Water Resources Research

RESEARCH ARTICLE
10.1029/2019WR026336

Key Points:
- DOC concentrations increased dramatically over 15 years in riparian forest soils and streams but not mire peats and wetland outlet streams
- Relative contribution of land cover in the catchment shapes heterogeneity in browning among streams in the network
- Changes in the depth profile of riparian soil DOC have altered C-Q relationships throughout the broader stream network

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2

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Citation:
Fork, M. L., Sponseller, R. A., & Laudon, H. (2020). Changing source-transport dynamics drive differential browning trends in a boreal stream network. *Water Resources Research*, *56*, e2019WR026336. https://doi.org/10.1029/2019WR026336

Received 12 SEP 2019
Accepted 17 JAN 2020
Accepted article online 22 JAN 2020

Changing Source-Transport Dynamics Drive Differential Browning Trends in a Boreal Stream Network

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Abstract Dissolved organic carbon (DOC) concentrations are increasing in freshwaters worldwide, with important implications for aquatic ecology, biogeochemistry, and ecosystem services. While multiple environmental changes may be responsible for these trends, predicting the occurrence and magnitude of "browning" and relating such trends to changes in DOC sources versus hydrologic transport remain key challenges. We analyzed long-term trends in DOC concentration from the two dominant landscape sources (riparian soils and mire peats) and receiving streams in a boreal catchment to evaluate how browning patterns relate to land cover and hydrology. Increases in stream DOC were widespread but not universal. Browning was most pronounced in small, forested streams, where trends corresponded to twofold to threefold increases in DOC production in riparian soils and increases in annual DOC export from a forested headwater. By contrast, DOC did not change in mire peats or streams draining catchments with high lake or mire cover, nor did we observe trends in DOC export from a mire-dominated headwater. The distinct long-term trends in DOC sources also altered concentration-discharge relationships, with a forested headwater shifting from transport-limited toward chemostasis, and a mire outlet stream shifting from chemostasis to source-limitated. Modified DOC supply to headwaters, together with altered seasonal hydrology and differences in the dominant water source along the stream network gave rise to predictable browning trends and consistent concentration-discharge relationships. Overall, our results show that the sources of DOC to boreal aquatic ecosystems are responding to environmental change in fundamentally different ways, with important consequences for browning along boreal stream networks.

1. Introduction

Throughout northern Europe and North America, concentrations of dissolved organic carbon (DOC) in surface waters have increased extensively and dramatically over the last several decades (De Wit et al., 2016; Monteith et al., 2007). Because DOC directly and indirectly modulates the physical, chemical, and biological conditions in surface waters, these "browning" trends have wide-ranging implications for the ecology of aquatic ecosystems (Prairie, 2008), provisioning of ecosystem services (Kritzberg et al., 2019), and the carbon (C) balance of broader landscapes (Webb et al., 2019). Elevated DOC concentrations in drinking water systems also require additional effort and expense in the treatment process (Keucken et al., 2017; Krzeminski et al., 2019). While considerable work has documented browning and its potential ecological and economic consequences, predicting changes in individual lakes and streams is limited by a lack of understanding of how hydrologic transport interacts with changes in landscape DOC sources to shape broader scale patterns.

Browning trends are attributed to a range of mechanisms reflecting the effects of long-term and contemporary environmental change on the production, solubility, and/or mobilization of DOC in soils (Clark et al., 2010). These drivers are not mutually exclusive and include recovery from acid deposition (Evans et al., 2012; Monteith et al., 2007), increased soil temperature (Freeman et al., 2001), biogeochemical interactions under shifting redox conditions (Knorr, 2013), elevated terrestrial productivity (Finstad et al., 2016), altered precipitation (De Wit et al., 2016), and land use/cover change (Finstad et al., 2016; Kritzberg, 2017; Oni et al., 2015; Steele & Aitkenhead-Peterson, 2012). Yet despite progress toward understanding the mechanisms, considerable uncertainty remains regarding what controls spatial heterogeneity in DOC trends, including the roles of local vs. broad scale drivers of browning in individual water bodies (Clark et al., 2010; Solomon et al., 2015). Processes operating at shorter temporal and smaller spatial scales may dampen or enhance the effects of long-term drivers and generate the heterogeneity in DOC trends among catchments

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(Clark et al., 2010). Proximately, however, all drivers of browning must act by either increasing the sources of DOC (through changes in concentration or solubility), enhancing hydrologic transport of DOC to surface waters, or a combination of these mechanisms.

Analysis of concentration-discharge (C-Q) relationships has emerged as a promising tool for resolving the potentially complex source-transport relationships that shape DOC concentrations in streams. C-Q analysis provides inference about the size and spatial distribution of resource pools based on whether solute concentrations in streams are unchanged (i.e., are chemostatic), enriched, or diluted as discharge increases (Moatar et al., 2017). In the context of DOC, published C-Q relationships span the full range of modalities and can be sensitive to land cover (Laudon et al., 2011) as well as network position (Creed et al., 2015). Despite this variability, DOC concentrations and fluxes most often increase with discharge across a broad range of streams, consistent with transport limitation in which higher flows connect and mobilize new pools of soluble organic matter (Raymond & Saiers, 2010; Zarnetske et al., 2018). Insights from these relationships are key to the development of mechanistic understanding and predictions for stream DOC concentrations across a range of flow conditions. However, projecting into the future requires the assumption of biogeochemical stationarity (Basu et al., 2010), which is unlikely to hold for DOC given multiple chemical and biological processes that can alter local soil pools (e.g., Evans et al., 2012). Indeed, in most cases, surface water browning cannot be attributed to transport processes alone, and unless changes in sources are manifest equally everywhere in a landscape, spatially heterogeneous changes in DOC sources imply a change in the C-Q relationships of small streams over time. At present, we lack understanding of how browning trends are connected to shifting source-transport dynamics at the catchment scale, which limits our ability to predict how ongoing environmental change may affect future DOC concentrations in surface waters.

Here we ask how the major sources of DOC in the boreal landscape have changed over the last 15 years and how these changes are influencing trends in stream chemistry at network scales. To answer these questions, we make use of the unique infrastructure and record length from the Krycklan Catchment Study (KCS) in boreal northern Sweden (Laudon et al., 2013). Globally, boreal landscapes store huge amounts of carbon belowground (Bradshaw & Warkentin, 2015) and mobilization of this organic matter from terrestrial to aquatic systems is key in regulating stream DOC concentrations. Like many boreal landscapes, coniferous forests and open mires (wetlands) dominate land cover in the KCS. Headwater mires store large amounts of organic matter in peat and support consistently high DOC fluxes to streams that drain them (Nilsson et al., 2008). Similarly, highly organic soils in riparian zones of forested catchments represent the primary source of DOC to their streams (Ledesma et al., 2018). Here DOC is transported from riparian soil sources via shallow subsurface flowpaths, where vertical patterns in water table elevation, hydraulic conductivity, and soil organic matter content interact to generate a dominant source layer that support the majority of lateral water and solute flux (Ledesma et al., 2018). In this study, we characterize the trends (from 2003–2017) in dominant sources of DOC. We link these patterns to trends in DOC concentration and flux in adjacent headwater streams using a source-transport framework. We then connect the observed heterogeneity in surface water DOC trends among streams to differences in catchment characteristics across the KCS network. Finally, we explore how differing patterns and trends in dominant DOC and water sources affect annual C-Q relationships over time, and how these patterns propagate through the stream network.

2. Methods

2.1. Site Description

The KCS is located in northern boreal Sweden (64°14′N, 19°46′E; see Laudon et al., 2013, for a full site description and map of catchments and sampling locations). Briefly, mean annual temperature (from 1981–2010) is 1.8 °C, with average monthly lows in January (−9.5 °C) and highs in July (+14.7 °C). Mean annual precipitation during the same period is 614 mm, much of this (40–60%) coming as winter snowfall. Annually, snow cover persists for ca. 167 days, but this has declined at a rate of ~0.5 days year^{-1} since 1980 (Laudon & Ottosson Löfvenius, 2016). Annual runoff is ~311 mm, with the largest water flux occurring during the spring snowmelt season (April–May). From 2003 to 2017 (the period of this study), there were no trends in maximum or minimum daily temperature ($p > 0.3$), but increases in both total annual precipitation (7.4 mm year^{-1}; $p = 0.05$) and maximum daily precipitation (0.21 mm day^{-1} year^{-1}; $p = 0.03$). Despite increases in precipitation, stream flow has not shown significant trends from 2003–2017.

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Elevation in the KCS ranges from 114 to 405 m a.s.l and the catchment is underlain by Svecofennian metasediments/metagraywacke (94%). The highest postglacial coastline traverses the KCS at approximately 257 m a.s.l. Above this line, quaternary deposits are dominated by glacial till; below it, soils are dominated by postglacial sedimentary deposits. Land cover in the KCS is primarily forest (86%), dominated by Scots Pine (*Pinus sylvestris* (L.); 63%) and Norway Spruce (*Picea abies* (L.) Karst; 26%), with relatively low cover by deciduous trees (~10%), primarily birch (*Betula pendula* Roth). Forests associated with our focal headwater catchments are mature with stands 50–100+ years in age, and have shown very little change in canopy cover between 1986 and 2015 (Kozii et al., 2017). Wetlands (oligotrophic, minerogenic mires) are also common in the basin, accounting for nearly 50% cover for some subcatchments.

2.2. Sample Collection and Analysis

We compiled DOC, sulfate (SO_4^{2-}), and pH data from the KCS monitoring program for streams, lysimeters, and piezometers sampled between 2003 and 2017. First, to evaluate potential changes in DOC sources to streams, we summarized soil water chemistry collected using ceramic suction lysimeters (P80, UMS, Germany) installed at six depths (10, 25, 35, 45, 55, and 65 cm) within the riparian zone of forest-dominated catchment C2, 4 m from the stream bank. Lysimeters were sampled between 2 and 12 (average: 4) times per year (total N ranged from 102–112 for each of the lysimeters between 25 and 65 cm depth, and was 56 for the 10 cm lysimeter). Additionally, to evaluate potential changes in the contribution of DOC from mires, we summarized data from 12 piezometers installed down to 450 cm at 25 cm increments in an oligotrophic, minerogenic mire located within catchment C4. Mire water samples were typically collected monthly from March to June, 2 to 9 (average: 4) times per year (total $N = 54$ to 56 for piezometers between 75 and 350 cm deep, 46 and 47 for piezometers at 25 and 50 cm, and 24 and 31 for piezometers at 400 and 450 cm). Finally, we analyzed data from 13 streams in the KCS with catchment areas that range from 12 to 6,790 ha, and encompass the full range of soil and land cover properties in the region (supporting information Table S1). The frequency of stream sampling is weighted by discharge (Q), with more frequent samples during snowmelt (one to three samples per week), biweekly sampling during summer and autumn, and monthly sampling during winter, for a total of 392–427 observations per stream between 2003 and 2017. All samples for DOC were filtered in the lab (0.45 μm MCE membrane, Millipore) and refrigerated prior to analysis within 10 days on a Shimadzu TOC analyzer (Shimadzu, Duisburg, Germany). Separate samples for pH were also analyzed in lab within 24 hr of collection using an Orion 8102BN ROSS low conductivity electron probe (Thermo Scientific). Finally, samples for SO_4^{2-} analysis were filtered and frozen prior to analysis on a Dionex DX-300 or DX-320 ion chromatograph system.

2.3. Analysis and Statistical Methods

We explored connections between trends in soil DOC sources and streams using multiple response variables and scales. We first evaluated how DOC production changed with depth and over time in riparian soils and mire pore waters. We then characterized the trends in DOC concentration and annual export from the headwater catchments C2 and C4, which are directly co-located with the riparian soil/mire sampling stations. Next, we evaluated the trends in stream DOC concentration across 13 sites in the broader KCS network and related the variation in these changes to land cover characteristics of their catchments. Finally, we assessed how trends in DOC have influenced the relationship between source and transport in these streams by examining how annual C-Q relationships have changed along a continuum from the headwaters C2 and C4 through to the KCS outlet.

To compare DOC concentration among depths for soil sources, we conducted ANOVA. We used the package “rkt” to perform Mann-Kendall tests for trends in climate variables and chemical parameters for sources and streams over the period of interest and to determine the Theil-Sen estimate of slopes (Marchetto, 2017). In addition to examining overall trends, we used the Seasonal Kendall Test to test for trends in stream chemistry in individual months among years (e.g., trends in June DOC concentrations from 2003–2017) using medians of samples collected within each month. We estimated the annual DOC fluxes at C2 and C4 by linearly interpolating DOC concentrations between measured values and multiplying by specific discharge before summing daily values for each year. We used simple linear regression to determine the relationship between annual DOC flux and water flux and examined interannual trends in the residuals of this linear relationship. Test assumptions for simple linear regression and ANOVA were validated by visual inspection of Q-Q and residual plots.

To explore the impact of land cover and catchment characteristics on DOC trends, we performed principal component analysis of characteristics of the catchments (as reported in Laudon et al., 2013) using the "vegan" package (Oksanen et al., 2017). Parameter values were standardized prior to running the ordination. We then used linear regression to compare scores on PC1 to trends in DOC. Lastly, we analyzed annual C-Q relationships for streams draining catchments C2, C4, C7, C9, C13, and C16 using the linear regression between log-transformed DOC concentrations and log-transformed daily specific discharge (q; following Godsey et al., 2009).

Estimates of DOC export and analysis of C-Q relationships both required discharge values going back to 2003. However, continuous discharge measurements for all but one of the sites (C7) only go back to 2010. Therefore, to characterize long-term trends, we used modeled flow data for the entire period of record as presented by Karlsen et al. (2016). Briefly, modeled daily discharge was generated using the Hydrologiska Byråns Vattenbalansavdelning (HBV) hydrologic model (Bergström, 1976; Seibert & Vis, 2012) calibrated with observed flow data. The R^2 between modeled and measured daily flow between 2010 and 2016 exceeded 0.82 for all catchments, and was 0.781 for C7 over the whole period from 2003–2016 (Figure S1). To evaluate whether the use of these modeled estimates biased our results, we also present the values of C-Q slopes at the different sites using both measured and modeled discharge for years when both were available.

3. Results

3.1. Trends in DOC Sources Differ With Depth and Correspond to Browning in Streams

DOC concentrations in riparian lysimeters increased significantly at most but not all depths (Figure 1; Table S2). At and below 35 cm, DOC in soil waters increased significantly (by 2–3 mg C L^{-1} $year^{-1}$; all $p < 0.0001$). At 25 cm there was no significant trend in riparian soil water DOC ($p = 0.58$) and in the shallowest lysimeter (10 cm) we found a decrease of 2.18 mg C L^{-1} $year^{-1}$ over time ($p = 0.02$). Over the whole record, DOC concentrations in forest riparian soil water were greater in shallower soils (10 cm = 25 cm > 35 cm > 45 cm = 55 cm = 65 cm). However, because of the increases in DOC at depth, by the end of the record (2016 and 2017), the only statistical differences in DOC concentration were between the shallowest lysimeter (25 cm, as the 10 cm well was dry during these final years) and those at 55 and 65 cm.

Vertical patterns and trends in DOC from mire peat were more subtle and less consistent than those observed in forest soils. Unlike forest soils, DOC concentrations decreased modestly over time at some depths within this mire. Specifically, the shallowest piezometers (25–50 cm) showed DOC decreases of 0.52 and 0.84 mg C L^{-1} $year^{-1}$, respectively ($p = 0.04$ and 0.0001). Similarly, DOC measured at 150 and 175 cm deep decreased 0.31 and 0.44 mg C L^{-1} $year^{-1}$, respectively ($p = 0.03$ and 0.006). No other depths showed significant DOC trends ($p > 0.1$ for depths 75–125 and ≥200 cm). DOC concentrations did not vary strongly with depth in the mire. In general, the piezometer at 150 cm had slightly greater and that at 450 cm had slightly lower DOC concentrations, as compared to the other depths.

We found high variability in the presence and magnitude of trends in stream water DOC concentration among subcatchments in the KCS network (Figure 2; Table S1). Specifically, DOC increased significantly ($p < 0.05$) for all but one of the 13 streams (mire-dominated C4). At the same time, the annual magnitude of increase (Theil-Sen estimate of slope) varied from 0.106 to 0.598 mg C L^{-1} $year^{-1}$ among sites, with a mean of 0.275 mg C L^{-1} $year^{-1}$. In addition, fluxes of DOC increased over time from the forested headwater catchment C2 by 1.4 kg DOC ha^{-1} $year^{-1}$ (Figure 3a) but not the mire-dominated catchment C4 (Figure 3d). In both catchments, annual fluxes of DOC were positively related to annual runoff (Figures 3b and 3e), with a stronger relationship in forested C2 ($R^2 = 0.88$, $p < 0.0001$) as compared to mire-dominated C4 ($R^2 = 0.43$, $p = 0.006$). However, the residuals of the annual DOC flux vs. water flux also increased over time for the forested catchment (Figure 3c), indicating a long-term increase in DOC export per unit runoff. In contrast, the residuals of DOC vs. water flux showed no consistent directional change over time in the mire-dominated catchment (Figure 3f).

Contemporaneously with increases in DOC, SO_4^{2-} concentrations decreased in the forest riparian soil water ($p < 0.005$ for all depths; Figure S2) and in stream water ($p < 0.001$ for all streams). However, these decreases in SO_4^{2-} were not correlated with increased pH in stream water. Instead, most streams became slightly more

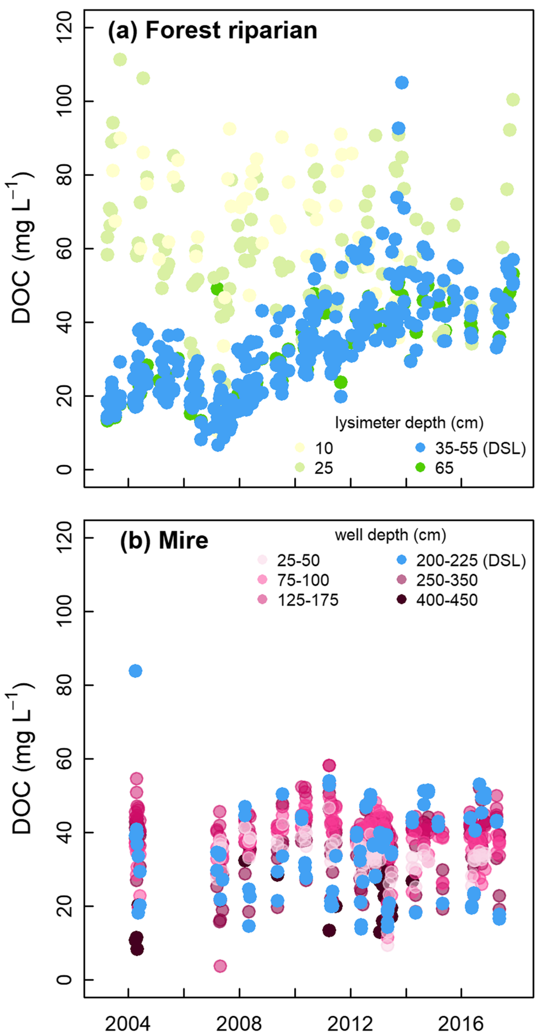

Figure 1. Long-term records (2003–2017) of DOC concentration in (a) forest riparian soils and (b) mire wells. Forest riparian lysimeters (4 m from the C2 stream) at and below 35 cm show positive DOC trends of 2 to 3 mg L^{-1} $year^{-1}$ (all $p < 0.0001$). The shallower lysimeters consistently have higher DOC concentrations than deeper layers; there is no significant DOC trend at 25 cm ($p = 0.58$), while the shallowest riparian soil (10 cm) have a long-term decrease of 2.2 mg L^{-1} $year^{-1}$ ($p = 0.02$). The Dominant Source Layer (DSL, soil layer with the greatest contribution to solute and water flux) in this catchment comprises the soils from 35–55 cm deep (blue points). Among sample wells in the mire (within catchment C4), there are no differences among depths in DOC concentration, and the shallowest wells (25–50 cm) show modest decreases in DOC over the period of record (0.52 and 0.84 mg L^{-1} $year^{-1}$, respectively; $p = 0.04$ and 0.0001). Similarly, wells at 150 and 175 cm deep show modest decreases in DOC (0.31 and 0.44 mg L^{-1} $year^{-1}$, respectively; $p = 0.03$ and 0.006). No other mire wells, including the DSL (200–225 cm deep, shown in blue) showed significant DOC trends ($p > 0.1$ for remaining depths).

acidic over time; slopes for streams with significant trends at $\alpha = 0.05$ ranged from −0.040 to −0.004 pH units per year with a mean of −0.024, and two streams did not show a long-term trend in pH.

3.2. Late Winter and Late Spring are Important for Driving Interannual Browning Trends

While browning trends were evident at annual scales, more detailed assessment revealed time windows within which most of this long-term change occurred. Seasonal Kendall tests revealed two months with significant trends in stream water DOC across pooled KCS streams (Table S4): DOC increased across streams in March (0.573 mg L^{-1} $year^{-1}$; $p = 0.0101$) and June (0.337 mg L^{-1} $year^{-1}$; $p = 0.0015$). While individual catchments varied in the temporal patterns in their DOC trends, the majority of catchments (8 of 13) showed statistically significant, positive trends in DOC concentration among years for these two months (Table S4). In general, individual streams with stronger trends showed a greater count of months for which Seasonal Kendall tests indicated statistically significant trends.

In June, stream DOC trends coincided with long-term increases in Q during this month. Seasonal Kendall tests on monthly streamflow showed a statistically significant increase of 0.12 L s^{-1} $year^{-1}$ in the median of daily average Q during June among years ($p = 0.01$; Figure S2). Similarly, the count of days in June for which the daily average Q exceeded 1 L s^{-1} (the approximate flow required to activate the dominant source layer; Ledesma et al., 2015, 2016) increased by 0.79 days $year^{-1}$ over the time period of our study ($p = 0.03$; Figure S3). In contrast, variation in March DOC did not coincide with trends in Q nor any metrics describing antecedent winter conditions (e.g., daily low temperatures, count of freeze-thaw days, winter precipitation).

3.3. Browning Trends Differed Among Catchments With Different Land Cover and Network Position

At broader scales, the magnitude of browning among streams in the KCS network could be predicted from the relative contribution of forest vs. mire DOC sources. Indeed, differences in the magnitude of trends among streams were strongly correlated with our integrated measure of catchment land cover (i.e., the first principle component of the ordination, PC1; Figure 4). Specifically, streams having catchments with greater tree volume and higher percentage of spruce (as opposed to pine or birch) had high scores on PC1 and greater magnitude of DOC increase. Catchments with more birch and higher percent cover of lake or mire had lower scores on PC1 and showed smaller magnitudes of browning or lacked a statistically significant trend. The streams draining the largest catchments (C14, 15, and 16) also had low scores on PC1 and small trends in DOC concentration over time. Finally, differences among these trends had the effect of homogenizing DOC concentrations among smaller streams (<1,000 ha in catchment area). Forest-dominated headwaters had relatively low initial DOC concentrations in 2003 and exhibited large increases in DOC, while the streams with higher initial DOC had relatively small or absent DOC trends (Figure 4c).

3.4. DOC C-Q Relationships Through the Stream Network Have Changed Over Time

In addition to the trends in stream DOC concentration and flux, C-Q relationships changed over time in forest- and mire-dominated headwater streams. For the forest headwater (C2), the slope of the annual C-Q relationship became shallower and the intercept greater over time (Figure 5). Early in the record, the

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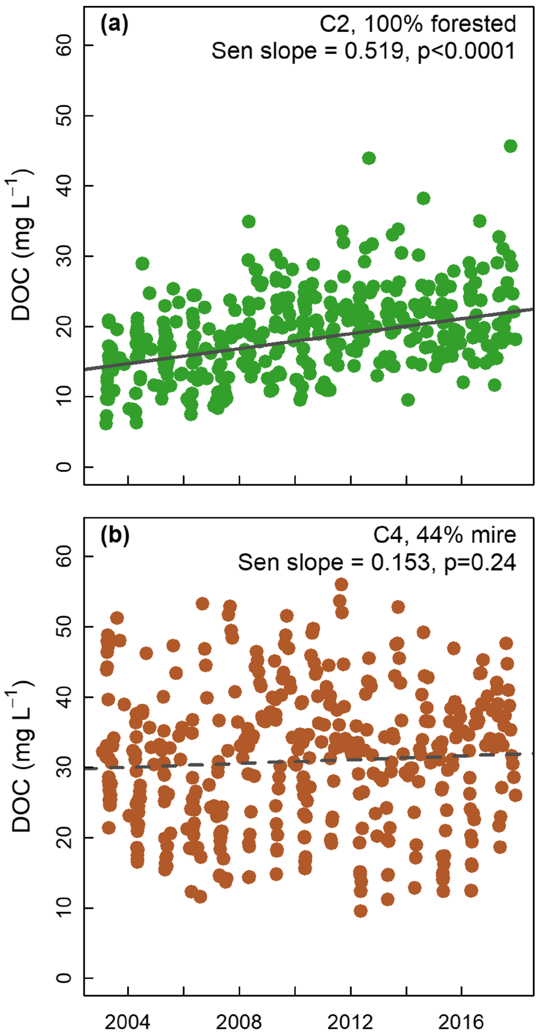

Figure 2. Long-term records (2003–2017) of DOC concentration for two streams in the Krycklan Catchment Study. The land cover in C2 (a) is primarily forest (dominated by spruce and pine), and stream water DOC shows a steady increase of 0.519 mg L^{-1} year^{-1} over the period of record. The land cover in C4 (b) consists of 44% mire with the rest of the catchment covered by spruce-pine forest. Here stream water DOC shows only modest, statistically nonsignificant increases over the 14 year period of record.

slope of the C-Q relationship at this site was about 0.25, with an intercept of 15 mg L^{-1}. By 2016, the intercept had increased to 20.9 mg L^{-1}, indicating an increase in DOC concentrations during low flow conditions. At the same time, the slope of the relationship at this site decreased to 0.087, suggesting less variability in DOC concentration among flow conditions in the catchment, i.e., a trend toward chemostasis. For the mire-outlet stream (C4), the changes in the annual C-Q relationship were more subtle (Figures 3c and 3d). Here, for the first several years, there were no significant correlations between DOC concentration and flow at the annual scale, indicating chemostatic behavior. Later in the record, we found negative C-Q relationships, i.e., dilution and source-limitation of DOC during high flows.

Patterns in C-Q relationships and their changes over time for streams further down the network reflect the changes in landscape DOC sources and transitions to different dominant source waters with network position (Figure 6). The stream draining catchment C7 (47 ha), just downstream of the confluence of the forested headwater C2 and mire-outlet C4, shows four years with positive C-Q relationships early in the record, but most years have C-Q relationships that do not differ significantly from zero (i.e., chemostasis). Moving downstream, catchment C9 (288 ha) includes a lake and its outlet stream and shows a consistently positive C-Q relationship, but the slope of annual C-Q relationships become shallower over time ($p = 0.02$). Yet further downstream, catchment C13 (700 ha) includes more forested land cover and shows a shift from positive C-Q relationships to chemostatic conditions over the course of our study ($p = 0.0008$). Finally, C16 drains the entire 6,970 ha of the KCS and shows strongly positive annual C-Q relationships for DOC across the period of record.

4. Discussion

While increases in surface water DOC are well documented in high latitude regions (De Wit et al., 2016; Monteith et al., 2007), predicting the magnitudes and locations of browning at finer spatial scales remains a challenge. Our study of long-term water chemistry in soils and streams of boreal northern Sweden connects differential changes in DOC source pools and increases in hydrologic transport to distinct and heterogeneous browning trends among streams in single drainage network. Specifically, in forest riparian zones, we observed clear increases in DOC concentrations within hydrologically active soils over the last 15 years, while trends in mire DOC concentrations showed only modest declines and were nonsignificant at most depths. These changes in sources were concurrent with long-term increases in DOC concentrations and fluxes for streams draining catchments with high forest cover, while streams draining catchments with high lake or wetland cover had weak or absent trends. Overall, our results show how patterns of browning can emerge at network scales as a result of variable changes in both source pools and seasonal flow regimes that fundamentally alter the relationship between hydrology and DOC concentration in streams.

4.1. Differential Changes in DOC Sources

Extensive peat accumulation in the riparian zones and mires of boreal landscapes constitute vast stores of organic C (Gorham, 1991) that support considerable export of DOC from terrestrial to aquatic ecosystems (Battin et al., 2009; Cole et al., 2007). These organic-rich, near-stream soils constitute the main source of DOC to boreal streams, which is mainly of relatively recent origin (i.e. C fixed since 1950; Ledesma et al., 2015, 2016). While both mires and riparian soils are important sources of DOC to streams (Laudon et al., 2011), a key message from our analysis is that these two major components of boreal landscapes are

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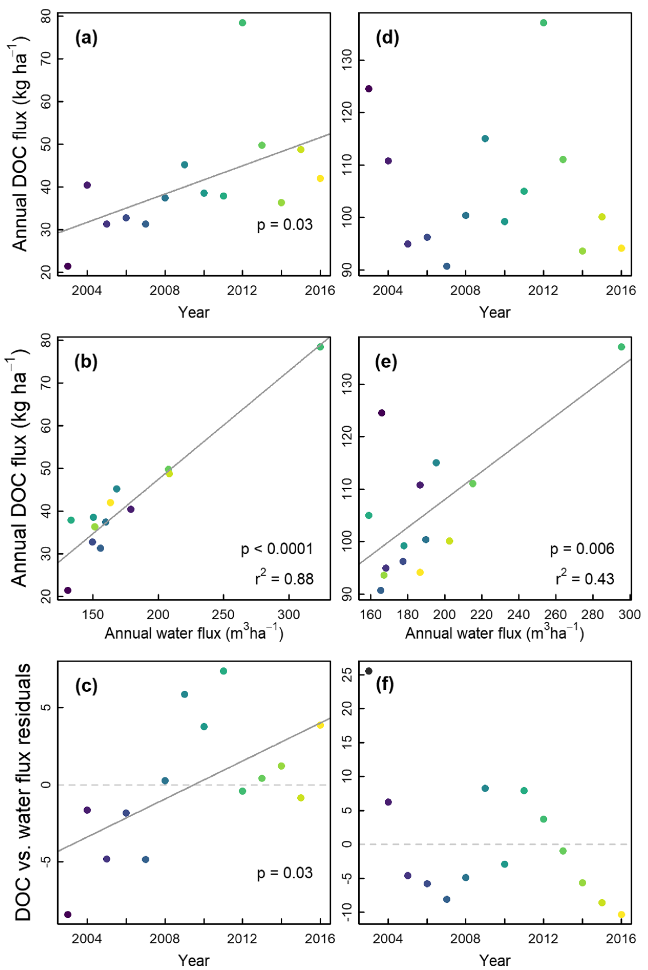

Figure 3. Trends in annual DOC flux, relationships between DOC flux and water flux, and trends in the residuals of DOC vs. water flux for streams draining catchments C2 (a, b, and c) and C4 (d, e, and f). In all panels, color corresponds to year. There is a long-term increase in DOC flux from the stream draining C2 (a) but no trend in DOC flux from the C4 stream (b). In both streams, there are positive, statistically significant relationships between DOC flux and water flux (b and e). For the C2 stream, the residuals of this linear model increased over time (c), demonstrating an increase in DOC flux per unit water flux in this stream. In contrast, the residuals of the DOC vs. water flux linear model showed no such long-term pattern in the C4 stream (f).

responding to environmental change in fundamentally different ways, with consequences for browning patterns across the stream network. Most notably, net DOC production in deeper riparian soils increased by as much 2–3 mg C L^{-1} $year^{-1}$, more than doubling DOC concentrations in these strata over the period of record (Figure 1). Recent work in the KCS suggests that this change likely reflects, at least in part, long-term declines in sulfur deposition, mediated in riparian soils by fluctuations in groundwater and redox state that control SO_4^{2-} concentrations and thus DOC solubility (Ledesma et al., 2016). Regardless of the mechanism, the lack of a concurrent DOC trend in mire pore waters suggests that these systems are shielded against the biogeochemical changes playing out in riparian soils. This may simply reflect the greater overall volume of peat in mires, which, together with more stable groundwater levels, results in less exposure to atmospheric inputs, C derived from plant roots, and fluctuating thermal and redox conditions that together shape DOC dynamics in riparian soils (Ledesma, Kothawala, et al., 2018). In any case, mires are dominant features of boreal landscapes worldwide (Gorham, 1991) and while they are major DOC sources to streams (Juutinen et al., 2013; Nilsson et al., 2008) and are documented elsewhere as systems vulnerable to environmental change (Monteith et al., 2015), our results highlight their potential to dampen or inhibit browning trends in this region.

4.2. Trends Across Streams and Propagation of Catchment-Scale Responses Through the Network

Nearly all of the KCS streams showed increases in DOC concentrations over the last 15 years, consistent with observations throughout aquatic ecosystems in northern Europe and North America (Evans et al., 2005; Monteith et al., 2007; Worrall et al., 2004). The magnitude of DOC increase among streams varied with land cover and could be predicted from changes in belowground source pools. Consistent with observations in the headwaters, streams whose catchments were dominated by older forests (greater tree volume), particularly spruce, showed the greatest browning while streams with higher coverage by mires or lakes, or those dominated by birch and pine forests, showed smaller or insignificant trends in DOC concentration. In addition, DOC trends of the largest magnitude occurred in streams with relatively low DOC concentrations at the outset of the study period (Figure 4c). These are the streams that browning most quickly and are converging with the more slowly changing streams that had higher initial DOC concentrations. At the current rate of change, the average DOC concentrations in small streams in the KCS network (catchments <1,000 ha) will converge with what is currently the brownest stream (mire-dominated C4) by ~2055. Further, these trends suggest that the smaller (first to third order) streams that make up approximately 80% of the channel length in this region will become homogenously brown in 30 years, and may eventually become browner if this trend continues.

Despite increases in DOC concentration of up to 72% among the smaller KCS streams over the last 15 years, we observed only modest trends in the larger streams they feed. This difference in behavior suggests a scale-break in the hydrologic processes driving stream flow and chemistry among catchments of different sizes (Jencso et al., 2009). In boreal Sweden, this break likely corresponds to a nonlinear shift in water (and corresponding DOC) sources from near-surface soils to deeper sediments with greater catchment size (Tiwari et al., 2017). In catchments smaller than about 1,000 ha, shallow flowpaths dominate the contributions to streamflow, making these streams sensitive to observed changes in the soil source pools. In catchments >1,000 ha, deep, DOC-poor groundwater constitutes much of the baseflow (Peralta-Tapia et al., 2015), diluting the effect of headwater DOC trends (Tiwari et al., 2014). During periods of high flow, the relative

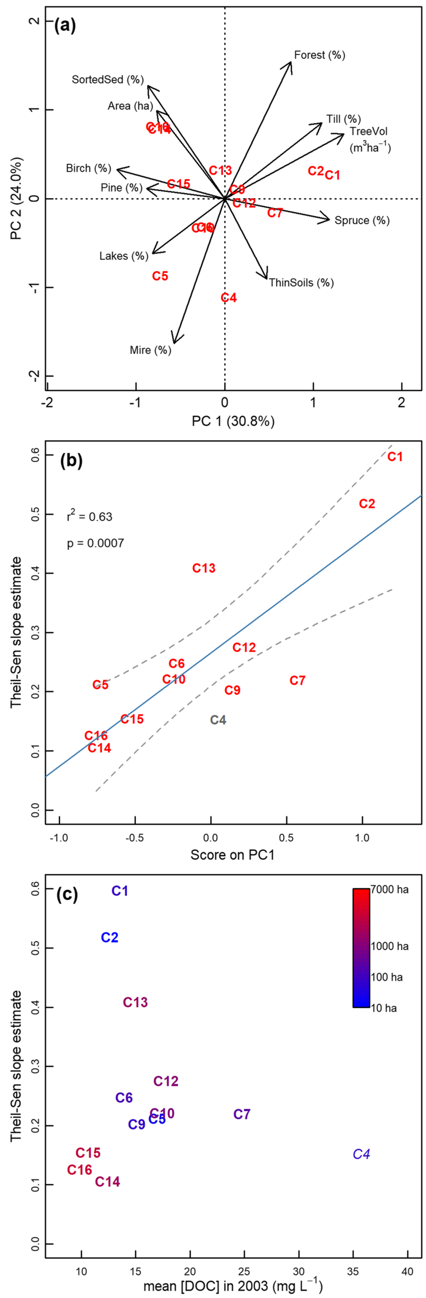

Figure 4. Principal component analysis of catchment characteristics for KCS catchments with selected loadings (a), the relationship of scores on PC1 with the Theil-Sen slope estimate of DOC trend in mg L^{-1} $year^{-1}$ (b), and initial (mean of 2003 measurements) DOC concentration vs. Theil-Sen slope estimate (c). Strong positive loadings on PC1 are associated with greater tree volume and higher percentages of spruce in forest patches. Low scores on PC1 are associated with greater areal coverage of lake and mire and higher percentages of birch in forest patches. The full description of catchment characteristics is given in Table S1 and full list of loadings given in Table S3. The score on PC1 describes 63% of the variation in the slope of the long-term TOC trends among catchments (b). In panel (b), catchments with significant trends ($p < 0.05$) are shown in red and that with $p > 0.05$ is shown in gray. In panel (c), catchments with significant trends are shown in bold text and that with $p > 0.05$ is shown in italics, while color of plotted text corresponds to the log of catchment area.

contribution of headwaters (and thus shallow flowpaths) to downstream channels increases (Buffam et al., 2007), which offers explanation for the significant DOC trends we observe in the larger streams during April and June (Table S4), when relatively high flows transmit the signals in browning headwaters down through the stream network. Thus, at the scale of the whole network, changes in the dominant water source between headwaters and larger streams lead to a disconnection in which the persistent browning signal in headwaters, driven by riparian soils, is only occasionally transmitted downstream to larger rivers. In addition, removal of DOC by instream processing may be responsible for some part of the spatiotemporal patterns we observe in the KCS network, as longer residence times during low flows allow greater removal by biotic and abiotic processes, while higher flows can shunt DOC downstream with less processing (Raymond et al., 2016). More broadly, recognizing these scale-dependent changes in water source is important for predicting the magnitude and occurrence of browning across northern freshwaters.

4.3. Changes in C-Q Relationships Along the Network Reflect Differences and Trends in Sources and Transport of DOC

The observed nonstationarity of riparian soil DOC concentrations has fundamentally changed the relationship between stream concentrations and discharge in these boreal streams. Historically, transport-limitation of DOC supply to forest streams arose because of strong declines in both concentration and hydrologic conductivity with greater depth in riparian soils (Bishop et al., 2004). Accordingly, increases in discharge activate surficial soil strata with exponentially greater capacity to supply DOC laterally to streams (Ledesma, Kothawala, et al., 2018), such that forest DOC signals propagate most strongly downstream during high flow periods (Buffam et al., 2007). However, increases in riparian soil DOC at depth have homogenized this vertical pattern, enriching soil strata that support the bulk of annual water flux and altering the associated pattern between DOC concentration and discharge in streams. Indeed, while C-Q relationships in the forest headwater were positive throughout the record, decreases in the slope indicate a clear transition from transport-limitation toward chemostasis over time. Decreases in the slope of the C-Q relationships are consistent with increasing DOC concentrations in the deeper riparian flowpaths that contribute at low- and baseflow conditions.

Changes in the relationship between DOC supply and catchment runoff are further evidenced by the long-term increase in the residuals of DOC flux vs. water flux from the forested catchment (Figure 3). This trend, which suggests an increase in the mass of DOC mobilized from the riparian source per unit annual runoff, is also consistent with increased flux of DOC at baseflow. In contrast to the forested stream, the mire outlet has transitioned from a chemostatic annual C-Q relationship to a negative chemodynamic relationship. This change suggests a shift toward greater dilution of DOC at high flows, indicating increasing source-limitation as hydrological transport increases. It is not clear whether this trend reflects the subtle declines in DOC concentration observed in mire pore waters or increases in snowpack that more strongly dilute chemical signals in these systems (Laudon et al., 2011). These contrasting trends in forested vs. mire-dominated catchment parallel predicted changes in DOC for dry vs. wet regions of Fennoscandia described by de Wit et al. (2016). Their work showed that increases in precipitation would alleviate source-

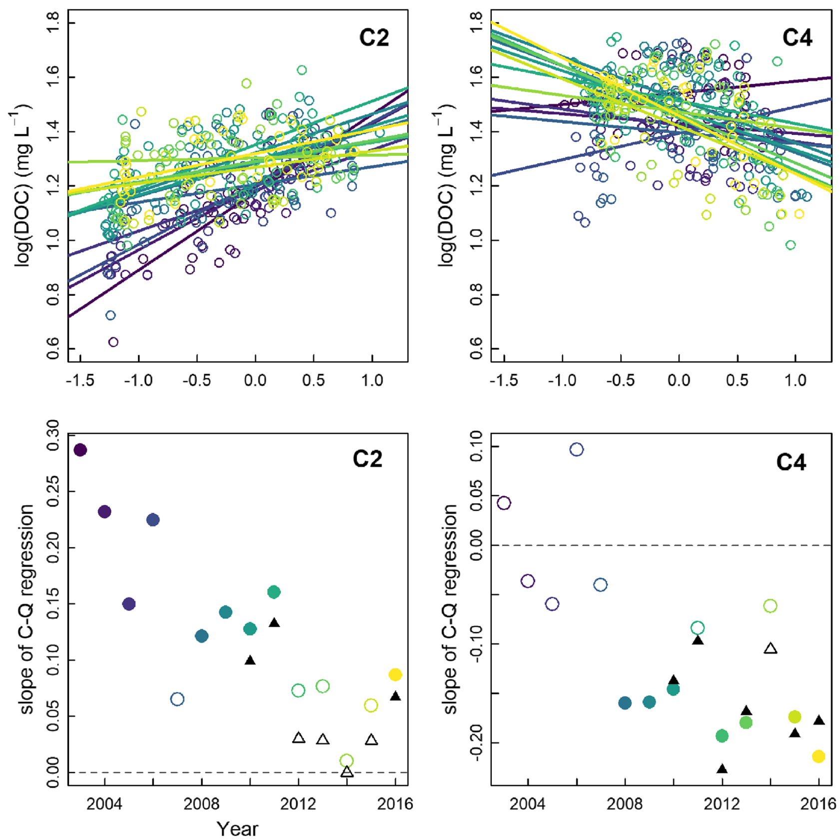

Figure 5. Concentration-discharge relationships among years for DOC at forested C2 and mire-dominated C4. Individual C-Q relationships are calculated for each calendar year (top panels) using the log of measured DOC vs. log of modeled discharge. Over time, the slope of the C-Q relationship at C2 (bottom-left) decreases toward zero. There are not significant correlations between C and Q at C4 (bottom-right) in the first several years of the record, while in later years significant negative relationships between C and Q develop. In all panels, color corresponds to year. In bottom panels, circles show annual C-Q relationships based on modeled flow data and triangles depict annual C-Q relationships calculated using measured flow data, for which records begin in 2010. Filled symbols indicate statistically significant linear regression between log-transformed C and Q ($p < 0.05$), while open symbols denote nonsignificant regressions ($p > 0.05$).

limitation and drive enrichment of DOC in drier catchments, but lead to dilution of DOC in wetter regions. Regardless, changes in the C-Q relationships for both forest- and mire-dominated sites represent emergent, hydro-biogeochemical responses to environmental change in the boreal landscape. Recognizing such changes can help us understand the flow conditions under which browning trends are likely to be most pronounced in the broader network.

The cumulative effects of catchment land cover and shifts in the dominant source of baseflow through the network also governed spatial and temporal patterns in annual C-Q relationships moving down the channel continuum (Figure 6). Overall, this assessment shows that while DOC concentration trends in the larger rivers of KCS may be modest, the pronounced long-term changes in source-transport dynamics we see in forested headwaters persist through broader stream network. For example, catchment C7 is sampled near the confluence of the streams draining forested headwater C2 and mire-dominated headwater C4, and the pattern in annual C-Q integrates the opposing trends and patterns in the C-Q relationships in these two headwaters. The confluence between C2 (which shifts from DOC enrichment at high flows to chemostasis over time) and C4 (which shifts from chemostasis to dilution) yields chemostasis over most of the record. Further downstream, a major lake outlet contributes to baseflow at C9, somewhat dampening the effects of increases in forest soil water DOC and driving a positive C-Q relationship. Over time, however, the slopes of these annual C-Q relationships have decreased as the effects of increased DOC in forest soils contribute to higher DOC in baseflow of their streams. The inclusion of more forest cover in C13 shifts the pattern even

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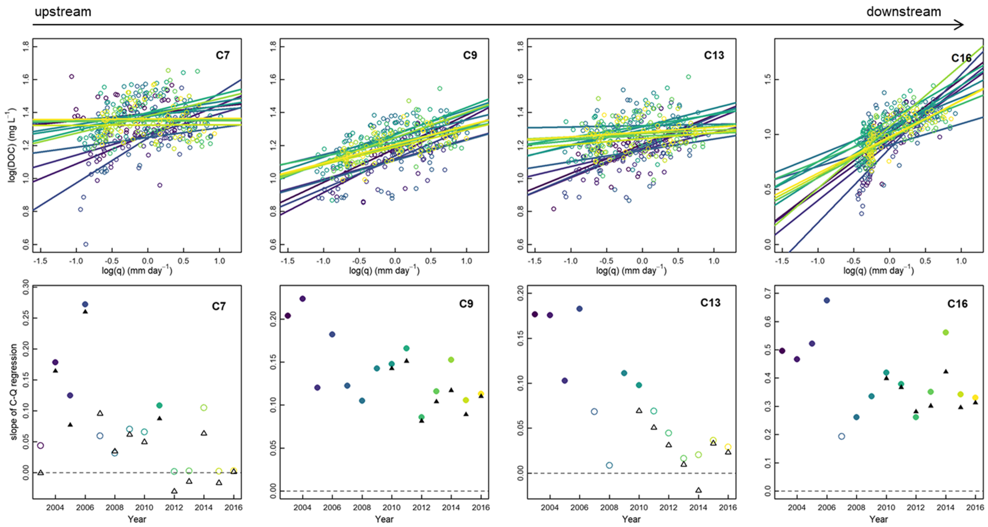

Figure 6. Concentration-discharge relationships among years for DOC at streams through the KCS network, beginning at the confluence of C2 and C4 (Figure 5) and moving downstream (left to right). Individual C-Q relationships are calculated for each calendar year (top) using the log of measured DOC vs. log of modeled discharge. In all panels, color corresponds to year. In bottom panels, circles show annual C-Q relationships based on modeled flow data and triangles depict annual C-Q relationships calculated using measured flow data, for which records begin in 2010. Filled symbols indicate statistically significant linear regression between log-transformed C and Q ($p < 0.05$), while open symbols denote nonsignificant regressions ($p > 0.05$).

more toward that observed at forested headwater C2, with positive annual C-Q relationships at the beginning of the record moving toward chemostasis over time. Finally, at C16 (the outlet of the entire KCS) we can observe the effect of the scale-break in baseflow source on the C-Q relationship. Here low-DOC groundwater contributes much of the baseflow and is strongly enriched at high flows when runoff and surface flows have a greater contribution to streamflow.

Nonstationarity in soil DOC sources and hydrologic connectivity combined with differential changes in C-Q relationships across the landscape make future browning difficult to predict. Despite differences in the direction and slope of relationships between DOC concentration and discharge among catchments, relationships between DOC flux (i.e., the product of concentration and flow rate) are almost universally positive (Zarnetske et al., 2018). Increases in hydrologic connectivity and stream flow are therefore likely to enhance transport of C from the terrestrial into the aquatic environment. Increases in flow, such as those we observed among June measurements over time, could result in both larger DOC loads from terrestrial sources as well as more frequent interaction with shallow riparian soils that have greater (but unchanged) DOC concentrations. It is possible that both changes to the pool size of DOC sources, as well as more frequent incursion of riparian flowpaths into shallower soils consistently high in DOC are responsible for the browning trends we observe. Increased transport of DOC from riparian soils is unlikely to exhaust this source, as much of the DOC transported to streams is of modern origin and current rates of net ecosystem production keep pace with export (Ledesma et al., 2015). Based on these results, riparian soil sources are likely able to continue to support browning in boreal headwater streams.

In conclusion, browning trends in boreal stream networks are not manifest equally among catchments because of different contributions and behaviors of the dominant DOC sources, with important consequences for broader boreal landscapes. Browning of surface waters is increasing the annual fluxes of DOC from forest landscapes, and seasonal increases in flow will mean changing temporal patterns of DOC flux even under chemostasis. Much of the DOC that enters surface waters is eventually converted to CO_2 through biotic and abiotic processes, so changes in the export of DOC from soils to streams can have significant implications for regional C budgets and CO_2 emissions (Cole et al., 2007; Öquist et al., 2014). In addition, the seasonal timing of consistent browning trends across this networks indicate the greatest changes early in summer, when the effects of DOC on receiving stream and lake communities and ecosystems are potentially most pronounced. Overall, interpreting the role of northern catchments as sources vs. sinks of carbon depends not only on understanding regional drivers of DOC change but also the landscape context of streams, including the interplay between changing soil source pools and hydrologic transport.

Acknowledgments
We acknowledge financial support for Krycklan Catchment Study, including the Swedish Science Foundation (VR), Swedish Infrastructure for Ecosystem Science (SITES), the VR extreme event project, Future Forests, Kempe Foundation, the Swedish Research Council for Sustainable Development (FORMAS), European Union's Horizon 2020 Research and Innovation Programme under the Marie Sklodowska-Curie Grant Agreement No 734317 (HiFreq), KAW (Branch Point program), and the Swedish Nuclear Waste Company (SKB). M. Fork was supported by a grant from the Knut and Alice Wallenberg Foundation (dnr: 2016.0083). We thank K. Lindgren for the help in preparation and management of data sets and R. Karlsen for preparing flow data for C-Q analysis. We also acknowledge the work of KCS technicians who collected and processed the samples that comprise these long-term records. Long-term flow and water chemistry data for KCS streams and lysimeters are available via the Svartberget data portal (https://franklin.vfp.slu.se/). Other data presented in this manuscript, including mire well chemistry and modeled discharge for streams draining C2 and C4, as well as R code used in analyses and generation of figures are available at the CUAHSI Hydroshare database (http://www.hydroshare.org/resource/55ea84cc5330424295c01f5cf208c517).

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