al., 2009], and DOC uptake parameters may also vary accordingly. Although detecting ambient DOC uptake at stream reach scales is difficult, the cumulative uptake at a river basin scale is likely a substantial flux [Lauerwald et al., 2012]. Our findings support that a sizeable portion (27 to 45%) of DOC exported from terrestrial ecosystems may be removed in river systems before reaching coasts.

5. Conclusions

Reach-scale measurements of DOC uptake using simple compound or leachate additions do not generate DOC v_f values that can be realistically applied to whole river networks. However, once we correct the median reach-scale DOC v_f from leachate additions for differences in bioavailability between leaf leachate and ambient in-stream DOC, we obtain a DOC v_f that can realistically be applied to whole river networks in small and large watersheds in the northeast U.S. Our use of the ratio K_{amb}/K_{LL} should be considered as preliminary at this point because we have few data points (with high variation) to assess this ratio and these values are not from the river for which we would like to assess DOC uptake. But this approach is promising for future field studies where one would add leachate and then measure its decay rate relative to the ambient decay of river water DOC. Such a scaling could be unique to each river and therefore more accurate than the approach we used here. Therefore, we encourage researchers to pair laboratory and field experiments to develop bioavailability conversion factors that are appropriate for their site. To improve the understanding and importance of DOC uptake in fluvial systems, we recommend using a multiscale approach, as we have done in this review, coupling laboratory assays, with reach-scale measurements, and modeling in a deliberate manner across a broad range of channel size and ecoregions. In addition, we recommend a more holistic approach to C budgets that simultaneously considers linked terrestrial and aquatic environments to adequately quantify DOC source, fate, and flux needed to evaluate the role of freshwater ecosystems at broader spatial scales.

Acknowledgments

Data used in this paper were gathered from published studies and associated references listed in supporting information Table S1. These data can also be obtained by contacting the corresponding author (m.m.mineau@unh.edu). Funding for the workshop where this review and synthesis was initiated was provided by NASA-NEWS grant NNX09AU89G. Additional support for M. Mineau was provided by the Northern States Research Cooperative through funding available by the USDA Forest Service and the Hubbard Endowment of the Earth Systems Research Center at UNH. We thank all participants of the "Strategies to Improve Understanding of DOC Dynamics through Time-Varying Regional to Continental Scale Models" workshop for stimulating conversations on this topic. We also thank Robert Stewart and Shan Zuidema for their assistance with the modeling.

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