LIMNOLOGY and OCEANOGRAPHY

ASLO

Limnol. Oceanogr. 68, 2023, 409–423

doi: 10.1002/lno.12282

Long-term changes in dissolved inorganic carbon across boreal streams caused by altered hydrology

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Abstract

A major challenge for predicting future landscape carbon (C) balances is to understand how environmental changes affect the transfer of C from soils to surface waters. Here, we evaluated 14 yr (2006–2019) of stream dissolved inorganic carbon (DIC) concentration and export data for 14 nested boreal catchments that are subject to climatic changes, and compared long-term patterns in DIC with patterns in dissolved organic carbon (DOC). Few streams displayed significant concentration or export trends in DIC at annual time scales. However, most streams showed decreasing DIC concentrations during spring flood over this 14-yr period, and about half showed declines during summer. Although annual runoff has generally not changed during this period, an intra-annual redistribution in runoff, with increases in spring flood discharge, explained much of the seasonal changes in DIC concentration. We observed negative DIC–discharge relationships in most streams, suggesting source limitation of DIC, whereas DOC mostly showed chemostatic behavior. The different trends and patterns observed for DIC vs. DOC underpin intra-annual changes in the composition of the total C pool (i.e., the DIC/DOC ratio) and reflect fundamental differences in how these C forms are produced, stored in riparian soils, and mobilized by hydrological events. Collectively, our results highlight the sensitivity of riverine DIC to the intra-annual distribution of runoff, but also important heterogeneity across the network that suggests local processes can also modify the mobilization of DIC in boreal landscapes.

Northern regions are experiencing widespread changes in climate and the future projection is that these will continue with important consequences for terrestrial and aquatic systems. In this context, one important unknown is how altered hydrometeorological conditions will affect the export of carbon (C) from land to surface waters. Potential changes in the export of C from soils have multiple biogeochemical implications for aquatic systems per se, but are also essential for capturing the overall landscape C balance, as the loss of terrestrial C to surface waters is a significant term in this overall mass balance (Öquist et al. 2014; IPCC 2021). Dissolved inorganic carbon (DIC), including carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) represents an important, yet often overlooked component of the C pool transferred from soils to water (Raymond and Hamilton 2018). DIC is also a key solute in aquatic systems, regulating pH, while also acting as the C source for aquatic primary production (Cole and Prairie 2014). Given these multiple ecological and biogeochemical roles, understanding the response in surface water DIC to changing environmental conditions is central for predicting future shifts in many biogeochemical processes.

Several studies have explored long-term patterns in stream and river inorganic carbon (IC) concentrations and exports to better understand effects of recovery from acidification (Clow and Mast 1999) and/or management change (Raymond et al. 2008; Stets et al. 2014; Räike et al. 2016), as well as responses to permafrost thaw (Tank et al. 2016; Drake et al. 2018). Common to most of these efforts is that time series rely on standard water chemistry monitoring where the IC component is restricted to data on alkalinity (i.e., HCO_3^-), or where DIC has been inferred from alkalinity measurements (Giesler et al. 2014). Since DIC comprises both a gaseous component, CO_2, and the nonvolatile ions, HCO_3^- and CO_3^{2-} in

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Additional Supporting Information may be found in the online version of this article.

Author Contribution Statement: M.B.W., H.L. and R.S. generated the idea. L.R. compiled data, performed the data analysis and wrote the first draft of the manuscript. H.L. acquired funding for maintaining the long-term data collection. M.B.W. conducted additional data analyses and wrote the final version of the manuscript with support from all coauthors.

equilibrium, the flux is two-dimensional (2D) with both a lateral and a vertical transport component. Thus, from a landscape C balance perspective, representative measurements of DIC transfer from soils to surface waters needs to be conducted close to the terrestrial source, as CO_2 is known to degas to the atmosphere shortly after passing the soil–water interface (Leith et al. 2015). This is especially true for weakly buffered systems that are low in pH and where a large share of the DIC is in the form of CO_2 (Wallin et al. 2010). Such conditions are common across the boreal biome where silicate weathering occurs at relatively low rates, and where carbonate containing bedrock and minerals are rare.

DIC is produced through aerobic and anaerobic respiration in soil, water, and sediments (Cole and Prairie 2014), but also through weathering of minerals in soils and bedrock (Gaillardet et al. 1999), and by photo-oxidation of organic matter in aquatic systems (Granéli et al. 1996). The relative importance of these sources for surface water DIC varies in time and space and seems highly site specific. For boreal headwaters, DIC inputs from soil respiration in the surrounding catchment generally outweigh in-stream production (Campeau et al. 2018; Riml et al. 2019), but aquatic respiration can also be a sizeable CO_2 source under some circumstances (Demars 2019; Lupon et al. 2019). Furthermore, the spatial variability in stream DIC is high due to discontinuities in terrestrial inputs (Lupon et al. 2019), and due to the 2D transport where local physical characteristics of the stream channel regulate the gaseous exchange with the atmosphere (Wallin et al. 2011; Raymond et al. 2012). Stream DIC is also temporally variable, as production, consumption, and transport are all regulated by variation in hydrometeorological conditions. As a result, DIC in low-order stream systems appears largely controlled by variation in runoff, often displaying a negative concentration-discharge relationship that reflects source limitation (Finlay 2003; Wallin et al. 2010; Jantze et al. 2015).

Concurrent changes in other water chemistry parameters may also influence the production, consumption, and transport of DIC. For example, for the last several decades, increases in dissolved organic carbon (DOC) concentrations have been rising in many inland waters across the northern hemisphere, both within individual catchments and across larger regions (Evans et al. 2005; Fork et al. 2020; Eklöf et al. 2021). The reasons for this are not completely resolved, but recovery from sulfur deposition, as well as changes in climate and land use are all potential drivers (Kritzberg et al. 2020). Regardless of the mechanism, positive relationships between DOC and CO_2 have been observed at multiple spatial scales across northern lakes and streams (Sobek et al. 2003; Lapierre and del Giorgio 2012; Wallin et al. 2014), and any increases in terrestrially derived DOC with subsequent mineralization has been suggested to increase aquatic CO_2 and hence DIC (Lapierre et al. 2013). However, although DOC and CO_2 are spatially related, evaluations over temporal scales suggest an uncoupling between these C components (Nydahl et al. 2017). Furthermore, detailed catchment studies suggest that DOC and DIC are sourced differently in the landscape, such that their export responds differently to changes in hydrology (Winterdahl et al. 2016; Campeau et al. 2019) and shifts in land cover (Gómez-Gener et al. 2021). Whether the difference in hydrological sourcing between DOC and DIC also affects the long-term evolution of the different C forms in response to environmental changes remains unknown. Resolving these responses is central to making future projections of the total export of C from soils to surface waters. A prerequisite for filling this knowledge gap is access to long-term time series of directly determined stream IC data that also include the CO_2 component (i.e., DIC).

Here, we examined patterns in stream DIC within the boreal Krycklan Catchment Study (KCS) over a 14-yr period (2006–2019). The area has experienced clear changes in hydrometeorological conditions during the last 40 yr with increasing air temperatures and shorter winters, resulting in altered seasonal runoff patterns (Laudon et al. 2021). In addition, increasing DOC concentrations have been observed for several of the KCS streams during the same period (Fork et al. 2020). We took advantage of these ongoing changes to ask how DIC concentrations have changed over time, and whether trends relate to changes in DOC or hydrology. Because the direct input from soils is expected to be a more important source of stream DIC than in situ DOC mineralization, we predicted that, if trends in DIC are present, these would relate to changes in runoff. However, if in situ (aquatic) mineralization is the more important DIC source, then we might expect DIC to increase at sites where DOC concentrations are also increasing. To test these alternatives, we analyzed temporal patterns in DIC and compared these trends with patterns in runoff and DOC for the same period. We addressed these patterns and the potential controls at seasonal and annual time scales. Finally, we integrated the trends for DIC and DOC (as DIC/DOC) to explore whether, and how, environmental changes are altering the overall composition of the C pool exported from this stream network.

Materials and methods

Site description

The study was conducted in the 68 km^2 boreal KCS, situated ca. 50 km northwest of Umeå, Sweden (64°14′ N, 19°46′ E; Fig. 1; Laudon et al. 2013). The catchment is primarily comprised of forest, mainly Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), as well as mires, streams, and lakes. The elevation ranges from 114 to 405 m.a.s.l., and the catchment is dominated by till and peat soils above the highest postglacial sea level (257 m.a.s.l.), and with primarily sorted postglacial sediments below. The underlying bedrock consists predominantly of base-poor Sveco-fennian metasediments/metagraywacke with no known carbonate

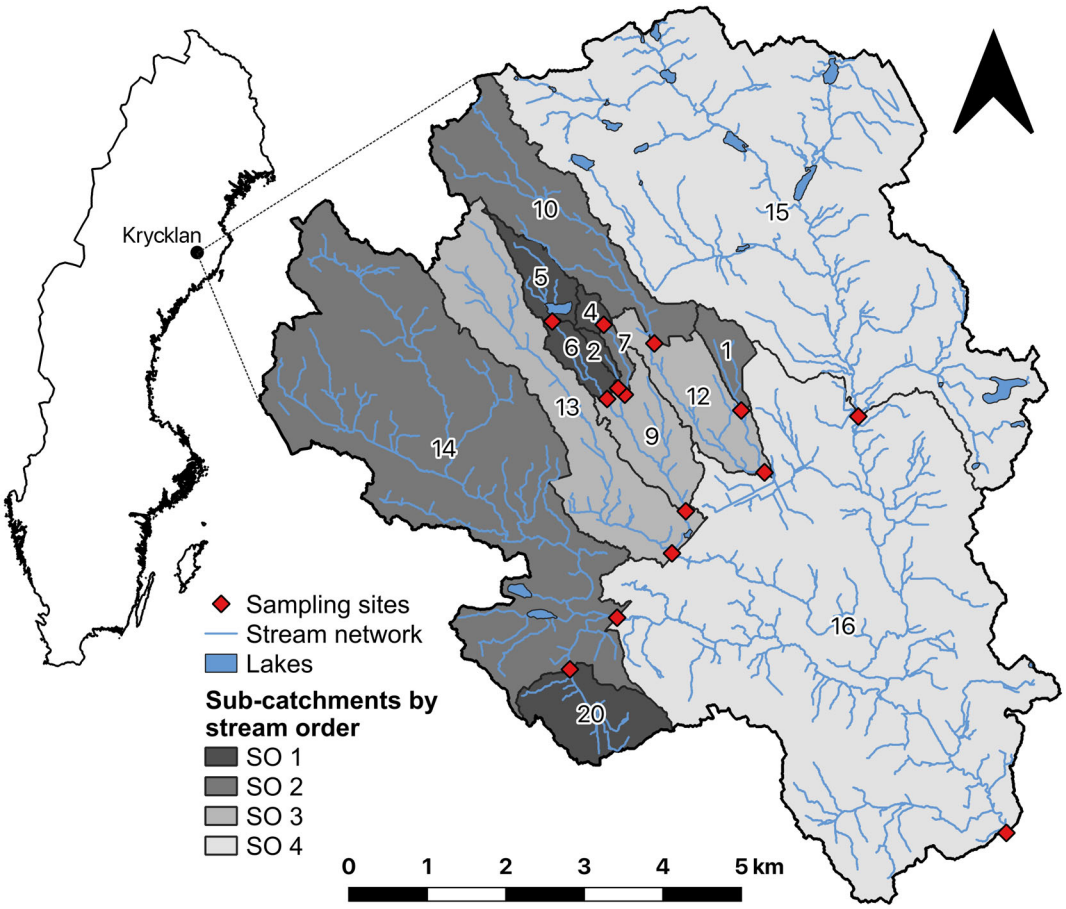

Fig. 1. The location of the KCS and with the subcatchments grouped by stream order, along with the stream network, lakes and sampling sites. The contour map of Sweden is taken from GADM (https://www.gadm.org/).

containing minerals (Ågren et al. 2007). Hence, any carbonate alkalinity is produced by weathering of silicate minerals, which is confirmed by the stable carbon isotopic composition of DIC (δ^{13}C-DIC) in groundwater typically ranging from −20‰ to −28‰ across the catchment (Venkiteswaran et al. 2014; Campeau et al. 2018; Nydahl et al. 2020). The mean annual air temperature was 2.1°C between 1981 and 2020, with monthly means ranging from −9.1°C in January to 14.5°C in July. The mean annual precipitation for the same period was 623 mm, of which ca. 30% as snow. The annual mean runoff was 298 mm with 40–50% occurring during the spring flood period in April–May. Importantly, changes in climate over the last 40 yr have led to increasing air temperatures (mean annual temperature increased by 2.5°C) with subsequent effects on snow cover duration and runoff patterns (Teutschbein et al. 2015; Laudon et al. 2021).

We used data from 14 sites, representing a nested set of subcatchments that span four Strahler stream orders and ranging in size from 0.12 to 68 km^2 (Laudon et al. 2013; Table S1). All subcatchments are mainly covered by forest and with various amounts of peatland. Subcatchments C4 and C5 are outlets of a peatland and a lake, respectively. Stream water pH within the catchment is typically ranging from 4–5 in the headwaters to 6–6.5 in the 4th-order streams (Buffam et al. 2008).

Sampling and analysis

We analyzed stream DIC and DOC concentration data collected from each site between February 2006 and June 2019. Each site was sampled on average 22 times per year, ranging from monthly frequency during late autumn and winter to almost daily frequency during spring peak flood. In total 4381 DIC and 4206 DOC samples were included in the analysis.

For DIC determination, a headspace method was used where a sample of bubble-free water (2 mL in 2006, 5 mL from 2007 and onward) was injected in a 22.5 mL glass vial sealed with a bromobutyl rubber septa. The injection was made by using a sterile syringe which was flushed with stream water before sampling. The vial was prefilled with 0.5 mL 0.6% HCl (between 2006 and 2011) or 0.1 mL 85% H_3PO_4 (from 2011 and onward) and N_2 at atmospheric pressure. The samples were stored dark and cold (4°C) for a maximum of 1 week prior to analysis. Samples were analyzed on a gas chromatograph equipped with a

methanizer and flame ionization detector (GC-FID). The GC-FID used between 2006 and 2011 was a PerkinElmer Clarus 500, after which a PerkinElmer Clarus 580 connected to a Turbo Matrix 110 autosampler was used instead. As the samples were acidified, DIC concentrations were determined from the headspace CO_2 considering water and headspace volumes and temperature-dependent equations for the carbonate equilibrium. *See* Åberg and Wallin (2014); Leach et al. (2016); Wallin et al. (2010) for further details of the DIC method. Water samples for DOC were collected and filtered in the lab using a 0.45 μm MCE membrane, Millipore. Samples were then stored refrigerated for up to 10 days after which they were analyzed using a Shimadzu TOC analyzer (Shimadzu, Duisburg, Germany). For further details on the DOC sampling and analysis *see* Laudon et al. (2011).

Stream discharge was measured at the outlet of each subcatchment. Measurements were performed in V-notch weirs or flumes using established stage height–discharge relationships. Stream discharge gauging for rating curve definition was done using salt dilution, velocity–area, and time–volume measurements (depending on site) covering most of the observed discharge ranges. Stage height was continuously recorded at each site using pressure or capacitance sensors. Missing days in the measured discharge data were gap-filled using the hydrological model HBV-Light, based on climate data collected at the Svartberget climate station. Gap-filling of discharge data was mainly performed during low-flow periods with snow and ice during early years in the time series. Site-specific daily discharge time series covered on average 12 yr, for details concerning start and end dates for each site see Table S2. For further information concerning discharge measurements and gap-fill modeling, *see* Karlsen et al. (2016).

Statistical analysis

We used nonparametric Mann-Kendall (MK) trend test and the related Theil-Sen (TS) slope estimator were used (Hipel and McLeod 1994; Helsel and Hirsch 2002) to examine temporal trends in DIC concentration. The MK test examines a data set for significant monotonic trends while the TS slope finds the median slope of all pairs of points within the data set, providing a robust estimate of rate of change within the data set (Helsel and Hirsch 2002). For the full time period (2006–2019), monthly median DIC concentration data were used for the MK tests to remove uneven weighting of data caused by the difference in sampling frequency across the year. We also analyzed MK trends over the 14-yr period for seasonally grouped DIC data: winter (December–March), spring flood (April–May), summer (June–August), and autumn (September–November). Spring flood is here defined as April–May as these months typically cover the clear majority of the runoff pulse (Fig. S6). For the MK tests on seasonal data, all available data for a season were used, which allowed for a more robust statistical assessment of seasonal change. Since the data for each season were generally evenly distributed, this method did not risk uneven weighting of data within a season. Finally, to identify the drivers of DIC trends, we also examined the temporal changes in DOC concentration and discharge at each site following similar approaches. MK tests for DOC, DIC/DOC and discharge were computed for the full time period using monthly medians and for the seasonally grouped data as described for DIC. The DIC to DOC concentration ratio (DIC/DOC) was computed to identify differences among sites, and changes over time, in the overall composition of the stream dissolved C pool. To be noted, Fork et al. (2020) recently published a similar MK analysis on temporal trends in DOC for KCS streams, using a different range of years and different approaches to seasonal partitioning. In the current study, we analyzed DOC trends solely as a complement to observed trends in DIC.

Daily DIC export was calculated for each site by first creating daily time series of DIC concentration data through linear interpolation between sampling days. Daily DIC concentration was then multiplied with mean daily stream discharge. Annual DIC export rates were estimated for each subcatchment by taking the sum for each year and dividing it by the subcatchment area. MK trends for the annual DIC export were calculated for the full study period.

To evaluate the response in stream concentrations of DIC and DOC to variable discharge, we constructed C–*Q* relationships (log C (mg L^{-1}) vs. log specific discharge (mm d^{-1})) for each site. The slope of the log-transformed relationship was used to characterize the C response pattern at each site and with the explanatory power (R^2) describing the fit of the relationship. Based on Meybeck and Moatar (2012) we characterized the sites as "source limited" when the slope of this relationship < -0.2, "chemostatic" when the slope was between -0.2 and 0.2, and "transport limited" when the slope ≥ 0.2. For the DOC–discharge assessment, our analysis of all data for a given site incorporates any changes in this relationship during the study period (Fork et al. 2020). Analysis of the corresponding DIC–discharge relationships within the current study suggested that these relationships did not statistically change over time (Fig. S3). Because our primary focus here is on DIC, we opted for an approach that provided an overall (i.e., cross year) assessment of this relationship with discharge at each site. To further examine the temporal interplay between DIC and DOC, we computed Kendall's τ correlations on all concentration data at each site. Statistical analysis of C–*Q* relationships and Kendall's τ were performed in JMP 15.0.0. Temporal trend tests (MK) were performed in RStudio, and where the MK trends were computed for each individual site using the *rkt* package (Marchetto 2017). The significance level $p \leq 0.05$ was used for all statistical analyses. For further information of data inclusion in respective analysis, *see* Table S3.

Results

Spatiotemporal variability in stream DIC

DIC concentrations varied considerably within and between streams during the study period, 2006–2019 (Fig. 2).

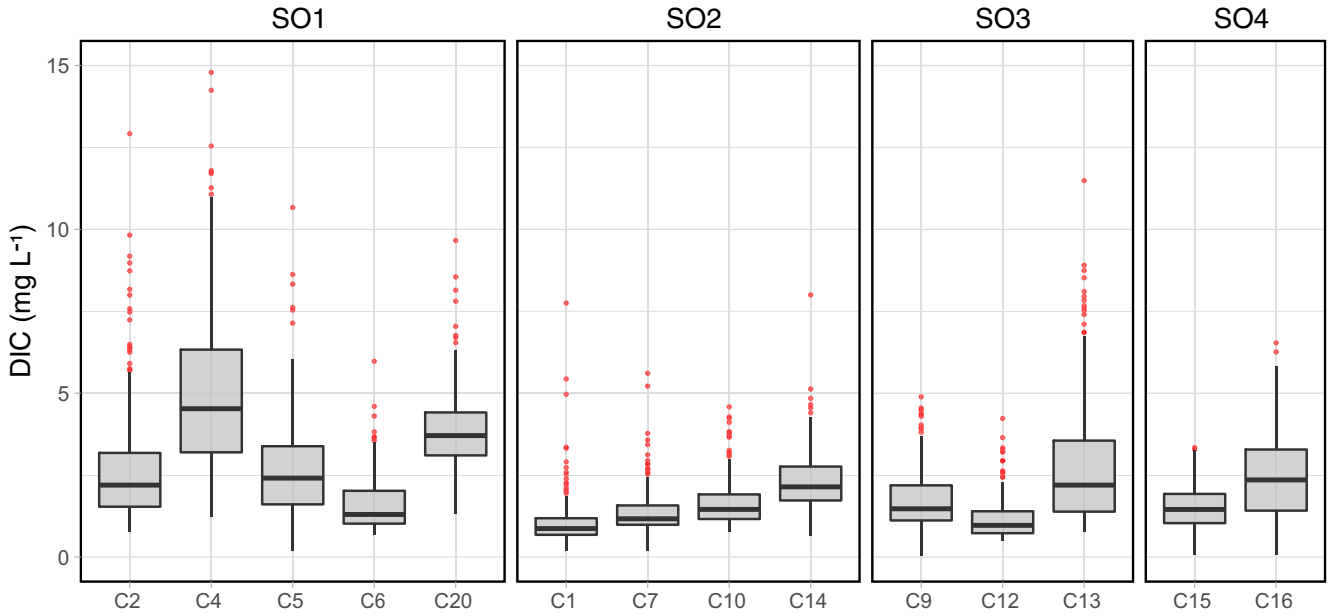

Fig. 2. Boxplots with DIC concentration data (2006–2019) for all 14 sites, grouped by stream order. Median concentration marked as horizontal line through each box, whiskers up to 1.5 times the interquartile range and outliers marked as red points. Two outliers exceeded the displayed range (18 and 22 mg L^{-1} for C2 and C5, respectively).

Site-specific median concentrations ranged from 0.9 to 4.7 mg L^{-1} and with interquartile ranges from 0.5 to 3.3 mg L^{-1}. The distribution in DIC for each site was generally skewed, with several high concentration outliers. The highest concentrations and variabilities were generally observed in the first order streams, with the exception of the 3rd stream order C13, which displayed higher variability in DIC than other 2nd–4th-order sites. The mean annual DIC export across the subcatchments ranged from 0.3 (± 0.1) to 1.4 (± 0.4) g C m^{-2} yr^{-1} (Fig. 3), with highest export rates found in three

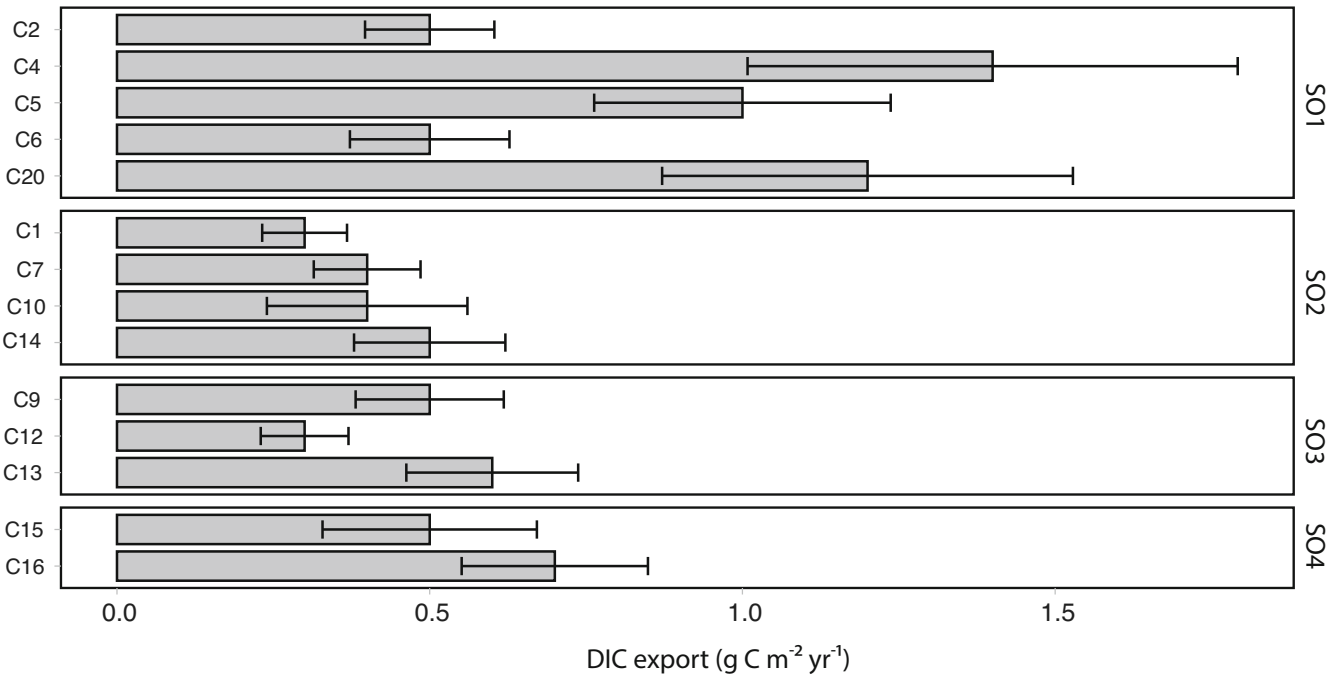

Fig. 3. Mean annual DIC export (g C m^{-2} yr^{-1}) and standard deviation (error bars) for each of the 14 stream sites (2006–2019) grouped by stream order.

Table 1. Mann-Kendall trend test results for DIC concentrations and annual DIC export rates in all sites for the full time period (2006–2019). Significant ($p \leq 0.05$) results marked in black bold font.

	DIC concentration trends		DIC export trends	
Site	Theil-Sen slope (mg L^{-1} yr^{-1})	*p* Value	Theil-Sen slope (g C m^{-2} yr^{-1})	*p* Value
C1	−0.01	0.11	−0.002	0.73
C2	−0.03	0.23	**−0.02**	**0.01**
C4	−0.03	0.46	−0.02	0.67
C5	+0.006	0.77	−0.02	0.15
C6	−0.02	0.35	**−0.03**	**0.01**
C7	**−0.02**	**0.02**	−0.01	0.13
C9	−0.008	0.62	−0.02	0.15
C10	−0.002	0.80	**−0.03**	**0.01**
C12	−0.01	0.36	+0.01	0.53
C13	−0.04	0.21	−0.02	0.06
C14	−0.03	0.07	−0.01	0.37
C15	−0.02	0.18	−0.003	0.85
C16	−0.03	0.30	−0.02	0.08
C20	+0.005	0.84	+0.001	0.80

1st-order streams (C4, C5, and C20). Finally, the importance of DIC to the broader C pool also differed by an order of magnitude across sites, with median DIC/DOC ratios ranging from 0.05 to 0.39 (Fig. S1). Highest median DIC/DOC ratios were typically observed in streams located at low-elevation areas within the catchment dominated by postglacial sediments (e.g., C14, C16, and C20).

Temporal trends in stream carbon and runoff

The MK tests for the full time period revealed that the DIC concentrations significantly decreased over time in one site (C7) with TS slope of −0.02 mg L^{-1} yr^{-1} (Table 1). No other sites displayed significant trends for the full time period. However, results from season-specific MK tests revealed distinct patterns across most sites during the 14-yr period (Fig. 4; Table S4). Here, no sites exhibited significant trends during the winter season, whereas 13 sites showed significant negative trends during the spring, with TS slopes ranging from −0.02 to −0.09 mg L^{-1} yr^{-1}. During summer, six sites exhibited significant negative trends, with TS slopes ranging from −0.03 to −0.06 mg L^{-1} yr^{-1}, while one displayed a significant positive trend (C5) with TS slope 0.05 mg L^{-1} yr^{-1}. Only two sites exhibited significant trends during autumn, one negative (C7) with TS slope −0.03 mg L^{-1} yr^{-1} and one positive (C16) with TS slope 0.07 mg L^{-1} yr^{-1}. Finally, the MK trends for the annual DIC export revealed that export decreased significantly in three sites (C2, C6, and C10), with TS slopes between −0.02 and −0.03 g C m^{-2} yr^{-1} (Table 1). No other sites displayed any significant trends in annual DIC export.

For DOC concentration, three sites displayed significant trends over the full time period: two increasing (C1 and C2) and one decreasing (C5; Table 2). As above, season-specific analyses revealed a wide range of changes. For example, declines in DOC concentration were widespread during

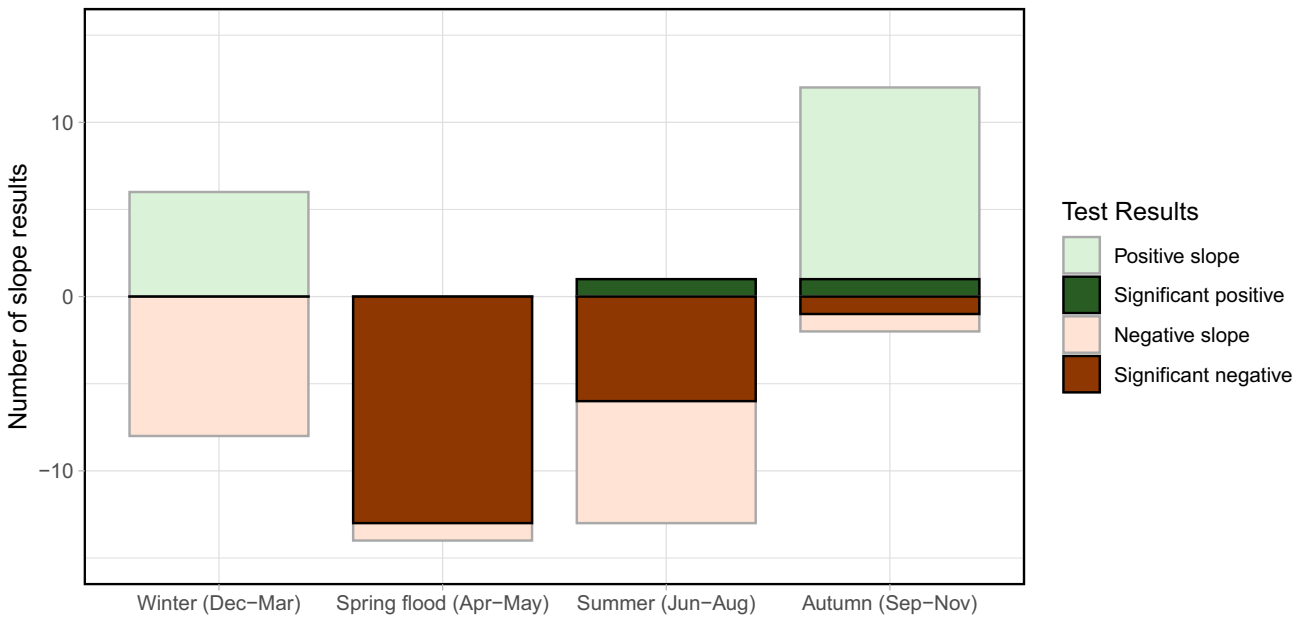

Fig. 4. Number of sites exhibiting significant ($p \leq 0.05$) and nonsignificant positive and negative Mann-Kendall test results for DIC concentration data (2006–2019) by season.

Table 2. Theil-Sen slopes for the Mann-Kendall trend tests for full time period (2006–2019) DOC concentration data and discharge data. Significant ($p \leq 0.05$) results marked in black bold font.

	Discharge trends		DOC concentration trends	
Site	Theil-Sen slope (mm d^{-1} yr^{-1})	*p* Value	Theil-Sen slope (mg L^{-1} yr^{-1})	*p* Value
C1	+0.008	0.17	**+0.3**	**0.02**
C2	**−0.01**	**0.02**	**+0.4**	**0.01**
C4	−0.0002	0.98	+0.03	0.86
C5	−0.003	0.66	**−0.3**	**0.01**
C6	**−0.2**	**0.01**	−0.06	0.46
C7	−0.005	0.35	+0.2	0.16
C9	−0.009	0.22	+0.02	0.79
C10	−0.02	0.06	+0.1	0.47
C12	+0.007	0.45	+0.2	0.22
C13	**−0.02**	**0.01**	+0.2	0.14
C14	−0.01	0.17	0	1.00
C15	−0.01	0.25	−0.004	0.96
C16	**−0.01**	**0.03**	+0.02	0.86
C20	−0.008	0.38	+0.06	0.50

autumn (10 sites; Fig. 5; Table S5). We also observed positive trends in DOC concentration during the spring flood (six sites) and summer (four sites). The only negative trends in DOC concentration during winter, spring flood, and summer were either at C4 or C5, the peatland and lake outlets. The different trends for DIC and DOC altered the relative composition of the total dissolved C pool over time, as expressed by

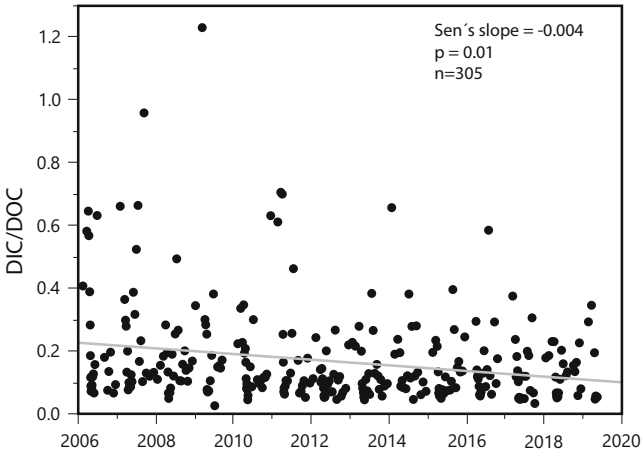

Fig. 6. The DIC/DOC concentration ratio over time (2006–2019) for site C2. Theil-Sen statistics are given based on analysis of monthly median values.

the DIC/DOC ratio. Here, three sites (C1, C2, and C7) showed decreasing DIC/DOC ratios across the full study period (range 0.001–0.004 yr^{-1}; Fig. 6; Table S6). At seasonal scales, 12 of 14 sites have decreased in DIC/DOC ratio during spring, and six sites during summer (Fig. S2). In contrast, nine sites have increased in DIC/DOC ratio during the autumn, whereas no changes in winter total C composition were detected. C5 (the lake outlet) was the only site with an increasing DIC/DOC ratio during summer.

Four sites (C2, C6, C13, and C20) displayed significant negative trends in stream discharge over the full time period, while the remaining sites did not show any change (Figs. S4, S5; Table 2). However, the number of sites that showed significant trends over time increased when making season-specific

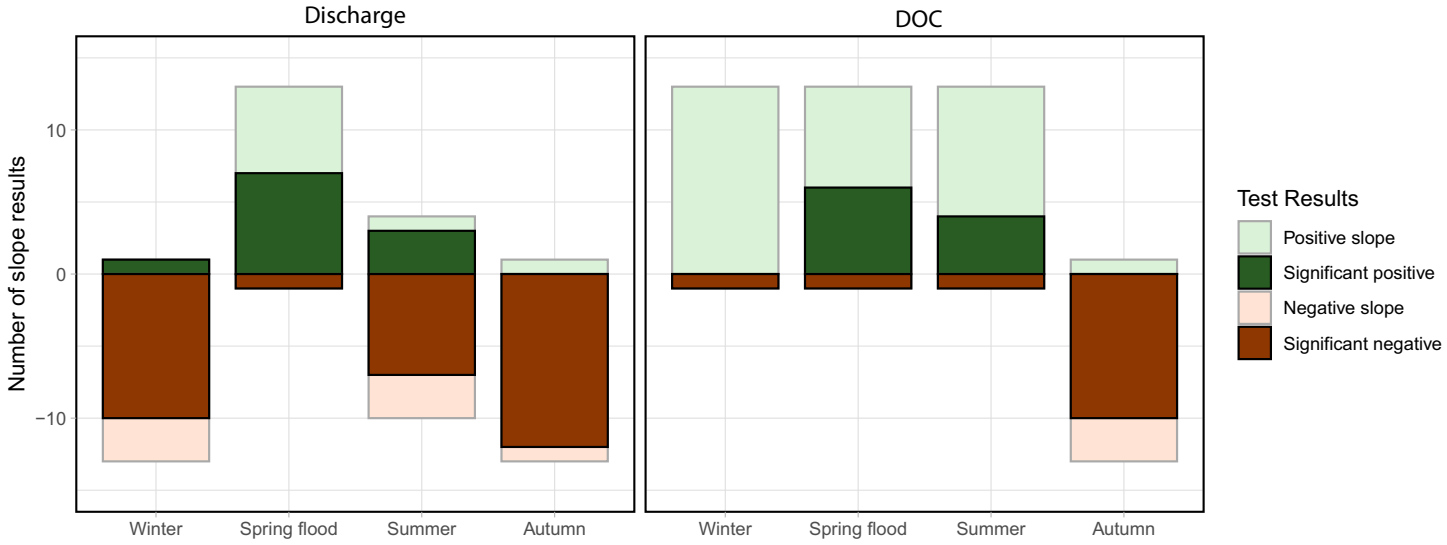

Fig. 5. Number of sites exhibiting significant ($p \leq 0.05$) and nonsignificant positive and negative Mann-Kendall test results for discharge and DOC concentration data (2006–2019) by season.

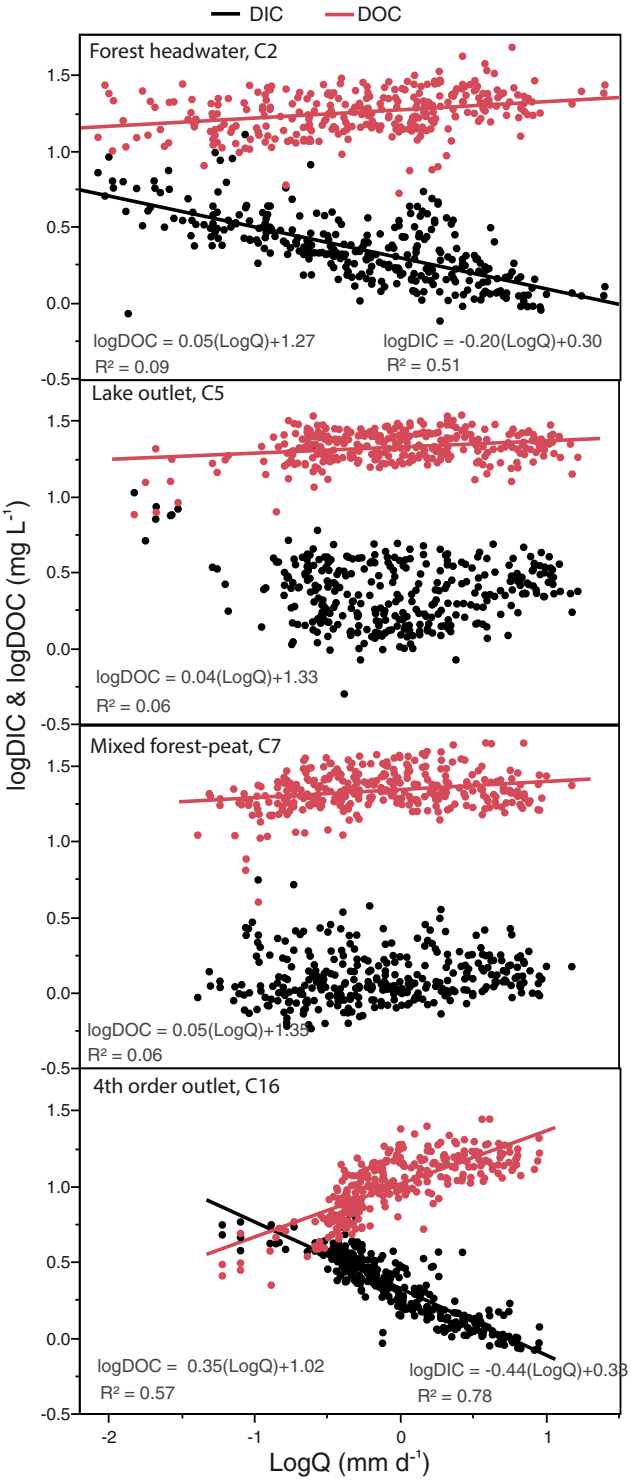

Fig. 7. logDIC and logDOC (mg L^{-1}) as functions of logQ (mm d^{-1}) for four example sites within the KCS. The four sites cover a wide range in conditions from fully forested headwater (C2), headwater lake outlet (C5), forest and wetland mixed 2nd-order stream (C7) and the 4th-order outlet of the Krycklan catchment (C16). Regression equations and R^2 are given for significant relationships. Note that C5 and C7 were the only sites among the 14 studied that did not display a significant DIC–discharge relationship.

analyses. Negative trends in discharge were widespread during autumn (12 sites) and winter (10 sites), but also during the summer (seven sites; Fig. 5). Three sites displayed positive trends in discharge during the summer. In contrast to these generally negative trends, we observed a positive trend in discharge during the spring flood period at seven sites, with only one site (C10) showing declines in flow during this season.

Hydrological controls on stream DIC and DOC concentrations

DIC concentrations were negatively related to discharge at 12 sites, with slopes of the C–Q relationship ranging from −0.09 to −0.46 (Fig. 7; Table S7). Eight sites had slopes < −0.2 suggesting source limitation of stream DIC and four sites were classified as chemostatic (slopes of −0.09–[−0.18]). For the two remaining sites (C5 and C7), DIC was unrelated to discharge (i.e., was chemostatic). DOC concentrations and discharge were positively related for 13 sites, with C–Q slopes ranging from 0.14 to 0.32, and negatively related at one site (C4), with a C–Q slope −0.13. Despite that a clear majority of the streams had positive C–Q slopes for DOC, 13 of 14 sites were classified as chemostatic and with only one site (C16) showing transport limitation. The difference in temporal behavior between DIC and DOC was further revealed by correlating the two C forms. DIC and DOC were negatively correlated in 10 sites, with Kendall's τ ranging from −0.14 to −0.56, and positively correlated at two sites (C4 and C5) with Kendall's τ 0.20 and 0.34, respectively.

Discussion

A major challenge for predicting future landscape C balances is to understand how environmental changes affect the transfer of C from soils to water. This is specifically important for boreal regions, which are subject to large climatic changes and store vast amounts of the global soil C stock (Bradshaw and Warkentin 2015). In this context, analysis of long-term data records can resolve temporal controls at different scales, which in turn can help us predict future changes. Overall, our results suggest that DIC across boreal streams is currently changing in response to altered runoff patterns, although these trends are largely manifested at seasonal rather than annual time windows, and are also variable across the stream network. Furthermore, trends in DIC contrast with those for DOC, and thus the overall composition of the C pool (DIC/DOC ratio) is also changing, something that is often overlooked in studies evaluating long-term C trends. Although beyond the scope of the current study such compositional changes could have multiple biological, chemical, and physical consequences for downstream ecosystem functioning.

The observed DIC concentrations across KCS streams, 0.9–4.7 mg L^{-1} (Fig. 2), are representative of many boreal and hemiboreal regions. For example, Hutchins et al. (2019) reported median values between 1.9 and 6.9 mg L^{-1} across

190 streams and rivers in Quebec, Canada. Similar stream DIC or TIC concentrations (0.7–10.4 mg L^{-1}) have also been observed in low-order boreal streams in eastern Finland (Rantakari et al. 2010) and south and mid-Sweden (Wallin et al. 2014). Finally, while the observed stream DIC export (0.3–1.4 g C m^{-2} yr^{-1}) is small in relation to other catchment C fluxes observed in KCS, including DOC export (4–10 g C m^{-2} yr^{-1}; Wallin et al. 2013) and terrestrial net ecosystem exchange (150–175 g C m^{-2} yr^{-1}; Chi et al. 2020), it is nonetheless a persistent loss term in the landscape C balance.

Annual changes in stream DIC concentration

Although unique in the context of DIC time series, a 14-yr study period is not especially long for evaluating long-term temporal trends in stream water chemistry. Hence, it was not surprising that only a few sites exhibited significant trends in either concentrations or export rates (one and three sites, respectively; Table 1). However, 12 out of 14 sites displayed negative slopes for both DIC concentration and export. Despite the nonsignificance, the consistency of negative slopes indicates that the transfer of DIC from soils to water in these headwaters is under change. This indication of decreasing DIC concentrations contrasts with the widespread increases in IC (mostly as measures of alkalinity) observed during the last decades across streams and rivers elsewhere in the northern hemisphere (Giesler et al. 2014; Stets et al. 2014; Räike et al. 2016; Drake et al. 2018). We can only speculate on reasons for these contrasting patterns, but differences in ecosystem size and investigated time periods are potential causes. Furthermore, reported increases in IC appear to arise from acid deposition recovery (Stets et al. 2014; Räike et al. 2016), or as a result of permafrost thaw (Giesler et al. 2014; Drake et al. 2018), neither of which operate as powerful drivers in the KCS.

Seasonal changes in stream DIC concentration

The occurrence of changes in stream DIC over time was clearer when analyzing the data seasonally, where we observed significant trends in DIC concentrations at most sites, despite considerable differences in catchment characteristics and background DIC concentrations. Specifically, DIC concentrations decreased during spring flood (at 13 sites) and summer (at six sites), but had few (or no) significant trends during autumn and winter. The negative trends in DIC concentration during spring flood were likely driven by increases in seasonal discharge, which may dilute DIC via greater contribution of meltwater and/or enhance the efficiency of gas exchange with the atmosphere. Indeed, seven KCS sites exhibited significant positive discharge trends during this season, and an additional six sites had a positive, but nonsignificant slope in the trend analysis. Furthermore, on average, the spring flood contributed 40–50% of the annual runoff among KCS sites, but accounted for up to 70% during extreme years (Table S8). Hence, any chemical and hydrological changes during this season likely has important influences on annual DIC export.

During summer, hydrological influences on changing DIC concentrations were less clear and likely complicated by the influence of in situ (aquatic) processes that can generate downstream chemical signals during low-flow periods (Hotchkiss et al. 2018). For example, we observed simultaneous decreases in DIC concentrations with increasing summer discharge (i.e., a dilution signal) at only three sites (C1, C7, and C12; Tables S4 and S5), whereas for the two largest streams (C15 and C16), DIC concentrations and discharge both decreased during this period. This longitudinal difference in summer DIC/discharge trends suggests a season-specific shift in the controls over DIC when moving from the headwaters to the catchment outlet. Here, decreasing discharge during summer in the larger streams results in longer water residence times, which may enhance in-stream C processing, including CO_2 fixation by primary production (Wallin et al. 2020). This change could also lead to less DOC transported downstream from more organic-rich headwater environments, and thus potentially reduced mineralization/CO_2 production in the larger recipient systems. Similar effects of in situ transformation may arise for streams with close connections to lakes. Indeed, the only site that displayed a positive trend pattern in stream DIC during summer was C5, the outlet of a headwater lake (Table S4). The most likely explanation here is that in-lake CO_2 production from breakdown of OC (biologically or photochemically) has increased due to longer water residence times resulting from reduced summer discharge. This is further confirmed by the decreasing trend in summer DOC at C5, which was also the only site in the KCS network showing this pattern. As a result of these contrasting DIC and DOC trends, C5 was the only stream with increasing DIC/DOC ratio during summer (Fig. S2). Hence, hydrological changes not only alter the terrestrial input of C to aquatic systems but also may affect the conditions for in situ metabolism at the relatively small scale of headwater systems.

DIC trends during the nongrowing seasons (autumn and winter) were even less evident during this period of record. During autumn, significant positive TS slopes in the DIC time series were only observed for the largest catchment (C16), however, 12 out of 14 sites indicated positive trends during this season (Fig. 3; Table S4). This suggests that autumn changes in DIC may be ongoing and potentially related to changes in hydrology, as 12 out of 14 sites also displayed significant decreases in autumn discharge. Decreasing trends in discharge likely shift the baseflow water composition, with a greater proportion originating from deeper groundwater sources. Deep groundwater (5–20 m depth) across KCS is known to be DIC-rich (typically 10–20 mg L^{-1}; Nydahl et al. 2020). Together with previous findings from KCS, that deep groundwater mostly enters the stream network at downstream locations (Peralta-Tapia et al. 2015), suggest that the increasing autumn stream DIC at the outlet (C16) could be

caused by an elevated deep groundwater contribution over time. Compared to autumn, there was no evidence for DIC trends during winter, despite the fact that winter discharge also decreased at 11 of 14 sites. Similarly, winter DOC concentrations were largely unchanged during the studied period with only one site displaying a significant trend, again the lake outlet (C5) where DOC concentration has decreased. Whether the apparent stable winter DIC (and DOC) concentrations over time reflect the relatively low sampling frequency (monthly) during the winter season (December–March) remains unclear and requires further investigation.

In the light of recent increases in stream DOC concentrations within the KCS (Fork et al. 2020), even the subtle declines in DIC observed here have altered the composition of the total C pool exported from these catchments. While just three sites showed decreases in the overall annual DIC/DOC ratio during this study period, most showed clear changes in the total C composition seasonally, with generally decreasing DIC/DOC ratios during spring and increasing ratios during autumn. Such shifts suggest that an increasing fraction of the total C exported from this landscape during spring is in organic rather inorganic form, whereas the opposite is true during autumn. Because these C forms play such different physical, chemical, and biological roles, and turnover at different temporal scales, the observed changes have multiple potential consequences for landscape and aquatic ecosystem functioning. Most importantly, bulk DOC can be much more persistent in stream systems than DIC (Öquist et al. 2009; Catalán et al. 2016), thus, changes in this ratio underpin a fundamental shift in the spatial scale at which the total C pool is cycled regionally, with a greater fraction that likely persists further downstream in the aquatic continuum following snowmelt.

Changes in the stream DIC/DOC ratio could also have implications that stretch beyond the C budget perspective and merit further study. For example, DIC serves as an important source for buffering ground- and stream water acidity, which in turn regulates the conditions for acid-sensitive stream biota (Petrin et al. 2007). The observed trend toward lower stream DIC/DOC ratios during spring flood suggests a decrease in the carbonate derived buffering capacity in relation to the amount of DOC (including organic acids). Interestingly, spring flood pH in one of these streams (C7) has increased over the last 35 yr in response to reduced sulfur deposition (Laudon et al. 2021), and it is possible that observed decreases in the DIC/DOC ratio at this site have slowed the rate of this recovery. However, disentangling such an effect is a challenge, and further investigations are needed to resolve the influence of a changing DIC/DOC ratio on stream acidity. Another potential effect of decreasing DIC is a reduction in aquatic primary production, as has been suggested for lakes (Hein 1997; Hamdan et al. 2018). However, primary production is generally low in these acidic, nutrient- and light-limited streams (Burrows et al. 2021), and DIC concentrations are usually elevated (or strongly elevated) in relation to atmospheric CO_2 equilibrium. Hence, given the subtle rates of declining DIC during spring and summer (site-specific median -0.03 mg L^{-1} yr^{-1}), it is unlikely that decreasing DIC concentrations would influence aquatic primary production.

Hydrological sourcing of terrestrial DIC to surface waters

Simultaneous measurements of DIC, DOC, and runoff from multiple streams in a network and that span more than a decade in time are rare in the literature. These data allowed us not only to detect long-term trends in C concentrations and total C composition, but also to test competing hypotheses related to the drivers of DIC dynamics in these streams. We hypothesized that any temporal trends in DIC would be related to changes in catchment hydrology that affect the mobilization of DIC, rather than changes in DOC concentrations, which have been observed during the same period (Fork et al. 2020). This hypothesis was supported by the opposing temporal trends in stream DIC and DOC concentrations (Fig. 7), and by the generally source limited (for DIC) vs. chemostatic (for DOC) character of the C–*Q* relationships. Source limitation of stream DIC was widespread across Krycklan streams, with 12 out of the 14 sites displaying strong negative DIC–discharge relationships (Table S7). Similar reports of source limitation of DIC in low-order stream are widespread in the literature, including early findings from the KCS (Wallin et al. 2010), but also across temperate, Arctic, and boreal systems (Finlay 2003; Polsenaere et al. 2013; Jantze et al. 2015). This diluting effect contrasts with the hydrological influences on DOC, which across the full study period was generally weak and positive (Table 2). However, recent detailed studies on the DOC–discharge relationship within the KCS streams indicate that DOC has transitioned from being transport limited 10–20 yr ago to being largely chemostatic in later years as a result of changes in riparian pore-water conditions (Fork et al. 2020; Gómez-Gener et al. 2021). In contrast, no systematic changes in the DIC–discharge relation were identified across these streams during the current study period (Fig. S3). This temporal stability further suggests that the hydrological controls generally override other long-term environmental changes affecting stream DIC within this boreal catchment.

We suggest that the distinct discharge responses on DIC and DOC reflect differences in the shape of the concentration profiles for the different C forms in riparian soils. Specifically, while DOC typically decreases with soil depth in forested ecosystems (Lyon et al. 2011), DIC shows the opposite pattern (Fig. 8) (Tang et al. 2003; Öquist et al. 2009; Stewart et al. 2022). Increases in DIC concentration with depth reflect, in part, the flux of CO_2 to atmosphere, which creates a vertical CO_2 concentration gradient with values close to atmospheric levels in near-surface strata. In addition, a large share of the total soil CO_2 derives from root and root-associated respiration further down in the soil profile (Högberg et al. 2001). Due to

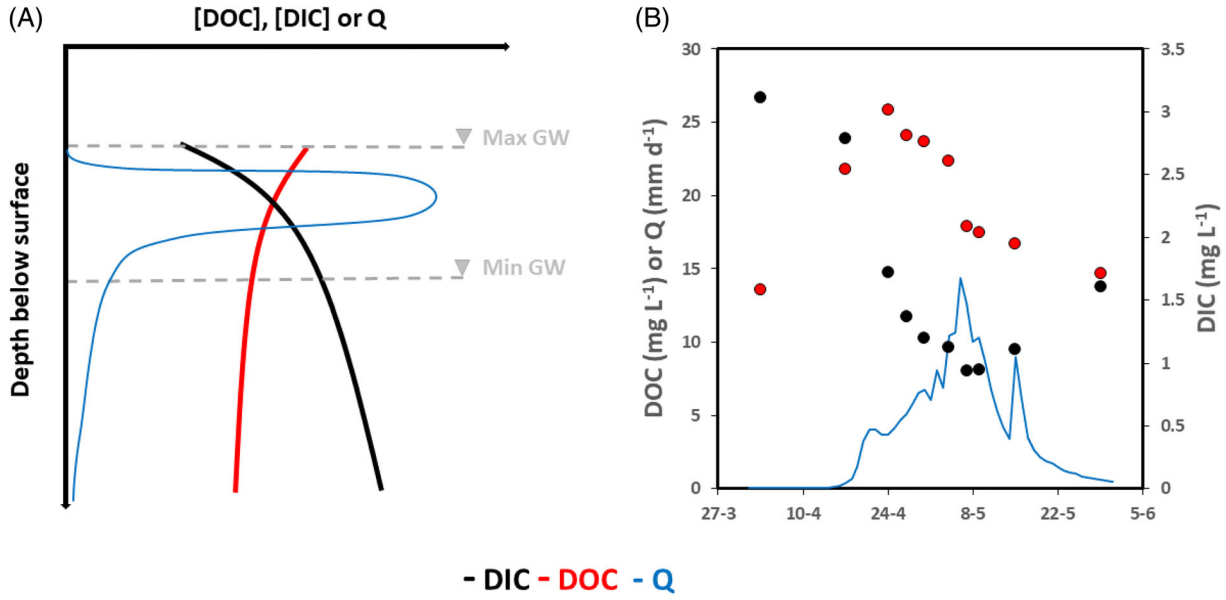

Fig. 8. Conceptual figure describing how (**A**) concentrations of DOC (red) and DIC (black) are typically distributed throughout near-stream soil profiles within KCS. In addition to C concentration profiles, typical vertical distribution in lateral water flux (*Q*) is shown in blue, with minimum and maximum groundwater level in dashed gray. The conceptual figure is based on empirical data from Öquist et al. (2009) (DIC), Grabs et al. (2012) (DOC) and Seibert et al. (2009) (*Q*). (**B**) A time series example on how DOC and DIC are responding during a typical spring flood (2018) at C2.

the differences in soil concentration profiles between DIC and DOC, variability in the groundwater table position and the subsequent lateral export of water through different source layers creates opposing response patterns between soil exports of DOC and DIC with changes in runoff (Gómez-Gener et al. 2021). This view supports previous findings that riparian soil exports of these two C species are mechanistically uncoupled, with differences in dominating terrestrial source areas at the catchment scale (Winterdahl et al. 2016; Campeau et al. 2019).

The different vertical patterns of DIC and DOC concentrations in riparian soils should also help us understand stream C responses to future hydrological change. Accordingly, any annual or seasonal increases in discharge will activate lateral groundwater flow paths that intersect soil strata with relatively lower DIC and higher DOC concentrations. In this study, we see the direct influence of this vertical pattern on stream chemistry most clearly in the seasonal declines in DIC and DIC/DOC ratios in response to a decadal increase in spring discharge (with the reverse in autumn). Whether such hydrological trends will continue is unclear, and hinge on how multiple climatic factors interact with terrestrial water storage and plant water use to regulate runoff. The long-term projection for the Krycklan catchment outlet (C16) suggests an increase in annual runoff by 20% until 2090, but also substantial changes in intra-annual runoff distribution, mainly in connection to winter and spring periods (Teutschbein et al. 2015). Our results indicate that such changes in the timing of runoff will have consequences for seasonal DIC mobilization to streams. Whether projected changes in hydrology will also result in an altered annual DIC export is more uncertain. Similar to any solute that display a negative C–*Q* relationship, decreased concentrations at higher runoff might be compensated by a higher water volume resulting in a uniform export. Regardless, recognizing the biogeochemical controls at the land–water interface are key to predicting how any future hydrological changes will alter the mobilization of terrestrial DIC (and DOC), as well as the potential for in situ, aquatic processes to contribute to changes in stream DIC through shifts in DOC inputs and water residence time.

Implications and future research needs

Analyzing temporal trends in stream water chemistry over a period of 14 yr ultimately raises the question of whether the observed patterns are part of real long-term trends, or of a natural variability including cyclic patterns. Hence, conclusions and potential implications from our findings should be drawn with care. Still, the consistent pattern observed among seasons and sites clearly shows that ongoing hydrological alterations in the region, likely driven by raising air temperatures, affect the timing of when terrestrial DIC is mobilized. The observed changes in DIC/DOC ratio also suggest that the composition of the total C pool being exported to boreal surface waters are under change, with a higher proportion being organic in character during the spring period. This rarely investigated aspect of C transport from soils to water has implications for where in the landscape the different C forms are processed, stored or emitted to the atmosphere (e.g., Raymond et al. 2016). Despite

the directional consistency in the seasonal DIC trends among the streams, we also observed considerable differences in the rate of DIC change across sites, illustrating the complexity and spatial variability of the boreal landscape. This heterogeneity across the network further highlights the need to understand local-scale processes and mechanisms to predict current and future patterns in C concentrations and export rates at larger scales. A prerequisite for detecting whether the observed intra-annual changes in DIC will persist in the future, whether these concentration changes are reflected in more long-term annual trends (longer than the 14 yr included in the current study) in lateral DIC export, and if similar patterns are occurring elsewhere across northern regions, require continued long-term monitoring within catchments like where this study was conducted (Laudon et al. 2017). By extending data records in time and across larger spatial scales, will allow a more direct connection to environmental changes, including climate. We further strongly recommend that such long-term monitoring programs include measurements of DIC, as it is an important, and often overlooked, variable in the landscape C balance determination. Based on our findings, it is evident that future changes in hydrometeorological conditions will affect the transfer of DIC from boreal soils to water, and that these changes are different from expected changes in DOC. Such information is critical for future projections on how total C transfer from boreal system will respond on environmental changes.

Data availability statement

Chemical and hydrological data from KCS are freely available via https://data.krycklan.se/. The specific data set used in the current study is accessible via https://github.com/XGP08L/KCS_DIC_DOC_Q.git.

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Acknowledgments

The study was supported by funding to M.B.W. from the Swedish Research Councils Formas (grant 2019:01105) and VR (grant 2021-04058_VR). The KCS infrastructure and long-term data collection have been funded by The Swedish Research Council VR (SITES), several individual Formas and VR grants, SKB, as well as by the Knut and Alice Wallenberg and Kempe foundations. The authors would also like to thank all skilled and dedicated field and lab personnel within KCS which have enabled the current study.

Conflict of Interest

None declared.

Submitted 27 October 2021
Revised 07 March 2022
Accepted 20 November 2022

Associate editor: Edward G. Stets