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# Spatial variability of dissolved organic and inorganic carbon in subarctic headwater streams

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## Abstract

The subarctic landscape is composed of a complex mosaic of vegetation, geology and topography, which control both the hydrology and biogeochemistry of streams across space and time. We present a synoptic sampling campaign that aimed to estimate dissolved C export variability under low-flow conditions from a subarctic landscape. The results included measurements of stream discharge and concentrations of both dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and carbon dioxide (CO<sub>2</sub>) for 32 subcatchments of the Abiskojokka catchment in northern Sweden. For these subarctic headwater streams, we found that DOC, DIC and CO<sub>2</sub> concentrations showed significant variability ( $p < 0.05$ ) relative to catchment size, discharge, specific discharge, lithology, electrical conductivity, weathering products, and the estimated travel time of water through the subcatchment. Our results indicate that neither vegetation cover nor lithology alone could explain the concentrations and mass flux rates of DOC and DIC. Instead, we found that mass flux rates of DOC, DIC, and CO<sub>2</sub> depended mainly on specific discharge and water travel time. Furthermore, our results demonstrate the importance of studying lateral carbon transport in combination with hydrological flow paths at small scales to establish a knowledge foundation applicable for expected carbon cycle and hydroclimatic shifts due to climate change.

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## Introduction

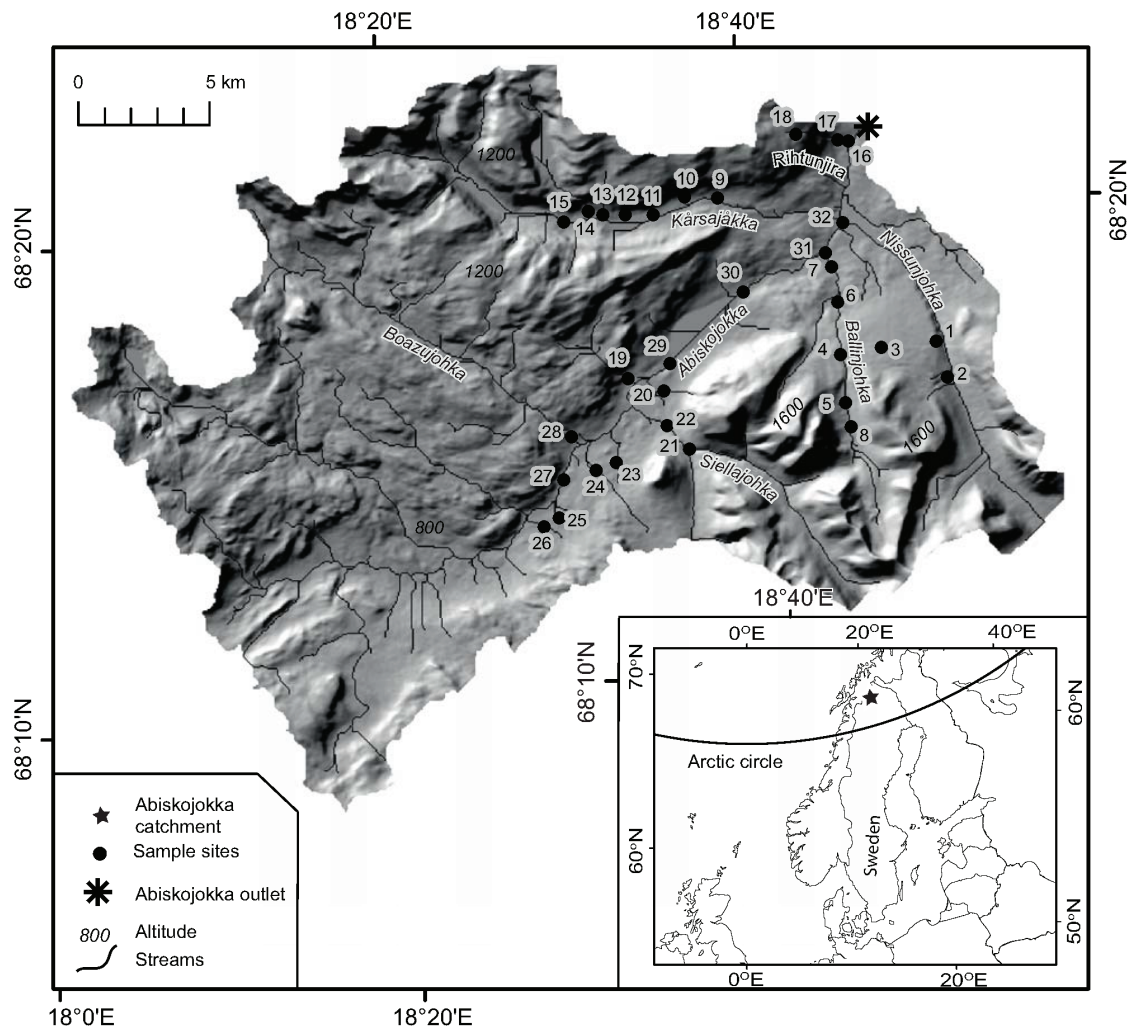
Lateral dissolved organic and inorganic carbon (C) exported from northern landscapes to and through streams forms an important and active part of the terrestrial C cycle (Cole et al., 2007; Aufdenkampe et al., 2011). The main C constituents found in aquatic systems can be divided between organic and inorganic forms measured as total organic carbon (TOC) and dissolved inorganic carbon (DIC). The former is made up by particulate organic carbon and dissolved organic carbon (DOC), and the latter is distributed between the carbonate components (CO<sub>2</sub>, HCO<sub>3</sub><sup>3-</sup>, and CO<sub>3</sub><sup>2-</sup>). Along the aquatic conduit (e.g., Cole et al., 2007), parts of the DOC are typically mineralized to CO<sub>2</sub> and outgassed to the atmosphere (Wallin et al., 2013) while the remaining portions can function as nutrients for organisms and/or eventually sediment in lakes or other recipient water bodies (Berggren et al., 2010). Moreover, a large part of the riverine DOC is transported through the aquatic conduit to downstream recipient waters where it sediments. Despite these active roles in the terrestrial C cycle and clear relevance for climatic change feedbacks, surprisingly little is known about the spatial variability of dissolved C in northern streams in general and subarctic headwaters in particular.

Regarding dissolved C transport in subarctic and arctic systems, much of the literature to-date has focused on the role of solute flow pathways (Carey and Woo, 2001; Lyon et al., 2010a; Giesler et al., 2014) and understanding mineralization processes of C in stream systems (Klaminder et al., 2011) and peatlands (Olefeldt et al., 2012; Limpens et al., 2008). Within the landscape, vegetation cover can alter the stream water biogeochemistry by affecting weathering rates and terrestrial C sequestration. Photosynthesis and respiration thus tend to dominate the terrestrial C cycle over shorter time scales, while at longer (i.e., geological) time scales weathering of silica and carbonate rock regulate the global C cy-

cle (Berner, 1992). Further, changes in hydrological flow pathway distributions due to permafrost thaw can also have large potential influence on dissolved C transport (Peterson et al., 2002; Hinzman et al., 2005; Déry and Wood, 2005; Lyon et al., 2010a; Jantze et al., 2013) in cold environments. The spatial heterogeneity of land cover (vegetation), subsurface characteristics (lithology and quaternary geology), biophysical characteristics, and associated terrestrial hydrology are thus important factors controlling the export of C within arctic and subarctic landscapes (Battin et al., 2008; Jorgenson et al., 2013) resulting in large variations in stream water chemistry especially in small streams (Buffam et al., 2008).

Large-scale studies of C transport in the Arctic with focus on fluxes, sources, and mechanisms have recently become more in focus due to a growing interest in climate change impacts and feedbacks (e.g., McGuire et al., 2009; Tank et al., 2012a; Pokrovsky et al., 2012). Small catchments and their subsequently low-order headwater streams, however, make up the majority of the total stream length in the landscape (Bishop et al., 2008). There is clearly a shortage of studies and data available for dissolved C export from small-scale arctic and subarctic systems (Giesler et al., 2013). Nevertheless, to fully characterize C variability and the associated transport mechanisms across various scales, more knowledge about the connections between landscape heterogeneity and resultant headwater C chemistry is needed (Olefeldt et al., 2012; Lundin et al., 2013; Giesler et al., 2014; Wallin et al., 2010). The remoteness and inaccessibility of arctic and subarctic environments together with technical challenges in measuring both lateral and vertical C fluxes of streams (Cole et al., 2007) have contributed to the current lack of observations from subarctic headwaters.

The potential linkages between lithology, vegetation, and hydrology form the pillars for our process understanding with regard to what regulates dissolved C along the aquatic conduit. The spatial distribution of dissolved C in stream networks across scales thus



**FIGURE 1.** Sample sites within the Abiskojokka catchment and its tributary streams Nissongjokka, Ballinsvaggi, Siellajokka, Boazojokka, Kårsajokka, and Rihtonjira. Elevation ranges from 345 to 1790 m a.s.l.

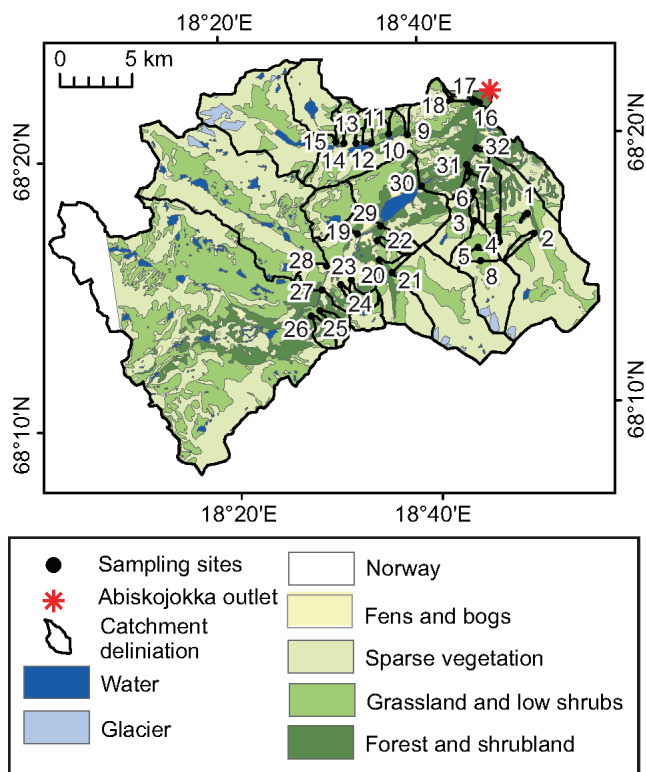
needs to be explored in order to improve our understanding of the processes that regulate C fluxes and how this may be affected by, for example, vegetation shifts and/or changes in flow paths due to warming and thawing of permafrost, which is relevant for many future cold environments. In this context, we present here a data-driven study in small headwater subarctic streams within the Abiskojokka catchment of northern Sweden (Fig. 1). The two main goals of this study were (1) to investigate the spatial variability of  $\text{CO}_2$ , DOC, and DIC in a subarctic alpine stream network and (2) to identify potential links between dissolved C and landscape characteristics. With regard to the latter goal, we explicitly assessed if the patterns and mechanistic understanding of dissolved C transport gathered for this region in previous work at catchment scales  $>500 \text{ km}^2$  (i.e., Lyon et al., 2010a; Jantze et al., 2013) are consistent with catchment scales  $<500 \text{ km}^2$ .

## Methods

### SITE DESCRIPTION

The central component of this study was a synoptic sampling campaign conducted in the  $576 \text{ km}^2$  Abiskojokka catchment,

which drains the Abisko valley, situated about 200 km north of the Arctic circle in northern Sweden (Fig. 1,  $68^\circ 21' 36'' \text{N}$ ,  $18^\circ 46' 48'' \text{E}$ ). The area has been well studied during the past century due to its proximity to the Abisko Scientific Research Station. Abiskojokka catchment is situated in the Scandinavian mountain range with subarctic climate characterized by short summers and long winters and discontinuous permafrost (Johansson et al., 2006; Lyon et al., 2010a). Elevation in the catchment ranges between 345 m above sea level (a.s.l.) at the catchment outlet to 1745 m a.s.l. at the highest point. Long-term mean annual precipitation was  $304 \text{ mm yr}^{-1}$  and mean annual air temperature was  $-0.8^\circ \text{C}$  for the period 1961–1990 (Swedish Meteorological and Hydrological Institute [SMHI], station no. 18880, Abisko), but the annual average temperatures have exceeded  $0^\circ \text{C}$  since 2000 (Callaghan et al., 2010). There is a strong precipitation gradient, decreasing eastward, and snow covers the ground from October to May (approximately 225 days of the year). The vegetation is dominated by birch forest (*Betula pubescens tortuosa*) in the subalpine zone that extends up to about 650 m a.s.l. on north-facing slopes and up to about 700 m a.s.l. on south-facing slopes. The deciduous forest transitions into willows (*Salix* sp.) in the low alpine zone and into dwarf birch (*Betula*



**FIGURE 2.** Vegetation map of Abiskoajokka catchment.

*nana*) heath in the middle to high alpine zone (Rafstedt et al., 1985, Fig. 2). The landscape is dominated by bedrock outcrops with non-continuous to thin quaternary deposit cover (about 68% of the total catchment). The Abiskoajokka catchment is further covered by till and regolith (29%), silt, sand, gravel, and fluvio-glacial material (2%). Glacier cover of the catchment is 1%. The quaternary deposits in the area are covered by a thin O-horizon that ranges between 0 and 50 cm; soils are cryoturbated at higher elevations (Becher et al., 2013). The main stream (Abiskoajokka) has been monitored by SMHI (Swedish Meteorological and Hydrological Institute) for the past 100 years. For the time period 1985–2012 the river had an annual average flow rate of  $14.2 \pm 2.4 \text{ m}^3 \text{ s}^{-1}$  (note: we are using the convention *average*  $\pm$  *standard deviation* throughout this paper) and ranged between approximately  $54.3 \pm 29.6 \text{ m}^3 \text{ s}^{-1}$  in spring freshet in June and  $1.0 \pm 0.68 \text{ m}^3 \text{ s}^{-1}$  during late winter low flows in March. The main stream Abiskoajokka is fed by several tributaries from which six subcatchments were sampled in this study: Nissunajokka, Ballinajokka, Siellajokkla, Boazujukka, Kårsajåkka, and Rihtunjira (Fig. 1). The mountainous part of the Abiskoajokka catchment likely receives more precipitation than measured at the rain gauge near the catchment outlet. Mean annual precipitation in the peak areas of the catchment has been estimated to reach over  $900 \text{ mm yr}^{-1}$  (1913–1990) (Josefsson, 1990; Alexandersson et al., 1991), which explains some of the discrepancy found between annual average flow and precipitation.

#### FLOW AND WATER CHEMISTRY

Water grab sampling and streamflow measurements were performed as a synoptic field campaign during a 10 day period in the first half of August 2012 across stable flow conditions. The

discharge ( $Q$ ) at the Abiskoajokka outlet was  $43.0$  and  $21.8 \text{ m}^3 \text{ s}^{-1}$  on the first and last day of the field campaign, respectively, with an average flow rate of  $28.4 \pm 6.3 \text{ m}^3 \text{ s}^{-1}$ . Between 1986 and 2012, the August average  $Q$  for Abiskoajokka was  $14.2 \pm 7.7 \text{ m}^3 \text{ s}^{-1}$  thus the average  $Q$  for August 2012 of  $21.0 \text{ m}^3 \text{ s}^{-1}$  falls within the 30th and 70th percentile range for the period.

For the synoptic campaign, 32 sample sites were identified through an initial geographic information system (GIS) study. These sites were selected to cover different vegetation zones and lithologies within Abiskoajokka catchment. The sites were mainly located at stream junctions where small creeks confluence with larger ones (Fig. 1). At all 32 sites, water samples were collected for DOC analysis in 100 mL polyethylene (PE) or high-density polyethylene (HDPE) bottles. Water samples for  $\text{CO}_2$  analysis were collected in 22 mL acidified gas-exchanged vials following the procedure from Wallin et al. (2010). In short, the bottles and the sterile syringes (used to fill the gas-exchanged vials) were rinsed three times with stream water before filling them with a water sample. The bottles and vials were kept dark and cool during transport to the laboratory where they were refrigerated until analysis. All water samples were analyzed for DOC ( $\text{mg L}^{-1}$ ) using a 5000 Shimadzu TOC-analyzer and for  $\text{CO}_2$  (ppm) using a Perkin Elmer Clarus 580 gas chromatograph with TurboMatrix 110 Head-space Sampler. DIC and  $\text{CO}_2$  were determined using the headspace method (see Wallin et al. [2010] for description of calculations). Streamflow was measured using either the velocity-area method by measuring cross-sectional areas and velocities with a current meter (Omni MiniWater Probe and Logger) or the dilution method involving the injection of rhodamine WT dye and recovery with a fluorometer (FL30 field fluorometer). A current meter (for the velocity-area method) was used in the smaller streams while the dilution method was used for both the smaller and the larger streams. Our previous work in the field with these two methods indicates that they produce similar levels of error and allow for comparable flow measurements. With these methods, however, it was not possible to measure flow at the largest streams within this synoptic campaign. Therefore, instantaneous discharge observations were available for only 18 out of the total 32 sampling locations.

The mass flux rate of a given constituent was calculated as the instantaneous concentration multiplied by instantaneous specific discharge ( $q$ ) in the stream at the 18 locations where both measurements were available. As such, it should be noted that all subsequent concentrations are expressed in units of  $\text{mg L}^{-1}$ , mass flux rates in  $\text{kg d}^{-1} \text{ ha}^{-1}$  and discharge flow rates in  $\text{m}^3 \text{ s}^{-1}$ . In addition to the streamflow and water chemistry observations, measurements of pH (–), electrical conductivity (EC,  $\mu\text{S cm}^{-1}$ ), and stream water temperature ( $^\circ\text{C}$ ) were performed at each sampling site with a calibrated Hanna Instruments HI98129 Combo meter. Silica and the base cations,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  ( $\text{mg L}^{-1}$ ) were analyzed with an ICP-OES analyzer (ICAP6500 duo, Thermo Scientific) with an error margin of  $\pm 5\%$ .

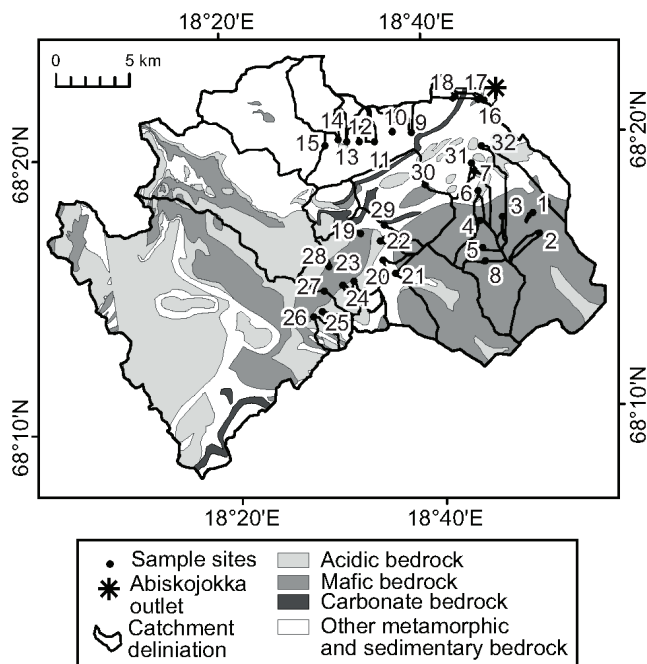
#### CATCHMENT CHARACTERISTICS AND STATISTICAL ANALYSIS

To investigate the potential first-order controls on the dissolved C concentrations and fluxes in this subarctic landscape, we determined several catchment-scale features for each sampling location (Table 1). Topographic data were available from the Swedish University of Agricultural Sciences (SLU; <http://maps.slu.se/>) in the form of a digital elevation model (DEM) at a horizontal resolution of 50 m. This DEM was then used to define the catchments for each sampling location using the hydrology toolkit within Arc-

**TABLE 1**  
**Physical and chemical characteristics of sampled streams in Abiskojokka catchment.**

Site	Average catchment altitude (m)	pH (-)	Area (ha)	EC ( $\mu$ S)	Average travel time (yr)	$q$ (mm day <sup>-1</sup> )	$Q$ (m <sup>3</sup> s <sup>-1</sup> )	DOC (mg L <sup>-1</sup> )	DIC (mg L <sup>-1</sup> )	CO <sub>2</sub> (mg L <sup>-1</sup> )	DOC (kg day <sup>-1</sup> ha <sup>-1</sup> )	DIC (kg day <sup>-1</sup> ha <sup>-1</sup> )	CO <sub>2</sub> (kg day <sup>-1</sup> ha <sup>-1</sup> )
1	871	7.6	10	5	0.37	5.12	0.006	1.33	1.07	0.09	6.8 × 10 <sup>-4</sup>	5.5 × 10 <sup>-4</sup>	4.6 × 10 <sup>-5</sup>
2	1122	7.3	95	1	0.77			0.55	0.91	0.14			
3	1285	6.9	49	1	3.26	0.45	0.003	0.85	0.71	0.24	3.6 × 10 <sup>-5</sup>	3. × 10 <sup>-5</sup>	1.1 × 10 <sup>-5</sup>
4	1277	7.4	1821	5	0.45	4.70	0.990	0.64	1.57	0.18	3.0 × 10 <sup>-4</sup>	7.4 × 10 <sup>-4</sup>	8.5 × 10 <sup>-5</sup>
5	1519	7.4	1432	8	0.49	1.89	0.314	0.94	1.79	0.25	1.8 × 10 <sup>-4</sup>	3.4 × 10 <sup>-4</sup>	4.7 × 10 <sup>-5</sup>
6	823	7.5	1923	9	0.44	5.63	1.252	0.55	1.69	0.15	3.1 × 10 <sup>-4</sup>	9.5 × 10 <sup>-4</sup>	8.7 × 10 <sup>-5</sup>
7	954	7.5	3005	11	0.55	4.10	1.425	0.70	1.69	0.18	2.9 × 10 <sup>-4</sup>	6.9 × 10 <sup>-4</sup>	7.5 × 10 <sup>-5</sup>
8	1326	7.2	1250	12	0.53			1.48	1.64	0.26			
9	972	7.4	94	25	0.66			0.65	2.14	0.23			
10	1087	7.6	80	20	0.86	1.91	0.018	1.26	3.03	0.26	2.4 × 10 <sup>-4</sup>	5.8 × 10 <sup>-4</sup>	4.9 × 10 <sup>-5</sup>
11	918	7.6	97	27	0.49			0.61	2.13	0.18			
12	1107	7.6	87	32	1.11	4.13	0.042	0.95	2.80	0.24	3.9 × 10 <sup>-4</sup>	1.2 × 10 <sup>-3</sup>	9.8 × 10 <sup>-5</sup>
13	1200	7.5	200	32	1.18	1.05	0.024	0.56	1.90	0.18	5.9 × 10 <sup>-5</sup>	2.0 × 10 <sup>-4</sup>	1.9 × 10 <sup>-5</sup>
14	1174	7.1	1242	20	0.49	6.05	0.870	0.44	1.08	0.22	2.6 × 10 <sup>-4</sup>	6.6 × 10 <sup>-4</sup>	0.00013
15	1100	7.6	3612	23	0.57			0.49	2.04	0.18			
16	931	7.6	57664	43	0.88			1.17	5.14	0.39			
17	1145	7.6	227	76	1.52	1.26	0.033	1.07	4.92	0.36	1.4 × 10 <sup>-4</sup>	6.2 × 10 <sup>-4</sup>	4.6 × 10 <sup>-5</sup>
18	1097	7.1	157	51	1.79	1.09	0.020	0.83	3.72	0.23	9.0 × 10 <sup>-5</sup>	4.0 × 10 <sup>-4</sup>	2.5 × 10 <sup>-5</sup>
19	942	7.7	1004	31	0.85	0.58	0.067	1.31	4.63	0.26	7.6 × 10 <sup>-5</sup>	2.7 × 10 <sup>-4</sup>	1.5 × 10 <sup>-5</sup>
20	1204	7.7	3978	21	0.35			0.79	3.07	0.20			
21	1167	7.5	2880	19	0.30			0.66	2.64	0.27			
22	1053	7.3	182	30	1.18	1.09	0.023	2.01	3.38	0.52	2.2 × 10 <sup>-4</sup>	3.7 × 10 <sup>-4</sup>	5.7 × 10 <sup>-5</sup>
23	792	8.0	189	60	2.04	0.42	0.009	3.73	8.74	0.30	1.6 × 10 <sup>-4</sup>	3.7 × 10 <sup>-4</sup>	1.3 × 10 <sup>-5</sup>
24	861	8.0	405	44	4.53	0.36	0.017	3.33	6.13	0.21	1.2 × 10 <sup>-4</sup>	2.2 × 10 <sup>-4</sup>	7.5 × 10 <sup>-6</sup>
25	1026	8.0	212	80	2.11	0.32	0.008	3.07	12.00	0.39	9.9 × 10 <sup>-5</sup>	3.9 × 10 <sup>-4</sup>	1.3 × 10 <sup>-5</sup>
26	1019	7.7	235	108	1.61	0.23	0.006	2.91	11.26	0.73	6.7 × 10 <sup>-5</sup>	2.6 × 10 <sup>-4</sup>	1.7 × 10 <sup>-5</sup>
27	1188	7.7	19384	27	1.06			1.02	3.15	0.19			
28	1204	7.5	7038	19	0.93			0.87	2.43	0.21			
29	1244	7.5	34661	27	0.97			1.32	3.41	0.36			
30	951	7.7	37257	21	0.98			1.30	2.87	0.19			
31	1140	7.5	3034	15	0.55			0.76	2.40	0.22			
32	1420	7.7	4823	35	0.54			1.26	4.30	0.37			
Average	1098	7.5	5885	29	1.1	2.24	0.28	1.23	3.45	0.26	2.1 × 10 <sup>-4</sup>	4.9 × 10 <sup>-4</sup>	4.7 × 10 <sup>-5</sup>
St.dev.	169	0.25	12898	24	0.88	2.02	0.47	0.85	2.68	0.12	1.5 × 10 <sup>-4</sup>	2.7 × 10 <sup>-4</sup>	3.5 × 10 <sup>-5</sup>

Notes: EC = electrical conductivity,  $q$  = instantaneous specific discharge,  $Q$  = discharge at the Abiskojokka outlet, DOC = dissolved organic carbon, DIC = dissolved inorganic carbon.



**FIGURE 3** The bedrock in the Abiskojokka catchment is dominated by acidic bedrock (34%), mafic bedrock (34%), other sedimentary and metamorphic bedrock (30%) and carbonate bedrock (2%).

GIS 10.0 (ESRI, Redlands, California). Topographic and spatial features considered as potential first-order control candidates included the catchment area, the average catchment elevation, and the percent land cover for various vegetation types, quaternary geology, and lithologies within each catchment. The vegetation map was derived from SLU (<https://maps.slu.se/>); lithology and quaternary deposits maps, from the Swedish Geological Survey (SGU, [www.sgu.se](http://www.sgu.se)). Vegetation was divided into the following three classes based on height and woodiness: (1) fens and bogs, (2) forest and shrubland, (3) grassland and low shrub, and (4) sparse vegetation (Fig. 2). Quaternary geology was divided into the following classes: (1) bedrock outcrops and thin sediments; (2) silt, sand, gravel, and fluvio-glacial material; and (3) till and regolith. The lithology was divided into the following four classes depending on the C content, acidity, and rock type: (1) carbonate bedrock, (2) acidic bedrock, (3) mafic bedrock, and (4) other sedimentary and metamorphic bedrock (Fig. 3).

Finally, to provide some proxy for the distributed hydrology in the region, the average travel time of water within each subcatchment was estimated based on the model from Lyon et al. (2010a). In that work they used a Darcy approach based on hillslope gradients, the distribution of flow pathway lengths estimated from surface topography, and literature-reported hydraulic conductivities to estimate a distributed travel time for the Abiskojokka catchment. Such a modeling approach has been considered in several studies as an approximation of subsurface hydrology at the hillslope to catchment scale (e.g., Darracq et al., 2010; Basu et al., 2012). For the Abiskojokka catchment, the results of the water travel time model were validated using stable water isotope estimates from the region (Burgman et al., 1987) and, thus, they can be considered here as a good approximation of the distributed hydrology by providing a metric of similarity between sampling locations. As

such, the travel times can be considered to quantify relative differences between locations in the catchment (e.g., Lyon et al., 2010b). It should be noted, however, that due to discrepancy between the modeled streams in the travel time model from Lyon et al. (2010a) and the real streams where the synoptic samples were collected, catchments with travel times greater than two standard deviations (there were 4 out of 32 sampled sites) were not included in the following statistical analysis.

We investigated the existence of simple (linear) relationships, performed multiple linear regressions, and computed Spearman's and Kendall's rank correlation coefficients ( $\rho$  and  $\tau$ , respectively) for C concentration and mass flux rates versus catchment area,  $Q$ ,  $q$ , landscape characteristics, EC, travel time, silica, base cations and alkalinity at the  $\alpha = 0.05$  significance level. Further, we tested the relationships of travel time versus silica, base cations and alkalinity, as well as  $q$  versus catchment area using the simple (linear) relationships, multiple linear regressions, and both Spearman's and Kendall's rank correlation coefficients. The multiple linear regressions, Spearman's  $\rho$  and Kendall's  $\tau$  were calculated using MATLAB (R2012a Student) at a significance level of  $\alpha = 0.05$ . It should be noted that several of the catchments in the study are nested, which can potentially lead to inflated correlations between C and the biophysical variables (Guse et al., 2009). We have opted to not "un-nest" catchments here due to the potential for introducing compound errors when differencing, for example, discharge along a stream system.

We performed one-sided F-statistics to test for significant variability of organic and inorganic C in relation to landscape homogeneity/heterogeneity with regard to the independent variables across the catchments. The aim was to test whether C export in catchments with a dominant landscape characteristic (e.g., high coverage of forest and shrubland cover) were different compared to catchments in which the landscape characteristic was not dominant (e.g., low coverage of forest and shrubland cover). The F-tests were performed by comparing the variance of measured concentrations and estimated mass flux rates between catchments with higher-than-median values of a given characteristic and catchments with lower-than-median values of a given characteristic. For example, to compare the variances of C concentrations and fluxes of relatively small catchments to those of relatively large catchments the first step was to sort the data from the smallest to largest catchment area (i.e., the characteristic of interest). In a next step, the variance of concentrations and mass flux rates were computed across the catchments that were larger than the median catchment area and those that were smaller than the median catchment area. For these calculations, variances for the mass flux rates only included catchments for which it was possible to estimate  $Q$  and thus have a lower number of samples. Finally, the variances of the two populations (i.e., catchments smaller than the median catchment area and catchments larger than the median catchment area) were compared using the one-sided F-test to determine if they were significantly different.

## Results

### SYNOPTIC CAMPAIGN

The physical and chemical characteristics of the sites and the sampled streams are summarized in Table 1. For all variables linear regression equations, Spearman's  $\rho$ , Kendall's  $\tau$ , and their associated  $p$ -values are shown in Table 2 and Table 3. The average concentration for the 32 catchments was  $1.2 \pm 0.8 \text{ mg L}^{-1}$  for DOC,  $3.4 \pm 2.7 \text{ mg L}^{-1}$  for DIC, and  $0.26 \pm 0.12 \text{ mg L}^{-1}$  for  $\text{CO}_2$  Concen-

TABLE 2

Linear regressions and associated  $p$ -values of the observed DOC, DIC, and CO<sub>2</sub> concentrations and mass flux rates (dependent variables) and selected landscape variables (independent variables). Bold numbers show significant variables.

Table 2a

Variables	DOC concentration (mg L <sup>-1</sup> ) Eq. linear regression ( $p$ )	DOC mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> ) Eq. linear regression ( $p$ )
Area	[DOC] = $-3 \times 10^{-6} \times \text{Area} + 1.2$ (0.8)	DOC = $3 \times 10^{-8} \times \text{Area} + 0.0002$ (0.5)
$Q$	[DOC] = $-1.0 \times Q + 1.8$ (0.05)	DOC = $9 \times 10^{-5} \times Q + 0.0002$ (0.3)
$q$	[DOC] = $-0.31 \times q + 2.2$ (0.009)	DOC = $6 \times 10^{-5} \times q + 7 \times 10^{-5}$ ( $2 \times 10^{-5}$ )
Forest and shrubland	[DOC] = $6.3 \times \text{Forest and shrubland} + 0.88$ (0.01)	DOC = $-0.0004 \times \text{Forest and shrubland} + 0.0002$ (0.1)
Grassland and low shrub	[DOC] = $1.1 \times \text{Grassland and low shrub} + 0.83$ (0.1)	DOC = $2 \times 10^{-4} \times \text{Grassland and low shrub} + 1 \times 10^{-4}$ (0.1)
Sparse vegetation	[DOC] = $0.29 \times \text{Sparse vegetation} + 1.2$ (0.7)	DOC = $-3 \times 10^{-4} \times \text{Sparse vegetation} + 3 \times 10^{-4}$ (0.1)
Acidic bedrock	[DOC] = $2.6 \times \text{Acidic bedrock} + 0.84$ (0.03)	DOC = $-3 \times 10^{-4} \times \text{Acidic bedrock} + 3 \times 10^{-4}$ (0.004)
EC	[DOC] = $0.023 \times \text{EC} + 0.55$ ( $5 \times 10^{-5}$ )	DOC = $-2 \times 10^{-6} \times \text{EC} + 3 \times 10^{-4}$ (0.05)
Travel time	[DOC] = $0.62 \times \text{Travel time} + 0.52$ ( $1 \times 10^{-4}$ )	DOC = $-2 \times 10^{-4} \times \text{Travel time} + 4 \times 10^{-4}$ (0.03)
Ca <sup>2+</sup>	[DOC] = $0.2 \times \text{Ca} + 0.4$ ( $1 \times 10^{-4}$ )	
K <sup>+</sup>	[DOC] = $1.4 \times \text{K} + 0.56$ ( $1 \times 10^{-4}$ )	
Na <sup>+</sup>	[DOC] = $2.6 \times \text{Na} - 0.39$ ( $1 \times 10^{-11}$ )	
Mg <sup>2+</sup>	[DOC] = $0.6 \times \text{Mg} + 0.60$ (0.002)	
Silica	[DOC] = $1.8 \times \text{Si} + 0.14$ ( $1 \times 10^{-8}$ )	
Alkalinity	[DOC] = $2.2 \times \text{Alk} + 0.68$ (0.003)	

Table 2b

Variables	DIC concentration (mg L <sup>-1</sup> ) Eq. linear regression ( $p$ )	DIC mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> ) Eq. linear regression ( $p$ )
Area	[DIC] = $8 \times 10^{-6} \times \text{Area} + 3.4$ (0.8)	DIC = $1 \times 10^{-7} \times \text{Area} + 0.0004$ (0.1)
$Q$	[DIC] = $-2.9 \times Q + 4.8$ (0.09)	DIC = $0.0003 \times Q + 0.0004$ (0.03)
$q$	[DIC] = $-1.0 \times q + 6.2$ (0.007)	DIC = $0.0001 \times q + 0.0003$ ( $2 \times 10^{-4}$ )
Forest and shrubland	[DIC] = $27.9 \times \text{Forest and shrubland} + 1.9$ ( $2 \times 10^{-5}$ )	DIC = $-0.0008 \times \text{Forest and shrubland} + 0.0006$ (0.2)
Grassland and low shrub	[DIC] = $3.0 \times \text{Grassland and low shrub} + 2.4$ (0.2)	DIC = $9 \times 10^{-5} \times \text{Grassland and low shrub} + 0.0005$ (0.7)
Sparse vegetation	[DIC] = $2.7 \times \text{Sparse vegetation} + 2.7$ (0.3)	DIC = $-9 \times 10^{-5} \times \text{Sparse vegetation} + 0.0005$ (0.8)
Acidic bedrock	[DIC] = $9.4 \times \text{Acidic bedrock} + 2.0$ (0.009)	DIC = $-0.0007 \times \text{Acidic bedrock} + 0.0006$ (0.07)
EC	[DIC] = $0.1018 \times \text{EC} + 0.47$ ( $3 \times 10^{-12}$ )	DIC = $-2 \times 10^{-6} \times \text{EC} + 0.0006$ (0.4)
Travel time	[DIC] = $3.1 \times \text{Travel time} + 0.51$ (0.01)	DIC = $-0.0002 \times \text{Travel time} + 0.0007$ (0.02)
Ca <sup>2+</sup>	[DIC] = $0.7 \times \text{Ca} - 0.04$ ( $1 \times 10^{-11}$ )	
K <sup>+</sup>	[DIC] = $6.3 \times \text{K} + 0.5019$ ( $6 \times 10^{-10}$ )	
Na <sup>+</sup>	[DIC] = $8.6 \times \text{Na} - 1.8893$ ( $4 \times 10^{-14}$ )	
Mg <sup>2+</sup>	[DIC] = $2.5 \times \text{Mg} + 0.81$ ( $2 \times 10^{-5}$ )	
Silica	[DIC] = $6.7 \times \text{Si} - 0.6$ ( $1 \times 10^{-8}$ )	
Alkalinity	[DIC] = $8.8 \times \text{Alk} + 1.3$ ( $7 \times 10^{-5}$ )	

Table 2c

Variables	CO <sub>2</sub> concentration (mg L <sup>-1</sup> ) Eq. linear regression ( $p$ )	CO <sub>2</sub> mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> ) Eq. linear regression ( $p$ )
Area	[CO <sub>2</sub> ] = $1 \times 10^{-6} \times \text{Area} + 0.26$ (0.5)	CO <sub>2</sub> = $2 \times 10^{-8} \times \text{Area} + 3 \times 10^{-5}$ (0.03)
$Q$	[CO <sub>2</sub> ] = $-0.11 \times Q + 0.31$ (0.2)	CO <sub>2</sub> = $5 \times 10^{-5} \times Q + 3 \times 10^{-5}$ (0.002)
$q$	[CO <sub>2</sub> ] = $-0.038 \times q + 0.36$ (0.03)	CO <sub>2</sub> = $2 \times 10^{-5} \times q + 1 \times 10^{-5}$ ( $1 \times 10^{-6}$ )
Forest and shrubland	[CO <sub>2</sub> ] = $1.1 \times \text{Forest and shrubland} + 0.20$ ( $8 \times 10^{-4}$ )	CO <sub>2</sub> = $-0.0001 \times \text{Forest and shrubland} + 5 \times 10^{-5}$ (0.2)

**TABLE 2**  
Continued

**Table 2c (Continued)**

Variables	CO <sub>2</sub> concentration (mg L <sup>-1</sup> ) Eq. linear regression ( <i>p</i> )	CO <sub>2</sub> mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> ) Eq. linear regression ( <i>p</i> )
Grassland and low shrub	[CO <sub>2</sub> ] = -0.043 × Grassland and low shrub + 0.28 (0.7)	CO <sub>2</sub> = -4 × 10 <sup>-5</sup> × Grassland and low shrub + 6 × 10 <sup>-5</sup> (0.3)
Sparse vegetation	[CO <sub>2</sub> ] = -0.0024 × Sparse vegetation + 0.26 (1)	CO <sub>2</sub> = -8 × 10 <sup>-6</sup> × Sparse vegetation + 5 × 10 <sup>-5</sup> (0.9)
Acidic bedrock	[CO <sub>2</sub> ] = 0.20 × Acidic bedrock + 0.25 (0.3)	<b>CO<sub>2</sub> = -0.0001 × Acidic bedrock + 7 × 10<sup>-5</sup> (0.004)</b>
EC	[CO <sub>2</sub> ] = <b>0.0038 × EC + 0.15 (1 × 10<sup>-6</sup>)</b>	CO <sub>2</sub> = -5 × 10 <sup>-7</sup> × EC + 7 × 10 <sup>-5</sup> (0.07)
Travel time	[CO <sub>2</sub> ] = 0.17 × Travel time + 0.12 (0.3)	<b>CO<sub>2</sub> = -4 × 10<sup>-5</sup> × Travel time + 9 × 10<sup>-5</sup> (0.006)</b>
Ca <sup>2+</sup>	[CO <sub>2</sub> ] = <b>0.03 × Ca + 0.1 (2 × 10<sup>-7</sup>)</b>	
K <sup>+</sup>	[CO <sub>2</sub> ] = <b>0.2 × K + 0.16 (6 × 10<sup>-5</sup>)</b>	
Na <sup>+</sup>	[CO <sub>2</sub> ] = <b>0.3 × Na + 0.097 (1 × 10<sup>-8</sup>)</b>	
Mg <sup>2+</sup>	[CO <sub>2</sub> ] = <b>0.06 × Mg + 0.20 (0.04)</b>	
Silica	[CO <sub>2</sub> ] = <b>0.2 × Si + 0.13 (4 × 10<sup>-4</sup>)</b>	
Alkalinity	[CO <sub>2</sub> ] = <b>0.2 × Alk + 0.20 (0.03)</b>	

trations ranged from 0.44 to 3.7 mg L<sup>-1</sup> for DOC, from 0.71 to 12.0 mg L<sup>-1</sup> for DIC, and from 0.090 to 0.73 mg L<sup>-1</sup> for CO<sub>2</sub>. The lowest and highest measured stream flows from the 18 catchments were 0.0026 and 1.4 m<sup>3</sup> s<sup>-1</sup>, respectively. The average stream flow measured across all 18 sites was 0.28 m<sup>3</sup> s<sup>-1</sup>. The lowest and highest estimated *q* were 0.23 and 6.0 mm d<sup>-1</sup>, respectively. Correspondingly, the average mass flux rates were 2.1 × 10<sup>-4</sup> ± 1.5 × 10<sup>-4</sup> kg d<sup>-1</sup> ha<sup>-1</sup> for DOC; 4.9 × 10<sup>-4</sup> ± 2.7 × 10<sup>-4</sup> kg d<sup>-1</sup> ha<sup>-1</sup> for DIC; and 4.7 × 10<sup>-5</sup> ± 3.5 × 10<sup>-5</sup> kg d<sup>-1</sup> ha<sup>-1</sup> for CO<sub>2</sub> (Fig. 4).

The average DOC (1.2 mg L<sup>-1</sup>) and DIC (3.4 mg L<sup>-1</sup>) concentrations found across the headwater systems considered in our synoptic study were similar to six catchments in the same region (e.g., Giesler et al., 2014) where DOC and DIC concentrations ranged from about 1 to 4 mg L<sup>-1</sup> and 3 to 5 mg L<sup>-1</sup>, respectively, during August. Pan-Arctic DOC concentrations for the same time period (August) typically range between 3 and 10 mg L<sup>-1</sup> (Raymond et al., 2007). The high variability of C concentrations that we found for small catchments is in line with previous studies. The downstream reduction in variability with increasing catchment area is mainly due to the mixing of water sources. Previous investigations in boreal landscapes have found large variability for headwater streams across the landscape (Lyon et al., 2012; Temnerud and Bishop, 2005, and references therein). The observed average silica (0.60 mg L<sup>-1</sup>), Ca<sup>2+</sup> (5.1 mg L<sup>-1</sup>), K<sup>+</sup> (0.47 mg L<sup>-1</sup>), and Na<sup>+</sup> (0.62 mg L<sup>-1</sup>) concentrations (Fig. 5) are in line with cation concentrations in the region (Beylich et al., 2004; Giesler et al., 2014).

#### SPATIAL VARIABILITY

The F-statistics for selected variables are summarized in Table 4, and the land cover and lithology characteristics are summarized in Table 5. The highest DIC concentrations were found in small catchments with low *q* (Fig. 4), whereas relatively low DIC concentrations were found across all catchment sizes. Relatively small catchments (areas between 10 and 1004 ha, *n* = 16) had significantly higher variability of DOC, DIC, and CO<sub>2</sub> concentrations compared to the larger catchments (areas between 1242 and 57,664 ha, *n* = 16, Fig. 4). The largest variability in C

mass flux rates was estimated for DIC. The greatest range in DIC concentrations was observed in small catchments and catchments with high *q* (Fig. 4). For the Abiskojojokka catchment, Jantze et al. (2013) found greater temporal variability in DOC compared to DIC concentrations; however, in this study, where time was held relatively constant due to the synoptic nature of the sampling, greater spatial variability was found for DIC concentrations relative to DOC.

There was significantly higher variability in the CO<sub>2</sub> mass flux rate in catchments with high forest and shrubland cover (8%–31%, *n* = 11) than in catchments with low cover (0.2%–8%, *n* = 10; Fig. 6). Catchments with high grassland and low shrub cover (34%–100%, *n* = 16) had significantly higher variability in DIC concentrations than catchments with low grassland and low shrub cover (6%–32%, *n* = 16; Fig. 6). Further, the variance of the DOC mass flux rate was significantly higher for catchments with high grassland and low shrub cover (34%–100%, *n* = 10) compared to low grassland and low shrub cover catchments (6%–32%, *n* = 8; Fig. 6).

Catchments with high acidic bedrock cover (38%–58%, *n* = 8) had significantly higher variability in DOC and DIC concentrations compared to catchments with low cover (1%–30%, *n* = 9; Fig. 7). There was significantly higher variability of all C concentrations for catchments with longer average travel times (0.8–1.8 yr, *n* = 13) compared to catchments with shorter travel time (0.3–0.7 yr, *n* = 13; Fig. 7).

#### POTENTIAL LANDSCAPE CONTROLS

Overall, both organic and inorganic C concentrations increased with increasing vegetation cover. Of the investigated vegetation classes, forest and shrubland cover had overall significant positive relations to C concentrations (Fig. 6, Tables 2 and 3). Grassland and low shrub cover was significantly positively related to DOC and DIC concentrations. Only DIC had a significant positive relation to sparse vegetation (Fig. 6, Tables 2 and 3). Counter to this, all vegetation cover classes showed weak negative relationships with C mass flux



TABLE 3

Coefficients for Spearman and Kendall rank correlations and associated *p*-values for relationships between C concentration and mass flux rates as dependent variables and biophysical characteristics as independent variables. Bold numbers show significant variables.

Table 3a: DOC concentration and mass flux rates

Variables	DOC concentration (mg L <sup>-1</sup> )		DOC mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> )	
	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )
Area	-0.05 (0.8)	-0.01 (0.94)	0.14 (0.6)	<b>0.12 (0.5)</b>
<i>Q</i>	<b>-0.66 (0.003)</b>	<b>-0.46 (0.01)</b>	0.45 (0.06)	<b>0.36 (0.04)</b>
<i>q</i>	<b>-0.66 (0.003)</b>	<b>-0.48 (0.01)</b>	<b>0.83 (2 × 10<sup>-5</sup>)</b>	<b>0.66 (4.6 × 10<sup>-5</sup>)</b>
Forest and shrubland	<b>0.43 (0.05)</b>	<b>0.34 (0.03)</b>	-0.49 (0.13)	-0.35 (0.16)
Grassland and low shrub	<b>0.39 (0.03)</b>	<b>0.28 (0.02)</b>	0.03 (0.91)	-0.03 (0.88)
Sparse vegetation	0.8 (-0.05)	0.81 (-0.03)	-0.37 (0.13)	-0.25 (0.15)
Acidic bedrock	<b>0.52 (0.03)</b>	<b>0.38 (0.03)</b>	<b>-0.81 (0.02)</b>	<b>-0.64 (0.03)</b>
EC	<b>0.48 (0.01)</b>	<b>0.33 (0.01)</b>	-0.44 (0.07)	<b>-0.37 (0.04)</b>
Travel time	0.36 (0.06)	0.23 (0.09)	<b>-0.71 (0.0041)</b>	<b>-0.56 (0.005)</b>
Ca <sup>2+</sup>	<b>0.48 (0.01)</b>	<b>0.34 (0.01)</b>		
K <sup>+</sup>	<b>0.38 (0.03)</b>	<b>0.25 (0.05)</b>		
Mg <sup>2+</sup>	<b>0.36 (0.04)</b>	<b>0.28 (0.03)</b>		
Na <sup>+</sup>	<b>0.75 (8.2 × 10<sup>-7</sup>)</b>	<b>0.54 (1.5 × 10<sup>-5</sup>)</b>		
Silica	<b>0.39 (0.03)</b>	<b>0.28 (0.03)</b>		
Alkalinity	<b>0.66 (4 × 10<sup>-5</sup>)</b>	<b>0.48 (1 × 10<sup>-4</sup>)</b>		

Table 3b: DIC concentration and mass flux rates

Variables	DIC concentration (mg L <sup>-1</sup> )		DIC mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> )	
	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )
Area	0.19 (0.31)	0.16 (0.22)	0.24 (0.34)	0.16 (0.37)
<i>Q</i>	-0.31 (0.21)	-0.33 (0.06)	<b>0.6 (0.01)</b>	<b>0.42 (0.01)</b>
<i>q</i>	<b>-0.73 (6 × 10<sup>-4</sup>)</b>	<b>-0.62 (4 × 10<sup>-4</sup>)</b>	<b>0.78 (1 × 10<sup>-4</sup>)</b>	<b>0.57 (7 × 10<sup>-4</sup>)</b>
Forest and shrubland	<b>0.48 (0.03)</b>	<b>0.37 (0.02)</b>	-0.37 (0.26)	-0.27 (0.28)
Grassland and low shrub	<b>0.45 (0.01)</b>	<b>0.34 (0.01)</b>	-0.05 (0.85)	-0.05 (0.82)
Sparse vegetation	<b>0.41 (0.02)</b>	<b>0.28 (0.02)</b>	-0.05 (0.84)	-0.06 (0.77)
Acidic bedrock	<b>0.55 (0.02)</b>	<b>0.42 (0.02)</b>	-0.57 (0.15)	-0.43 (0.18)
EC	<b>0.88 (2.7 × 10<sup>-11</sup>)</b>	<b>0.73 (6 × 10<sup>-9</sup>)</b>	-0.19 (0.44)	-0.16 (0.38)
Travel time	<b>0.58 (0.0012)</b>	<b>0.42 (0.002)</b>	-0.42 (0.13)	-0.3 (0.16)
Ca <sup>2+</sup>	<b>0.9 (2 × 10<sup>-12</sup>)</b>	<b>0.79 (3 × 10<sup>-10</sup>)</b>		
K <sup>+</sup>	<b>0.71 (5 × 10<sup>-6</sup>)</b>	<b>0.55 (1 × 10<sup>-5</sup>)</b>		
Na <sup>+</sup>	<b>0.82 (8 × 10<sup>-9</sup>)</b>	<b>0.65 (2 × 10<sup>-7</sup>)</b>		
Mg <sup>2+</sup>	<b>0.73 (2 × 10<sup>-5</sup>)</b>	<b>0.58 (3.5 × 10<sup>-6</sup>)</b>		
Silica	<b>0.5 (0.004)</b>	<b>0.33 (0.01)</b>		
Alkalinity	<b>0.81 (2 × 10<sup>-8</sup>)</b>	<b>0.75 (2 × 10<sup>-9</sup>)</b>		

Table 3c: CO<sub>2</sub> concentration and mass flux rates

Variables	CO <sub>2</sub> concentration (mg L <sup>-1</sup> )		CO <sub>2</sub> mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> )	
	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )
Area	0.03 (0.86)	0.02 (0.91)	0.28 (0.3)	0.16 (0.4)
<i>Q</i>	-0.36 (0.14)	-0.32 (0.07)	<b>0.71 (9 × 10<sup>-4</sup>)</b>	<b>0.50 (0.003)</b>
<i>q</i>	<b>-0.6 (0.01)</b>	<b>-0.47 (0.01)</b>	<b>0.89 (6 × 10<sup>-7</sup>)</b>	<b>0.75 (1 × 10<sup>-6</sup>)</b>

TABLE 3

Continued

Table 3c: CO<sub>2</sub> concentration and mass flux rates (Continued)

Variables	CO <sub>2</sub> concentration (mg L <sup>-1</sup> )		CO <sub>2</sub> mass flux rate (kg day <sup>-1</sup> ha <sup>-1</sup> )	
	Spearman's Rho (p)	Kendall's Tau (p)	Spearman's Rho (p)	Kendall's Tau (p)
Forest & shrubland	<b>0.46 (0.04)</b>	0.31 (0.06)	-0.45 (0.17)	-0.35 (0.2)
Grassland & low shrub	0.06 (0.8)	0.03 (0.8)	-0.24 (0.3)	-0.20 (0.3)
Sparse vegetation	0.04 (0.8)	0.03 (0.8)	-0.20 (0.4)	-0.11 (0.6)
Acidic bedrock	0.23 (0.4)	0.17 (0.4)	-0.67 (0.08)	-0.50 (0.11)
EC	<b>0.57 (6 × 10<sup>-4</sup>)</b>	0.42 (0.001)	-0.41 (0.1)	-0.26 (0.1)
Travel time	0.36 (0.06)	0.26 (0.06)	-0.5 (0.07)	-0.34 (0.1)
Ca <sup>2+</sup>	<b>0.57 (7 × 10<sup>-4</sup>)</b>	0.43 (8 × 10 <sup>-4</sup> )		
K <sup>+</sup>	<b>0.44 (0.01)</b>	0.33 (0.01)		
Na <sup>+</sup>	<b>0.65 (5 × 10<sup>-5</sup>)</b>	0.49 (1 × 10 <sup>-4</sup> )		
Mg <sup>2+</sup>	<b>0.48 (0.01)</b>	0.36 (0.005)		
Silica	<b>0.41 (0.02)</b>	0.28 (0.03)		
Alkalinity	<b>0.47 (0.01)</b>	0.36 (0.004)		

rates (Fig. 6, Tables 2 and 3). Out of the four lithology classes (carbonate bedrock, acidic bedrock, mafic bedrock, and other sedimentary and metamorphic bedrock), only acidic bedrock cover was found to have a significant positive relationship with C concentrations. Acidic bedrock cover showed a positive significant relationship to both DOC and DIC (Fig. 7, Tables 2 and 3).

Stream water EC averaged  $29 \pm 24 \mu\text{S cm}^{-1}$  (Table 1) for the 32 sampled streams. EC showed strong significant positive regressions to concentration of DOC, DIC, and CO<sub>2</sub> and significant negative relationship to mass flux rate of DOC. All C concentrations showed positive relationship with travel times and they were significant for DOC and DIC concentrations (Fig. 7, Tables 2 and 3). Similar to EC, alkalinity, silica, and the base cations (Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>) showed significant positive relationships to all C concentrations (Fig. 5, Tables 2 and 3). Travel time showed a significant positive relationship to EC, silica, K<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup> (Fig. 8, Table 6). Specific discharge had no significant relationship to catchment area (Fig. 9).

The multiple linear regression analysis indicated that the hydrological factors were important for predicting C export whereby both  $q$  and travel time were found to be significantly correlated to all variables except the DIC concentrations (Table 7, Equations 1–6). Travel time was found to be important for DOC and CO<sub>2</sub> concentrations and for the DOC mass flux rates (Equations 1, 3, and 4). EC was the most important variable for prediction of DIC concentration (Equation 2) and grassland and low shrub cover was most important for predicting DOC flux (Equation 4).

## Discussion and Concluding Remarks

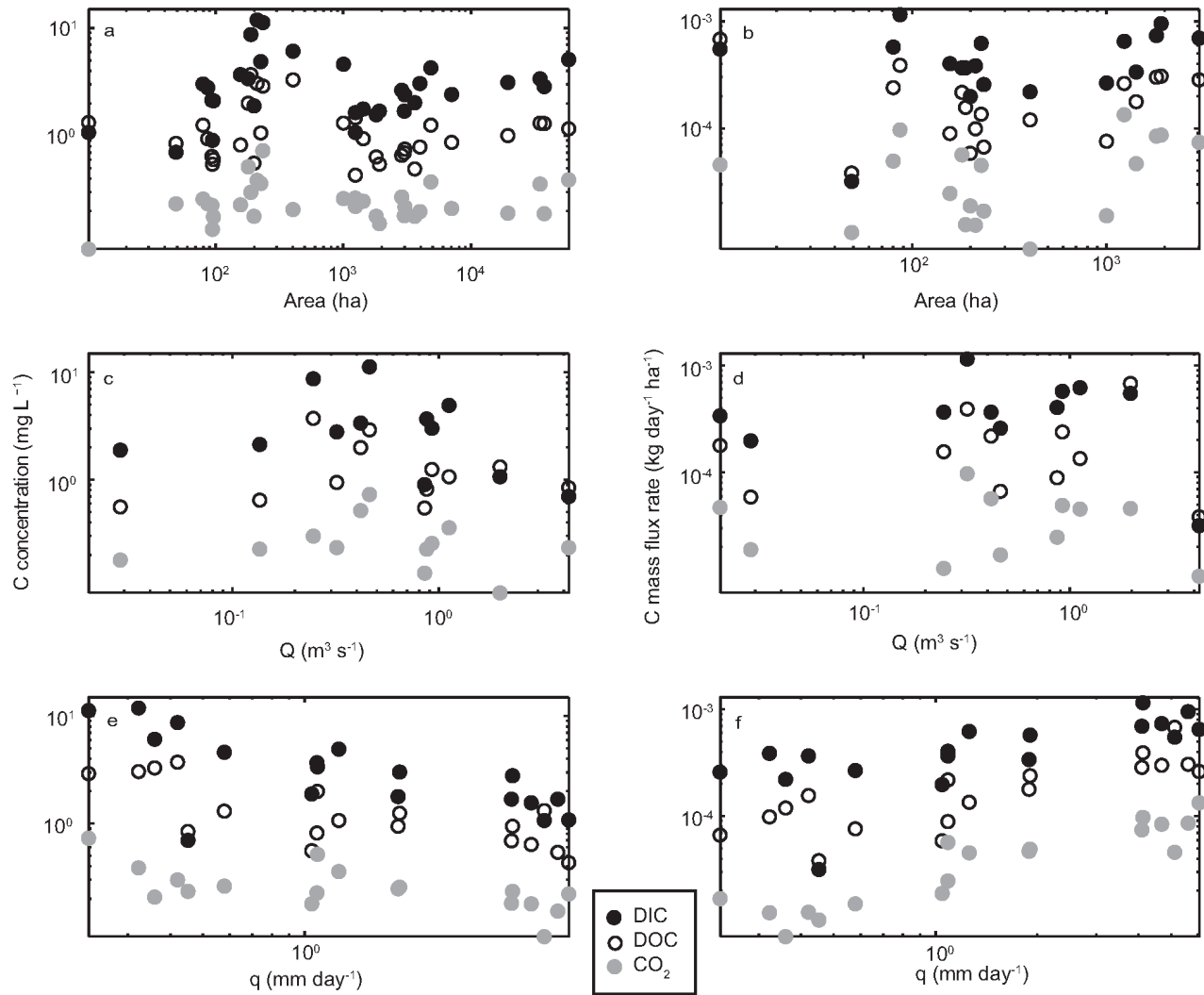
### ON THE SPATIAL VARIABILITY OF C IN SUBARCTIC HEADWATER STREAMS

The high variability of both organic and inorganic C concentrations within the Abiskoajokka headwater streams is consistent

with previous studies in other cold climate systems. Previous investigations in boreal landscapes for example have found large variability in DOC for headwater streams (Temnerud and Bishop, 2005; Dawson et al., 2011). This high variability may in part be attributed to the travel time of water through the landscape. From the multiple linear regressions, travel time was found to be a strong predictor of DOC and CO<sub>2</sub> concentrations during this synoptic campaign. The importance of travel time is likely due to a combination of catchment altitude and size given that the small catchments are situated at higher elevations with little vegetation (thus little biomass production and soil organic carbon) while larger catchments are lower down in the valley with a higher extent of shrubs and forest cover. As such, there was significantly higher variability of all C concentrations in catchments with longer travel times (0.8–1.8 yr,  $n = 13$ ) compared to catchments with shorter travel times (0.3–0.7 yr,  $n = 13$ ; Fig. 5, Table 3).

The data from the synoptic campaign presented here also confirms that DIC is the major component of dissolved C in small Arctic and subarctic rivers, which is consistent with previous work from both Sweden (Lyon et al., 2010a; Giesler et al., 2014) and rivers in the pan-arctic drainage basin (Gordeev et al., 1996; Striegl et al., 2007; Tank et al., 2012b). For all but two catchments sampled here, the stream water DIC concentration was higher than DOC (Table 1). In addition to the general dominance of DIC concentrations in this landscape, these low DOC concentrations relative to DIC are likely related to the relatively low flow conditions during the sampling campaign. During late summer, the active layer is likely at its deepest (Åkerman and Johansson, 2008; Sjöberg et al., 2013) and relatively deep hydrological flow pathways are maintaining the streamflow (i.e., baseflow). During this time of the year, DIC concentrations are typically increasing (to reach their maximum during winter) in this region (e.g., Giesler et al., 2014). DOC concentration is generally high during the snowmelt season when shallow flow pathways dominate the groundwater domain (Lyon et al., 2010a; Laudon et al., 2011).

For DIC, which originates from weathering of unconsolidated sediments and bedrock (e.g., Tank et al., 2012b), the high vari-

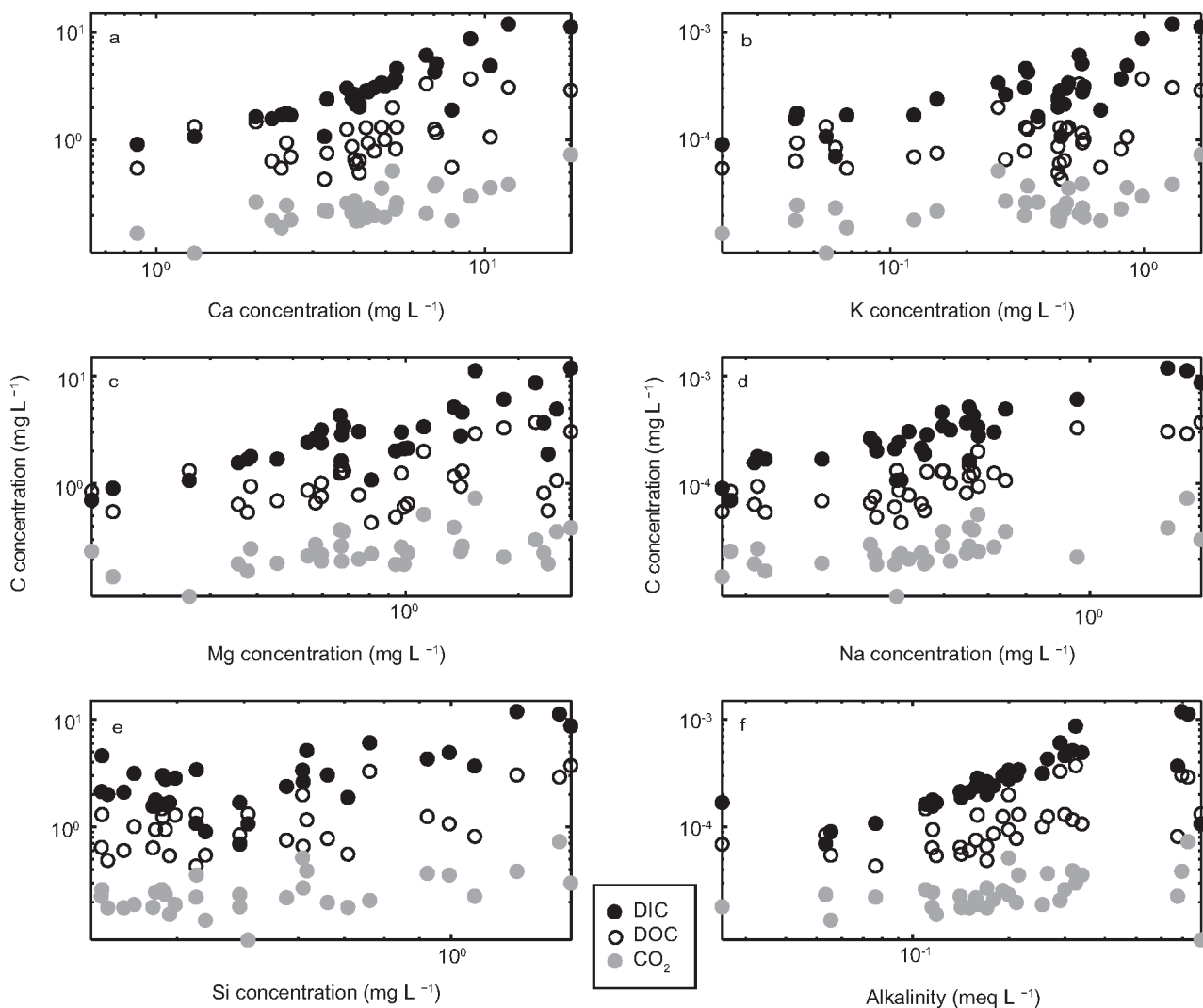


**FIGURE 4.** Dissolved C concentrations measured within Abiskojokka catchment and its tributaries. Concentration was measured at 32 sites; mass flux rate was estimated for 18 sites. (a), (c), and (e) Dissolved C concentration vs. catchment area,  $Q$ , and  $q$ , respectively. (b), (d), and (f) Dissolved C mass flux rate vs. catchments area,  $Q$ , and  $q$ , respectively.

**TABLE 4**

Results of one-sided variance  $F$ -test and associated  $p$ -values on the variances of the observed DOC, DIC, and  $\text{CO}_2$  concentrations and mass flux rates and selected landscape variables. Bold numbers show significant variables, and (–) indicate no significant difference between high and low values.

Variables	DOC ( $\text{mg L}^{-1}$ ) $F(p)$	DOC ( $\text{kg day}^{-1} \text{ha}^{-1}$ ) $F(p)$	DIC ( $\text{mg L}^{-1}$ ) $F(p)$	DIC ( $\text{kg day}^{-1} \text{ha}^{-1}$ ) $F(p)$	$\text{CO}_2$ ( $\text{mg L}^{-1}$ ) $F(p)$	$\text{CO}_2$ ( $\text{kg day}^{-1} \text{ha}^{-1}$ ) $F(p)$
Area	<b>11.2 (0.005)</b>	<b>13.4 (0.005)</b>	<b>10.6 (0.005)</b>	1.8 (–)	<b>4.5 (0.005)</b>	1.3 (–)
$Q$	<b>15.3 (0.005)</b>	2.9 (–)	<b>9.2 (0.005)</b>	<b>3.6 (0.05)</b>	<b>9.5 (0.005)</b>	4.2 (–)
$q$	<b>12.2 (0.005)</b>	<b>8 (0.005)</b>	<b>12.6 (0.005)</b>	<b>3.9 (0.05)</b>	<b>5.2 (0.025)</b>	<b>4.2 (0.025)</b>
Forest and shrubland	1.8 (–)	1.3 (–)	6.2 (–)	3 (–)	<b>5.9 (0.05)</b>	1.4 (–)
Grassland and low shrub	1.7 (–)	<b>4.3 (0.025)</b>	<b>5.2 (0.025)</b>	1.2 (–)	2.4 (–)	2.4 (–)
Sparse vegetation	1.1 (–)	2.1 (–)	1.6 (–)	1.1 (–)	1.1 (–)	1.1 (–)
Acidic bedrock	<b>6.3 (0.025)</b>	7.6 (–)	<b>9.7 (0.005)</b>	14.8 (–)	2.3 (–)	<b>66.5 (0.005)</b>
EC	<b>1.1 (0.005)</b>	3.2 (–)	<b>10.7 (0.005)</b>	1.7 (–)	<b>15.6 (0.005)</b>	8.3 (–)
Travel time	<b>2.4 (0.025)</b>	2.1 (–)	<b>3.5 (0.005)</b>	1.3 (–)	<b>8.3 (0.005)</b>	6 (–)



**FIGURE 5.** Dissolved C and (a)  $\text{Ca}^{2+}$ , (b)  $\text{K}^+$ , (c)  $\text{Mg}^{2+}$ , (d)  $\text{Na}^+$ , (e) silica concentrations, and (f) alkalinity for tributary streams within the Abiskojokka catchment, were measured at 32 sites.

ance of concentrations found in the small catchments is coupled to variability in subsurface conditions and the time that water takes to travel through the catchments. Jantze et al. (2013) highlighted the importance of travel time through catchments for connecting DIC sources across the landscape to the stream. Further, and consistent with Olefeldt et al. (2012), we found that DIC mass flux rate was positively related to  $q$ , which has also been found in studies of solutes that originate from geogenic sources (Basu et al., 2010). This is consistent with the view that inorganic carbon loadings are derived ubiquitously across the entire landscape, while additional factors (e.g., biological) and flow pathway variability through the catchment potentially influence the export of DOC. Our results thereby imply that in-stream DIC fluxes from small headwater catchments (<500 km<sup>2</sup>) are controlled by the same mechanisms as Jantze et al. (2013) found in large-scale (>500 km<sup>2</sup>) catchments.

The DOC concentration data presented here confirm the low DOC concentrations typical for most alpine subarctic systems. The organic soil horizon is the main DOC source in these landscapes (Olefeldt et al., 2012). Thus, the spatial variability of the C export and the vegetation cover is linked to the different C content in

the soil, which varies with vegetation type, organic carbon's ability to dissolve, and the connectivity between groundwater and the organic-rich soil horizons. In this mountainous region of northern Sweden, the combination of complex vegetation patterns and the topography, which has great influence on travel time (Lyon et al., 2010a), clearly complicates the interpretation of DOC and CO<sub>2</sub> export. As previously mentioned, travel time is the variable that best predicts DOC and CO<sub>2</sub> concentrations, thus the terrain appears to be more important than the vegetation cover in the late summer for concentration of DOC and CO<sub>2</sub> in the stream system. The relatively deep groundwater tables during baseflow conditions in combination with thin organic soil horizons lead to limited potential interaction between (and/or subsequent solute movement along) flow pathways. In addition, the DOC storage in the organic layer is typically flushed during spring freshet in this landscape (Jantze et al., 2013; Giesler et al., 2013). The size of the soil organic C pools in the catchment and the connection between these pools and the streams are the most important determinant of DOC export. However, adsorption to mineral soil and in-stream processes can regulate organic C concentrations in streams, especially for smaller

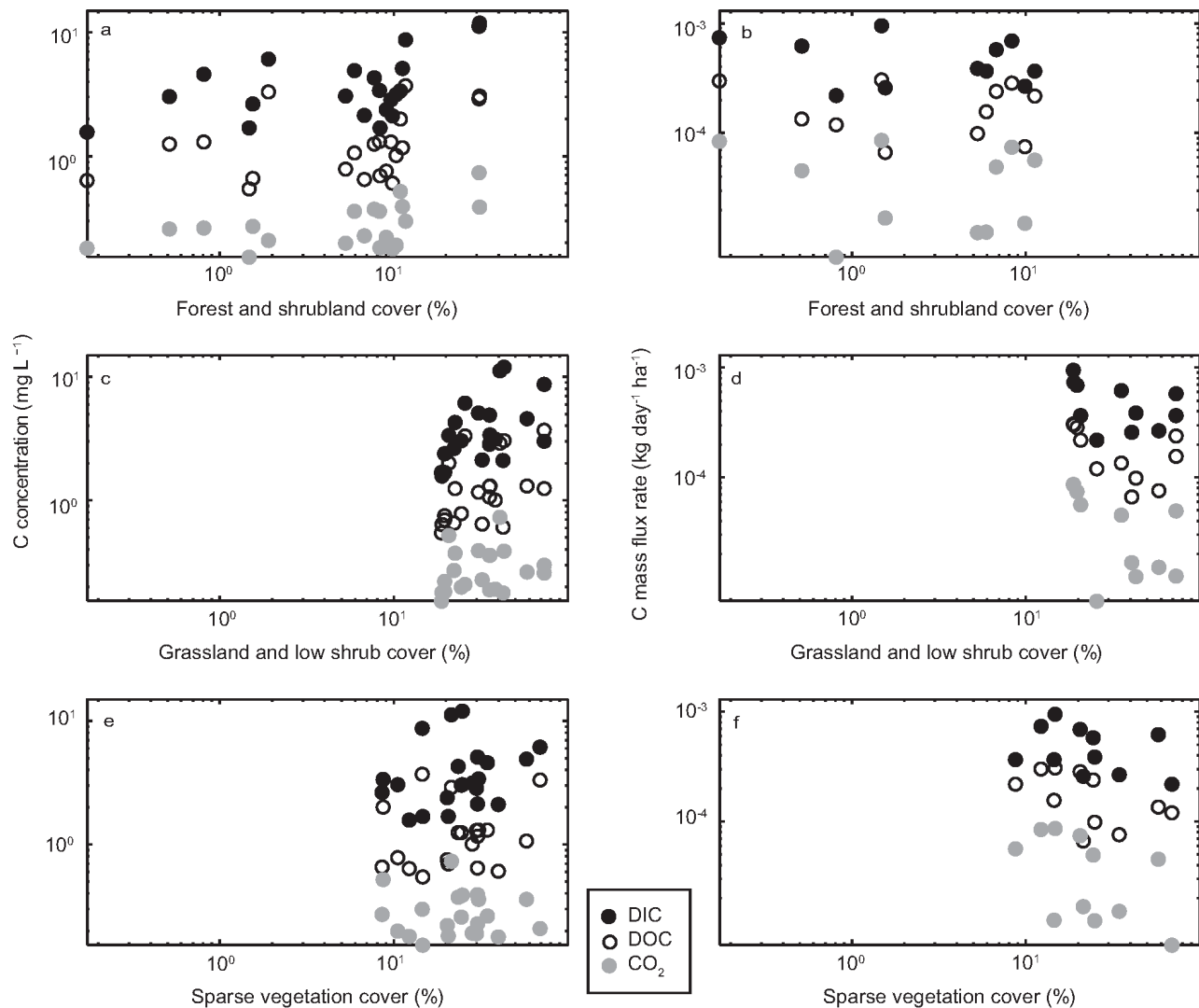
**TABLE 5**  
**Land cover and lithology characteristics of sampled streams in Abiskojokka catchment.**

Site	Other sedimentary and metamorphic bedrock cover (%)	Acidic bedrock cover (%)	Mafic bedrock cover (%)	Carbonate bedrock cover (%)	Forest and shrubland cover (%)	Lake cover (%)	Grassland and low shrub cover (%)	Sparse vegetation cover (%)
1			100				100	<0.5
2			100				34	8
3			100				7	2
4			100		<0.5	<0.5	19	12
5			100			<0.5	15	10
6	1	1	98		1	<0.5	19	15
7	8	4	88		8	1	20	21
8						<0.5	10	12
9	100				7	<0.5	32	30
10	100				1		74	25
11	100				10	2	43	40
12	100						67	20
13	100					2	60	32
14	100					6	6	55
15	98		2			4	24	35
16	38	30	20	2	11	3	31	30
17	95		<0.5	5	6	<0.5	36	58
18	100					<0.5	35	65
19	45	30	6	19	1	5	58	35
20	14	11	75		5	<0.5	25	11
21	4	14	82		2	<0.5	22	9
22	22	1	77		11		21	9
23	60	40			12		74	15
24	50	38			2	3	26	70
25	38	55			31	<0.5	43	25
26	27	58			31		41	22
27	21	56	2	2	10	4	38	28
28	41	43				5	34	45
29	25	45	10	2	8	3	36	31
30	27	42	12	3	10	4	36	30
31	9	4	87		9	1	20	20
32	6	10	84		8	1	23	23

catchments (<5 km<sup>2</sup>) (Aitkenhead et al., 1999). Further, the low DOC concentration in stream water is coupled to the dissolution rate of organic matter (Jantze et al., 2013) and the low percentage of organic-rich wetlands and mires in this alpine/subalpine landscape (Fig. 2). The low wetland cover in the Scandinavian Mountains thus keeps DOC concentrations at consistently low levels during late summer. The range of wetland cover is a fundamental difference between these systems and more boreal landscapes where DOC concentrations are higher than DIC concentrations

(e.g., Grabs et al., 2009; Wallin et al., 2010). Simply put, there is not much DOC available in this landscape in the late summer and the DOC that is present is not interacting with hydrological flow pathways.

While many studies have shown positive relationships between wetland extent and DOC (e.g., Laudon et al., 2004; Creed et al., 2008), there are other surface and subsurface processes known to regulate the C flux in streams (Tank et al., 2012a, 2012b). The relatively constant CO<sub>2</sub> concentrations across all catchment sizes



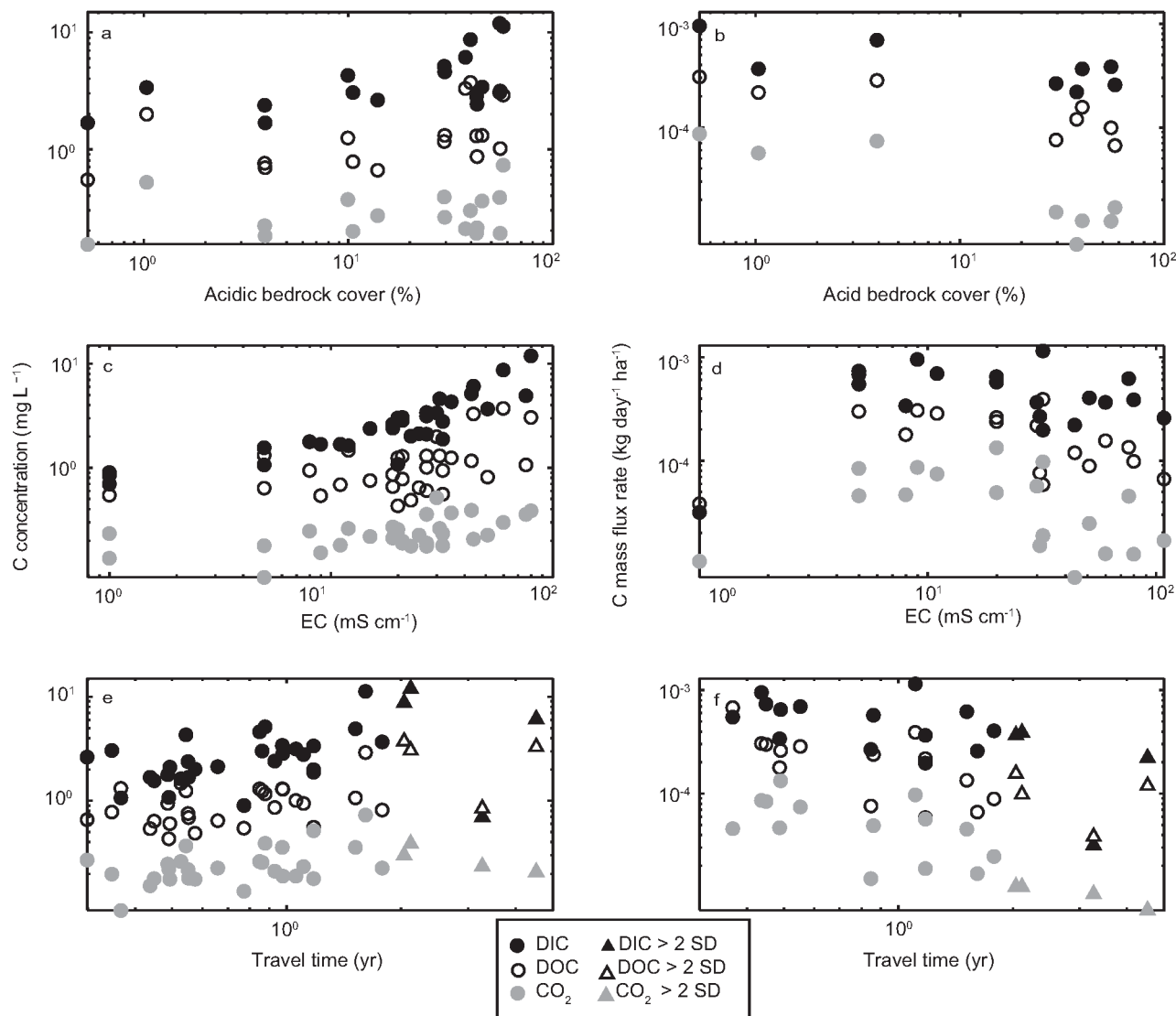
**FIGURE 6.** Dissolved C concentrations measured within Abiskojokka catchment and its tributaries. Concentration was measured at 32 sites; mass flux rate was estimated for 18 sites. (a), (c), and (e) Dissolved C concentration vs. forest and shrubland cover, grassland and low shrub cover, and sparse vegetation cover, respectively. (b), (d), and (f) Dissolved C mass flux rate vs. forest and shrubland cover, grassland and low shrub cover, and sparse vegetation cover, respectively.

(Fig. 4) can be explained by the inflow of  $\text{CO}_2$  supersaturated groundwater and the low decomposition rates of organic matter compared to photosynthesis rates. Supersaturation of  $\text{CO}_2$  in stream water has previously been found in studies of boreal (Wallin et al., 2013) and subarctic (Giesler et al., 2013) streams and across Swedish rivers (Humborg et al., 2010). Further, in-stream and lake bacterial respiration and photochemical degradation of DOC influence the temporal and spatial variability of DIC and  $\text{CO}_2$  in stream water (Sobek et al., 2003; Wallin et al., 2010). For boreal regions, where DOC levels are relatively higher, both terrestrial and freshwater aquatic respirations tend to contribute equally to atmospheric emission of  $\text{CO}_2$  (Humborg et al., 2010). Supersaturated streams with high emissions of  $\text{CO}_2$  in tundra-dominated systems of the subarctic have been reported by Lundin et al. (2013), which is consistent with our results. Because of the significant positive relationship between C and EC (Fig. 7), silica, and the base cations considered (Fig. 5), we interpret that the majority of the aquatic  $\text{CO}_2$  originates from terrestrial respiration in shallow to deep

groundwater, as previously seen by Hope et al. (2001, 2004) and Dawson et al. (2001).

#### ON THE POTENTIAL LINKS BETWEEN C AND LANDSCAPE CHARACTERISTICS

We found significant positive relationships between forest and shrubland, grasslands and low shrub cover, and DOC and DIC concentrations with the linear regression as well as Spearman's rho and Kendall's tau tests (Tables 2 and 3). In addition, sparse vegetation cover was significantly positively related to DIC (Table 3, part b). Thus, areas at higher altitudes with relatively small amounts of living biomass show similar positive relationship to DOC and DIC concentration as low-lying forest and shrubland covered areas with high amounts of living biomass (Fig. 6). This result is consistent with findings that soils at higher altitude, where grassland, shrubs, and sparse vegetation are common, have greater C storage than at lower altitudes due to the

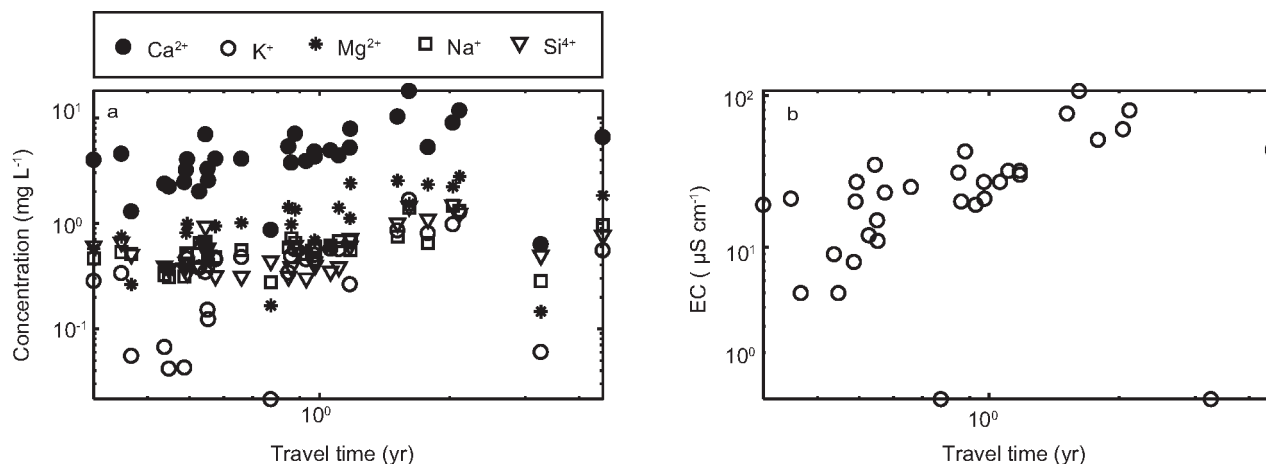


**FIGURE 7.** Dissolved C concentrations measured within Abiskojokka catchment and its tributaries. Concentration was measured at 32 sites; mass flux rate was estimated for 18 sites. (a), (c), and (e) Dissolved C concentration vs. acidic bedrock cover, electrical conductivity (EC), and travel time, respectively. (b), (d), and (f) Dissolved C mass flux rate vs. acidic bedrock cover, EC, and travel time, respectively.

**TABLE 6**

Coefficients for Spearman and Kendall rank correlations and associated *p*-values as well as linear regressions and associated *p*-values for relationships between travel time as dependent variable and EC, silica, and base cations as independent variables.

Variables	Travel time (yr)		
	Spearman's Rho ( <i>p</i> )	Kendall's Tau ( <i>p</i> )	Eq. linear regression ( <i>p</i> )
EC	<b>0.7 (0.00003)</b>	<b>0.54 (0.00007)</b>	<b>EC = 0.014 × Travel time + 0.44 (0.02)</b>
Silica	0.23 (0.2)	0.14 (0.3)	<b>Si = 0.84 × Travel time + 0.35 (0.01)</b>
Ca <sup>2+</sup>	<b>0.67 (0.00008)</b>	<b>0.53 (0.00004)</b>	Ca = 0.078 × Travel time + 0.43 (0.07)
K <sup>+</sup>	<b>0.73 (0.00001)</b>	<b>0.56 (0.00001)</b>	<b>K = 0.89 × Travel time + 0.42 (0.04)</b>
Na <sup>+</sup>	<b>0.66 (0.0001)</b>	<b>0.47 (0.0003)</b>	<b>Na = 1.2 × Travel time + 0.11 (0.008)</b>
Mg <sup>2+</sup>	<b>0.66 (0.0001)</b>	<b>0.49 (0.0002)</b>	<b>Mg = 0.48 × Travel time + 0.35 (0.007)</b>



**FIGURE 8.** Dissolved C concentrations and alkalinity measured within Abiskoajokka catchment and its tributaries. Concentration was measured at 32 sites. (a) Dissolved C concentration vs. travel time. (b) Alkalinity vs. travel time.

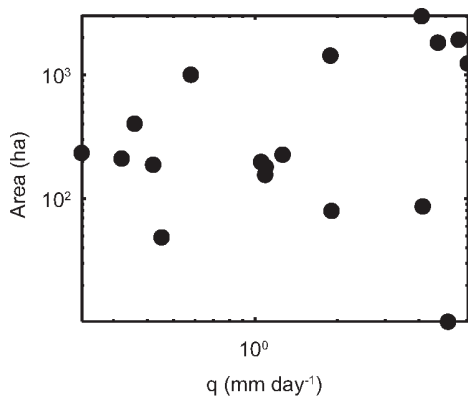
slower decomposition rates (Sjögersten and Wookey, 2009). In addition, the upper horizons of the low-lying areas are potentially hydrologically disconnected from the stream at low flows. Grassland and low shrub cover were also found to be the landscape characteristics that best predicted DOC mass flux rate within the multiple linear regression (Equation 4). The negative nature of the relationship between C mass flux rate and vegetation most likely comes from the fact that  $Q$  is an intrinsic component of mass flux rate.

Aitkenhead-Peterson et al. (2007) found that DOC concentration is strongly linked to peat cover in catchments where peatlands dominate. In the same study, however, Aitkenhead-Peterson et al. (2007) observed that this relationship between peat cover and stream water DOC concentration did not hold for landscapes with more heterogeneous land cover. Such as the case in our study area, the draining of mineral soils can be seen to be a more important process, since the rate with which the water passes through the mineralogenic soil has an impact on the degree of mineralization from organic to inorganic carbon (Ågren et al., 2007; Koch et al., 2013). Although we did find significant positive relationships between vegetation and C export, we had initially expected them to

be stronger than those observed due to the connection between vegetation and the organic matter in the soil (Hongve, 1999; Sjögersten and Wookey, 2009). The relationships between DOC in stream water and vegetation cover would most likely have been stronger in this landscape earlier in the year (i.e., during the early summer season) when the subsurface water has more contact with the organic rich upper soil horizon. However, the role of hydrologic connectivity between the landscape and the stream system, particularly with regard to probable shifts and distribution of vegetation zones as a consequence of climate change, as this could influence the export under different flow conditions, is presently not known. Vegetation shifts, for example, are likely to have an impact on the terrestrial C cycling in the future due to changes in the litter production, soil moisture (water holding capacity), soil C dynamics, and respiration, which will likely change soil profile characteristics and export of dissolved C in stream water.

Considering bedrock cover, only acidic bedrock was found to be significantly positive correlated to stream-dissolved C concentrations. Relationships to acidic bedrock cover for DOC and DIC concentrations showed significant positive relationships, as did the mass flux rates of DOC and  $\text{CO}_2$  (Fig. 7, Tables 2 and 3). Previous studies have demonstrated that carbonate-rich bedrock is often strongly correlated to inorganic C in streams (Blum et al., 1998; Tank et al., 2012b). The small coverage of carbonate-rich bedrock within the Abiskoajokka catchment and the poor resolution of lithology mapping are likely explanations for this lack of relationship. Regardless, there are strong relationships between DIC concentrations and the weathering products, namely silica and the base cations  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  (Fig. 5). The strong DIC relation in combination with low DOC concentrations in the stream suggests deep flow pathways are actively connecting the bedrock and the till-dominated unconsolidated sediments to the streams. This is consistent with other arctic and subarctic streams during low flow conditions (e.g., Holmes et al., 2012; Frey et al., 2007). Similar to previous work conducted in the Arctic (Tank et al., 2012b), we found that catchment size,  $q$ , and lithology, which is likely best represented by EC, silica, and base cations in this study (Figs. 5 and 6), were the main drivers of C flux during low flow conditions.

While the geology of the region governs the loading sources under low flow conditions, the movement of water through the landscape connects these sources to the streams. The travel time



**FIGURE 9.** Area vs.  $q$  measured for 18 sites within Abiskoajokka catchment.



**TABLE 7**  
**Multiple linear regression equations and corresponding *p*-values.**

Multiple linear regression equations	<i>p</i> -value	Equation
[DOC] = $-0.39 + 2.0 \times \text{Travel time}$	$p = 1.8 \times 10^{-5}$	(1)
[DIC] = $0.19 + 0.092 \times \text{EC} + 2.7 \times \% \text{Grassland and low shrub}$	$p = 7 \times 10^{-4}$	(2)
[CO <sub>2</sub> ] = $-0.11 + 0.513 \times \text{Travel time}$	$p = 1.7 \times 10^{-3}$	(3)
DOC flux = $4.7 \times 10^{-4} - 4.9 \times 10^{-4} \times \% \text{Grassland and low shrub} - 1.3 \times 10^{-4} \times \text{Travel time} - 1.1 \times 10^{-5} \times Q$	$p = 1.2 \times 10^{-3}$	(4)
DIC flux = $2.3 \times 10^{-4} + 1.4 \times 10^{-4} \times q - 3.8 \times 10^{-8}$	$p = 3 \times 10^{-4}$	(5)
CO <sub>2</sub> flux = $2.1 \times 10^{-5} \times 1.2 \times 10^{-5}$	$p = 0.032$	(6)

distribution model from Lyon et al. (2010a) used here reflects the topography of the region and provides a first order approximation of these hydrologic flow pathways. DOC and DIC concentrations both have significant positive relationships to travel time estimates (Fig. 7, Table 3, parts a and b). All C mass flux rates are significantly negatively correlated to travel time. This could be hydrologically explained as travel time is negatively related to *q* in this landscape during this low flow study period (not shown). Moreover, the negative relationships could further be related to some combination of increased gaseous emission of CO<sub>2</sub>, mineralization of DOC through infiltration in mineral soils, and increased bacterial consumption of C with increased travel time of water through the landscape. Emission of CO<sub>2</sub> is especially high in high gradient streams where water is likely turbulent (Wallin et al., 2013), which is the case in this mountainous environment. In this landscape, high DOC concentrations are associated with the spring freshet, while relatively low DOC concentrations (such as those presented in this study) are seen in late summer and the winter season (Giesler et al., 2014). The concentrations and mass flux rates of dissolved C in stream water are dependent on the dynamics of subsurface water travel time in relation to the release time (dissolution time) of C from the organic or inorganic (mineral) source material, respectively. Simply put, it is a combination of the time scale over which water moves through a source and how that source releases a solute in question that determines export from the landscape. Organic carbon has a short release rate (i.e., the time it takes for C to dissolve into the groundwater) and the soil C storage is effectively flushed out every year during the spring flood (Hongve, 1999), whereas the inorganic carbon has long release rates and ubiquitous weathering across the entire catchment. The seasonal variation of DOC and DIC in stream water is thus dependent on the subsurface dissolved C transport dynamics (Lyon et al., 2010a; Jantze et al., 2013). Moreover, the rate at which water passes through the mineral soil has an impact on the degree of mineralization from organic to inorganic C (Ågren et al., 2007; Koch et al., 2013).

Our results based on measurements of dissolved C during late summer show that DOC and DIC both are positively related to many of the biophysical variables, which demonstrate that neither vegetation nor geology alone can explain the dissolved organic and inorganic C in stream water in this northern landscape. Our results highlight the complexity of processes regarding C and hydrological cycles. The relationships for these low flow conditions are consistent with the annual estimates from Lyon et al. (2010a) and highlight the consistency of mechanisms as we move from smaller to larger catchment systems. Different landscape units in this subarctic alpine environment contrib-

ute to aquatic C export with great variance with respect to space and system characteristics. Our findings demonstrate a significant spatial variation in C concentration across Abiskoajokka catchment that appears connected to the local geology and travel time of water, indicating that the stream biogeochemistry is dominated by subsurface characteristics under low flow conditions. To estimate accurate transport of DOC, DIC, and CO<sub>2</sub>, we therefore stress the need to work across scales and landscape types to better inform future modeling efforts and help complement existing data sets.

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