Long term patterns in dissolved organic carbon, major elements and trace metals in boreal headwater catchments: trends, mechanisms and heterogeneity

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Abstract

The boreal landscape is a complex, spatio-temporally varying mosaic of forest and mire landscape elements that control surface water hydrology and chemistry. Here, we assess long-term water quality time-series from three nested headwater streams draining upland forest (C2), peat/mire (C4) and mixed (C7) (forest and mire) catchments. Temporal trends in weather and runoff (1981–2008); dissolved organic carbon concentration [DOC] (1993–2010) and other water quality parameters (1987–2011) were assessed. There was no significant annual trend in precipitation or runoff but a significant monotonic increasing trend existed in air temperature and length of growing season. Stream [DOC] was positively correlated with some trace metals (copper, iron and zinc) and negatively with several other chemical parameters (e.g. sulfate, conductivity, calcium). Both sulfate and conductivity showed declining trends, while a significant increase was observed in pH during winter and spring. Calcium and magnesium showed monotonic decreasing trends. The declining trajectories of stream base cation and sulfate concentrations during other times of the year were not accompanied by changes in pH and alkalinity. Water temperature increased significantly both annually and in most months while iron and DOC concentrations showed significant increases in autumn months. Though all streams showed significant positive trends in [DOC] in autumn, only C2 had a significant annual increasing trend. There was also a shift in the magnitude of variability in spring [DOC] and increasing trend of summer baseflow [DOC] in C2 and C7.

1 Introduction

Understanding seasonal and long term trends in dissolved organic matter is needed to explain nutrient, carbon, trace metals and base cation cycling in boreal forest ecosystems (e.g. Berggren et al., 2009; Schindler et al., 1997). Dissolved organic carbon (DOC), the fraction of natural organic matter able to pass through a 0.45 µm filter,
a heterogeneous mixture of complex-structured organic compounds of various terrestrial and in-stream origins (Kalbitz et al., 2000; Selberg et al., 2011).

In recent years, several studies have reported increasing trends in DOC concentration [DOC] in surface waters in different parts of the Northern Hemisphere (Evans et al., 2005; Erlandsson et al., 2008; Monteith et al., 2007). Several factors (or combination of factors) have been recognized as the driver of the observed trend in [DOC] in streams and lakes. However, regional differences, effects of scale and local processes have not allowed a unified consensus to be reached (Clark et al., 2010). In the United Kingdom for example; sea salt, declines in acid deposition (Dawson et al., 2009; Evans et al., 2006; Monteith et al., 2007), nitrogen enrichment (Worrall et al., 2004) and elevated atmospheric CO$_2$ (Fenner et al., 2007; Freeman et al., 2004) have all been recognized as possible drivers of trends. In North America; changes in precipitation and runoff regimes (Eimers et al., 2008), acid deposition and nitrogen enrichment (Findlay, 2005) as well as weather variability (Striegl et al., 2005) have also been noted amidst some other factors. In Scandinavia; change in acid deposition (de Wit et al., 2007), change in weather and/or runoff regimes (Hongve et al., 2004; Lepistö et al., 2008), or a combination of the two (Erlandsson et al., 2008) have been identified as the drivers of observed [DOC] trends in streams and lakes. This conclusion has been supported by modelling studies (Futter et al., 2009, 2011). Other factors reported as drivers of DOC in literature include drought (Worrall and Burt, 2005), landscape disturbance such as land use (Aitkenhead-Peterson et al., 2009) clear cutting (Schelker et al., 2012) and climate change (Oni et al., 2012a; Schindler et al., 1997).

These widely reported increases have implications on the overall catchment carbon budget and water quality, as DOC is a master variable controlling the chemistry of boreal surface waters. Because DOC can bind protons and modify the redox properties of other organic ligands, both the chemical and physical properties of some other key water quality parameters will be affected. Changes in production or transport of DOC will modify the mobility, toxicity, speciation and bioavailability of elements such as mercury (Ravichandran, 2004), silica (e.g. Klaminder et al., 2011a), copper (Brooks et al.,
2007; Shank et al., 2004), lead (Klaminder et al., 2006) and cesium (Tegen and Dorr, 1996) as well as persistent organic pollutants (e.g. Bergknut et al., 2011). In addition, DOC cycling strongly influences base cation dynamics and exports in forest ecosystems (Raulund-Rasmussen et al., 1998). Increases in DOC following acidification recovery of a catchment can also influence base cation exports and as a result control the buffering capacity of soil and surface waters acidity (Evans et al., 2005). Evaluation of recovery from acidification is therefore important in boreal systems as the associated changes in stream chemistry can have large impacts on overall aquatic health status.

Headwaters exert an important control on the overall carbon budget and water quality status of catchments but there is a lack of understanding of headwater biogeochemical processes since most monitoring efforts are focused on higher order streams or downstream of larger catchments (Oni et al., 2011; Temnerud and Bishop, 2005). This has been described as “Aqua Incognita” by Bishop et al. (2008). Large river basins will contain a mixture of DOC of different quality from various landscape sources making the DOC dynamics more uniform over time and space (Oni et al., 2012b). In contrast, the DOC processes in headwater reaches are dependent on both local soil conditions and hydrology that both have a heterogeneous nature. As a result, headwater [DOC] can be highly variable (Temnerud et al., 2010; Buffam et al., 2008). While relating downstream chemical parameters to upstream reaches might partly provide useful understanding about headwater biogeochemistry, studying the smallest units of the landscape mosaic such as wetland and upland forest landscape units is important to understand the processes driving the long term water quality trends in boreal catchments.

Climate variables control both the in-soil and in-stream carbon processes and increases in temperature can increase the rate of both biological and chemical processes (Futter et al., 2007; Köhler et al., 2008, 2009). Land use and hydrology also influence DOC. The DOC from forest dominated catchments can be more labile and bioavailable for microbial degradation or utilization in the aquatic food web (Berggren et al., 2009). DOC originating from wetlands is often less susceptible to degradation (Ágren et al., 2008; Berggren et al., 2007). Biotic processes such as microbial production and
mineralization (Berggren et al., 2009) are important second order controls on surface water DOC concentration. There can be both positive and negative discharge/[DOC] relationships in boreal headwaters, depending on whether the stream drains a forest or mire landscape element. Hydrological mobilization from organic rich soils adjacent to streams is an important control on DOC dynamics in forest dominated boreal catchments (Winterdah et al., 2011a). The riparian soil-stream interface is important for DOC production in boreal forest catchment due to strong hydrological connectivity between soil, groundwater and surface water (Bishop et al., 1994; Laudon et al., 2011). Riparian zones are characterized by wetter conditions than upland parts of a catchment (McGlynn and McDonnell, 2003) and can react rapidly to changing groundwater levels (Bishop et al., 2004). As a result, riparian zone can contribute more to stream DOC during the rising limb of runoff hydrograph than the corresponding falling limb (McGlynn and McDonnell, 2003). However, forest and mire landscape elements can display markedly different seasonal responses (Bishop and Pettersson, 1996; Köhler et al., 2008, Eimers et al., 2008; Laudon et al., 2004a, 2011).

Differences in environmental factors including climate influence catchment water retention and residence time in boreal ecosystems. As a result a series of interdependent biogeochemical processes controlling DOC production such as solubility and mobilization in the terrestrial-aquatic continuum of headwater basins and small scale processes occurring at plot scales are not fully integrated at catchment scales due to landscape heterogeneity. Complex interactions exist in the landscape-stream biogeochemical mechanisms, as relationships between surface water chemical parameters are not always linear. Therefore long term data are valuable to identify major drivers of trends in water quality and are a complement to seasonal trend and/or other short term process based studies.

The objectives of this study are (1) to evaluate the temporal pattern of long term and seasonal trends in stream chemical parameters and surface water [DOC] in three contrasting headwater streams draining forest, mire and a mixture of both (2) identify the driver(s) of trend and plausible linkages between DOC dynamics and mechanisms.
controlling the cycling of other carbon dependent parameters such as trace metals, base cations etc. in a small boreal catchment (3) evaluate riparian controls on stream [DOC] in a headwater boreal catchment. In this study, we use long-term monitoring data from the Svartberget catchment which is the most intensively monitored part of the Krycklan Catchment Study (KCS), a nested set of boreal catchments in Northern Sweden. The monitored parameters include both deposition and stream chemistry. Chemical monitoring includes [DOC] and other representative in-stream chemical parameters (absorbance, pH, chloride, conductivity, alkalinity and sulfate), trace metals (iron, copper, zinc and silicon) and base cations (calcium, magnesium, potassium and sodium). Several studies report on parts of this record (Grip and Bishop, 1990; Köhler et al., 2008; Winterdahl et al., 2011a; Yurova et al., 2008) but none has examined the entire record that is over a quarter century for some parameters and their possible linkages with DOC dynamics. It is our expectation that this study will contribute to the understanding of the dominating mechanisms and lead to improved process-modelling efforts in pristine boreal headwater catchments in the future.

2 Methods

2.1 Site descriptions and stream monitoring

This study was conducted in the Svartberget catchment (64°14′ N, 10°46′ E) located about 60 km northwest of Umeå city in Northern Sweden (Fig. 1). Svartberget is an unmanaged 50 ha boreal catchment, centrally located within the Krycklan study catchment. Streams in the catchment were ditched in the late 19th and early 20th centuries to improve drainage (Esseen et al., 1997). The catchment receives limited deposition of sulfate (∼2 kg ha⁻¹ SO₄⁻ s yr⁻¹) and inorganic nitrogen (<2 kg ha⁻¹ N yr⁻¹). As a result, Svartberget is probably only slightly acidified. However, episodic acidification of streams has been observed in the region (Bishop et al., 2000; Laudon and Bishop, 2002). The catchment consists of two headwater streams draining contrasting
landscape elements of forest and mire, which dominate the boreal landscape (Fig. 1). Forests in the catchment are dominated by approximately century old Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) (Laudon et al., 1999). Vegetation in the mires mainly consists of *Sphagnum* sp. (Yurova et al., 2008). The region has a long-term mean air temperature of 1.7 °C (1981–2008) with the highest temperatures occurring in July. Total annual precipitation in the catchment averages about 610 mm yr$^{-1}$, of which about 35–50% falls as snow (Köhler et al., 2008) and peak precipitation occur in late summer. The spring snowmelt is the dominant hydrologic event and lasts for about six weeks (Buffam et al., 2007). On average the snow cover in the catchment lasts ~ 170 days from October to May (Köhler et al., 2008; Laudon et al., 2011; Löfvenius et al., 2003). Annual runoff is about 320 mm yr$^{-1}$ with subsurface pathways dominating the delivery of runoff especially in the forest catchment (Laudon et al., 2007).

The geology of the catchment consists of gneissic bedrock overlain by till of varying thickness (Bishop et al., 2000; Buffam et al., 2007). The presence of well-developed iron-podzol soils enhances the formation of organic soils in the forest-dominated part of the catchment. These soils are mostly located in riparian areas in close proximity to streams (~ 50 cm depth). Shallower organic soils (~ 5 cm) are also found in upland areas (Blomberg, 2009; Köhler et al., 2009). In the wetland part of the catchment the organic soil depth is on average 3–4 m but extends to 7 m in some places. The catchment elevation ranges from 235–310 m a.s.l. The catchment was delineated using a combination of digital elevation model (DEM) and Light detection and ranging (LIDAR) into three subcatchments (Laudon et al., 2011). These comprise the forest dominated Västrabäcken (C2), mire dominated Kallkälsmyren (C4) and mixed Kallkälsbacken (C7) draining both mire and forest landscape elements. These subcatchments will be referred to as C2, C4 and C7 throughout this study (Fig. 1).

### 2.2 Data collection

The availability of long term time series provided an opportunity to test for trends in climate, deposition chemistry and water quality related parameters in the catchment.
both on long term (annual) and seasonal time scales. Long term measurements of atmospheric deposition of sulfate (1990–2007), chloride (1990–2007), dissolved inorganic nitrogen (1990–2006) and base cations (1990–2007) were used in evaluating the temporal trends of deposition in the catchment. Dissolved inorganic nitrogen (DIN) was estimated as the sum of nitrate (N-NO$_3$) and ammonia (N-NH$_4$) deposition.

Continuous daily time series of stream flow, air temperature and precipitation were available. Some 27 yr of air temperature and precipitation data (1981–2008) were used in estimating seasonal and long term trends as well as water temperature from 1987–2011 (Table 1). Streamflow was measured with a V-notch weir located in a heated dam house at the outlet of the catchment in C7.

Discrete water quality data from grab samples taken at approximately biweekly intervals in C7 stream were also available. Twenty four years (1987–2011) of trace metals, base cations and other in-stream chemical parameters in C7 were used in the analyses presented here (Table 1). While some DOC data were available from prior to 1993, only 17 yr of data (1993–2010) was used in this study to facilitate comparison between C2, C4 and C7. The streams were sampled weekly or biweekly and analyzed for DOC, metals and other water quality parameters listed in Table 1, as described in previous studies (Cory et al., 2007; Köhler et al., 2008, 2009; Laudon et al., 2011; Winterdahl et al., 2011a). Though differences exists between the frequency of DOC sampling in the catchments (C7 > C4 > C2). The frequency of sampling was highest in the spring and more intense in earlier than later part of the record.

Soil water [DOC] from the S4 riparian soil transect lysimeter from 2002–2011 was used to trace the pathways of DOC in the riparian-stream conduit. Soil solution chemistry samples were obtained from three soil profiles, established in 1996 along a 25 m transect in C2 (Laudon et al., 2004b, Cory et al., 2007). These profiles were at a distance of 4m (S4), 12 m (S12) and 22 m (S22) from the C2 stream. The transect was aligned based on the topography to follow the assumed lateral flow paths of the groundwater toward the stream. Only the S4 lysimeter located a distance of 4m from the stream was used in this study. Samples were collected from the S4 suction lysimeter
at a series of depths between 10 and 65 cm denoted as S4_{10} to S4_{65} in this study (Table 2). The S4 profile was dominated by organic material with a transition from organic to organic rich mineral soil at 30 cm depth. The organic enrichment continues to a depth of 60 cm.

### 2.3 Data analysis

A principal component analysis (PCA) of all chemical parameters was performed to evaluate the overall pattern of the relationships between the water quality parameters in the catchment over time. This was followed by Mann Kendall trend test (MKT) analysis to assess the significance of monotonic trends (increase and/or decrease) in runoff, weather-related parameters, stream [DOC] and trace metals, base cations and atmospheric deposition chemistry. This analysis was conducted on the monthly average values of the raw data. Annual as well as monthly trends were calculated since many water quality time series are characterized by strong seasonal variation. The MKT test is ideal for fulfilling the objectives of this study as it is a robust non-parametric statistical method that has been widely used to detect temporal changes in water quality (Leppistö et al., 2008; Libiseller and Grimvall, 2002; Worrall et al., 2004; Yue et al., 2002). The MKT test is insensitive to missing values and outliers in the data set or seasonality, autocorrelation and non-normality of the water quality data sets (Evans et al., 2005; Worrall et al., 2004). Sen’s slope was also calculated from monthly data to show rates of change in long term deposition and stream chemistry data. Soil solution [DOC] from S4 lysimeters were similarly subjected to MKT tests both on seasonal and long term basis. Seasonal MKT test was performed using MULTMK/PARTMK (Libiseller and Grimvall, 2002) and annual trend with MAKESEN (MKT test and Sen’s Slope estimates) (Salmi et al., 2002). Change in growing degree days and growing season length were also calculated. Growing degree days were estimated as the sum of air temperature for all days in a year where temperature was above a threshold of 5°C. The growing season length was based on the number of days with air temperature greater than 5°C.
3 Results

3.1 Change in climate, runoff and growing season

Our results showed that the temperature time series was not homogenous as years 1985–1987 were colder (due to cold winter periods) while 1981–1984 and 1989 onward were warmer (Fig. 2). The long term mean of air temperature was estimated to be about 1.7 °C (1981 to 2008) and mean stream water temperature was about 3.5 °C (1987–2011). The precipitation was about 610 mm yr⁻¹. The temporal pattern in annual runoff was similar to precipitation, with the largest variability between 1997–2002 (Fig. 3). Specific discharge was approximately 320 mm yr⁻¹.

There was a significant monotonic increasing trend in air temperature (MKT = 3.03, $p < 0.05$) with a Sen’s slope of 0.058 °C yr⁻¹ (Fig. 2) over the 27 yr period. In addition to the overall trend, monthly air temperature showed significant increases in January, April, August, September and December. Change in growing season was also evaluated for the entire period using air temperature (Fig. 2). There was a significant monotonic increase in growing degree days above 5 degree (MKT = 2.90, $p < 0.05$) as growing season length increased from 140 days (1981–1999) to 156 days (2000–2008) (Fig. 2). Water temperature followed a similar overall monotonic increase at $p < 0.05$ level (Table 1). The increase in monthly water temperature was statistically significant in most months except February, October, November and December. Unlike air temperature, no statistically significant overall trend could be detected in long-term precipitation series but there was a borderline decline in October monthly precipitation at $p < 0.1$ (Table 1). No detectable trend was observed for long term runoff series, but trends in monthly flows do exist. There was an increase in March ($p < 0.05$) and decline in May and October ($p < 0.1$) monthly flows. These trends were consistent with warmer temperatures leading to earlier spring melt and possibly greater summer evapotranspiration.
3.2 Atmospheric deposition chemistry

In terms of precipitation chemistry, atmospheric deposition in Svartberget is low with long-term depositional fluxes of $0.07 \text{ g m}^{-2} \text{ yr}^{-1}$ for calcium, $0.02 \text{ g m}^{-2} \text{ yr}^{-1}$ for magnesium, $0.09 \text{ g m}^{-2} \text{ yr}^{-1}$ for sodium, $0.19 \text{ g m}^{-2} \text{ yr}^{-1}$ for sulfate-S and $0.32 \text{ g m}^{-2} \text{ yr}^{-1}$ for DIN (Fig. 4). The low levels of acid deposition suggest that the catchment is only slightly acidified and thus subtle effects of recovery from acidification may be influencing stream water chemistry. Our results showed a significant long-term decline in the annual deposition of magnesium ($\text{MKT} = -2.12, p < 0.05$), calcium ($\text{MKT} = -1.89, 0 < p < 0.1$), sodium ($\text{MKT} = -1.74, p < 0.1$), sulfate ($\text{MKT} = -1.74, p < 0.1$) and DIN ($\text{MKT} = -2.27, p < 0.05$) (Fig. 4).

3.3 Long term pattern and trend in DOC concentrations

3.3.1 Stream DOC concentrations

Both the pattern and magnitude of stream DOC variability were significantly different in the three streams (Fig. 5). The highest [DOC] was observed in the wetland dominated C4 with flow-weighted [DOC] of $27 \pm 6.7 \text{ mg L}^{-1}$ (un-weighted = $31 \pm 0.4 \text{ mg L}^{-1}$). The lowest [DOC] was observed in the upland forest C2 with flow-weighted concentration of $19 \pm 3.7 \text{ mg L}^{-1}$ (un-weighted = $15 \pm 0.3 \text{ mg L}^{-1}$). The C7 stream draining both forest and mire landscape elements has an intermediate [DOC] of about $22 \pm 3.4 \text{ mg L}^{-1}$ (un-weighted = $21 \pm 0.2 \text{ mg L}^{-1}$).

We observed a change in both concentration and seasonal variability of DOC (Fig. 5). There appeared to be a shift in the magnitude of variability in spring [DOC] around 2002 and an increasing [DOC] during summer baseflow in C2 (Fig. 5). Similar shifts in magnitude of spring [DOC] were observed in C7 with a corresponding increasing trend in the low DOC values associated with the summer baseflow condition but the change occurred around 2004 instead. The shift in variability of [DOC] was synchronous with the long-term shift in the magnitude of daily runoff variability where runoff changed
by about 17% between the earlier (1992–2001; mean = 341 mm yr\(^{-1}\)) and later part of the record (2002–2008; mean = 284 mm yr\(^{-1}\)). This corresponds to the period of 2002 onward when we observed the longest growing seasons (Fig. 2). Differences exist between the seasonal dynamics of DOC in the three catchments. While a dilution effect dominates in C4 in spring, both C2 and C7 showed [DOC] increased with runoff.

There was no detectable overall trend in [DOC] in C4 and C7. However, significant monotonic trends do exist in C2 (Table 1). Stream [DOC] at all sites showed significant positive trends in autumn but only C2 showed an overall increase in concentration over the long term. In addition to the autumn increase, there were positive trends in [DOC] in April and November in C2 (Table 1). The lowest spring [DOC] in C4 was observed in May, corresponding to the month with the highest spring runoff. There was also a slight increase in DOC leaching from the mire in March prior to the onset of the spring melt.

The hydrological responses of the three catchments were different. Non-linear relationships existed between the stream [DOC] and specific discharge (Fig. 6). While logarithmic relationships existed between the stream [DOC] and runoff in C2 and C7, the relationship is complex in the mire dominated C4 (Fig. 6). The flow/[DOC] relationship at C4 showed that runoff alone cannot account for variability in both the low spring and high summer [DOC]. DOC production and concentration in C2 and C4 appeared to respond almost linearly to increasing runoff until a specific discharge of about 0.5 mm day\(^{-1}\) (in C2) or 0.2 mm day\(^{-1}\) (in C7) is reached. At this threshold, additional runoff does not seem to cause any further increase in [DOC]. Therefore runoff explained up to 44% of the variability in [DOC] in the forest dominated C2 catchment but only 22% in C7 draining the mixed landscape (Fig. 6).

### 3.3.2 Riparian soil DOC concentrations

Riparian soil water from the S4 suction lysimeter array was used to evaluate long term patterns of riparian soil [DOC] and possible controls on stream [DOC] (Fig. 7). These lysimeters were placed at various soil depths (10–65 cm) at an interval of 10 cm
(Table 2). Too few data were available from the S4_{10} lysimeter placed at 10 cm to run the MKT test, so it was therefore excluded from the analysis (Table 2). Concentrations of DOC in the S4_{25} lysimeter placed at 25 cm soil depth showed an overall borderline decline ($p = 0.041$) and in April ($p < 0.01$) and May monthly values ($p = 0.050$). Lysimeter S4_{35} at a depth 35 cm showed no detectable overall trend but a significant increase was observed in April monthly concentrations ($p = 0.024$). Lysimeter S4_{45} placed at 45 cm depth showed a borderline increase in April and October monthly concentrations ($p < 0.05$) but no detectable trend was observed (both on monthly and overall) in the S4_{55} lysimeter placed at a depth of 55 cm in the riparian soil. In contrast to S4_{55}, there was a statistically significant increase in [DOC] in the deepest S4_{65} lysimeter at 65 cm soil depth. The monotonic increase were significant both on overall ($p = 0.02$) as well as in April and May ($p < 0.05$).

### 3.4 In-stream chemical parameters

In addition to stream [DOC], trends in other chemical parameters were also evaluated using available long term data from the C7 stream (Fig. 8). Annual flow-weighted mean concentration of sulfate-S and chloride in the stream were $4.56 \pm 1.34 \text{ mgL}^{-1}$ and $0.73 \pm 0.12 \text{ mgL}^{-1}$ respectively (Fig. 8). Stream water chemistry suggests that the catchment was slightly acidified. There was a significant increase in pH in spring months while sulfate and conductivity decline significantly ($p < 0.05$) over the entire study period (Table 1). The decline in alkalinity that we observed was peculiar to late summer-early winter months (August–December) and early spring (April–May) regimes (Table 1). There was also a significant monotonic increase in absorbance in most months and on annual scale ($p \leq 0.05$) (Fig. 9).

### 3.5 Base cations and trace metal concentrations

The long term flow-weighted mean concentration of calcium was $2.0 \pm 0.4 \text{ mgL}^{-1}$ while magnesium was $0.64 \pm 0.12 \text{ mgL}^{-1}$ (Fig. 9). When the un-weighted concentrations of
base cations were subjected to MKT test, our results showed that calcium and magnesium displayed monotonic declining trends in most months and overall (Table 1). The decline in calcium was observed in most months except June and October ($p < 0.05$). The decline in monthly magnesium concentrations mostly occurred in winter and early spring (December–April) after which no trend was detected until August (Table 1). No annual and monthly trends were observed in sodium concentrations, except for monthly concentrations in June ($p < 0.05$). No overall trend was observed in potassium but increasing trends exist in March ($p < 0.05$) in contrast to declining trends in April and May.

Trace metals also showed significant long term trends with both monotonic decline (copper and zinc) and increases (iron) observed at a $p = 0.05$ probability level (Table 1). Both zinc and copper decline significantly in most months. However we observed a unique pattern in monthly iron concentrations, where increases were observed in August to December (Table 1). This is mostly consistent with the period where we observed significant increases in stream [DOC]. No major change in long term silica concentrations were observed except the borderline decline (in February and April) and increase (in December) at $p < 0.1$ level.

The overall pattern of relationships from the PCA showed that stream [DOC] was negatively correlated with many other water quality parameters, including base cations and positively correlated with trace metals (Fig. 10). Weak negative relationship existed between base cations and trace metals as they spread on the other side of the axis but strong correlation existed between DOC and absorbance. Zinc, copper and iron are orthogonal to the first principal axis while iron and temperature were close to the centre of the axes.
4 Discussion

4.1 Climate control on DOC

The drivers of long term trends in headwater stream chemistry can be both process and scale dependent (Clark et al., 2010). A recent long term, cross-regional scale study by Laudon et al. (2012) has concluded that long term average stream [DOC] is related to the prevailing mean annual temperature on a regional scale. When catchments across a 1000 km latitudinal gradient between Northern and Southern Sweden were compared, temperature and flow both appeared as major controls, but differed in their importance for specific catchments (Winterdahl et al., 2011b, Futter et al., 2011). However, no consensus on how climatic factors are affecting stream chemical parameters in individual catchments has been reached for the northern boreal ecozone. The almost three decades of temperature measurements for the Svartberget showed that the region is moving towards warmer conditions (Fig. 2).

Large natural variability exists in precipitation and runoff patterns over the period of record (Fig. 3). There was a shift in the magnitude of variability in the spring runoff hydrograph by about 17 % between 1992–2002 and 2002–2008. The shift in the magnitude of variability in runoff can be attributed to a long term monotonic increase in temperature and a longer growing season (Fig. 2). The warmer temperatures and longer growing season would suggest that a smaller fraction of precipitation is falling as snow in recent years, and the magnitude of the spring runoff peak may be reduced. This shift in runoff regime can further explain the reduction in the amplitude of spring [DOC] variability in the late period in contrast to early period of record where there was high variability (Fig. 5). The drop in the flashy spring [DOC] in the later period of record in (C2 and C7) suggest that stream DOC is driven more by intermittent rainfall flushing the top or subsurface layers than prolonged soil inundation from rising groundwater level. This might have large implications for the catchment carbon dynamics as changing flowpaths can influence the sources and mobilization of carbon and other carbon dependent processes (Laudon et al., 2011). There were pronounced differences in
year-to-year runoff regime in the catchment as some years are wet while some are very dry (Table 2).

Stream [DOC] responds differently to runoff as spring dilution was observed in wetland dominated C4 while increases in [DOC] were observed in the forest dominated C2 as reported earlier by Köhler et al. (2008). The C4 dilution can be attributed to less water infiltrating and subsequent reduced contact time with peat (Laudon et al., 2011; Yurova et al., 2008). Similar autumn dilution pattern in C7 (Köhler et al., 2008) can be attributed to the influence of upstream mire during the autumn season. The autumn dilution behavior has been attributed to late summer or early autumn rainfall (Köhler et al., 2008). This is also expected in C7 as the effect of forest and wetland are combined in the catchment despite similar seasonal trends. This explains why runoff can only explain about 22 % of the total variability in [DOC] in the C7 stream (vs. 44 % in C2) despite the large hydrologic changes. It appears that the presence of wetlands stabilizes or offsets the hydrologic changes associated with dry-wet regimes in C4. The increases in DOC during snowmelt in C2, especially in April where we observed a monotonic increase (Table 2), can be as a result of the influences of the riparian processes in upland forest catchments (Ågren et al., 2010).

4.2 Riparian controls on stream DOC concentration

The riparian soil-stream interface is important for DOC production in boreal forest catchment due to strong hydrological connectivity between soil, groundwater and surface waters (Laudon et al., 2011). The timing and change in groundwater levels can be an important driver of fluxes through the riparian zone, which have a strong influence on in-stream [DOC] (Bishop et al., 1995; Lyon et al., 2011; Grabs et al., 2012). Typically, soil solution [DOC] exceeds stream [DOC] and decreases with depth down the soil profile (Köhler et al., 2009). This apparent disconnect might be accounted for by the vertical differentiation in the later flux of water through the riparian zone (Bishop et al., 1993). The Riparian Profile Integration Model (RIM, Seibert et al., 2009), uses this interaction of flow and concentration in the riparian profile to predict stream [DOC]
(Winterdahl et al., 2011a, b). The increase over time in soil solution [DOC] in the deeper riparian soil layer may be the result of changing long term patterns in weather and runoff.

Though the available data from S4_{10} lysimeter could not give us enough statistical power to test for a trend in [DOC] concentrations in the topmost soil layers, useful inferences can be drawn from the S4_{25} lysimeter. Declining trends in [DOC] during the snowmelt in April and May are an indication that the organic or litter layer in the riparian zone is contributing less flashy DOC to the stream in recent years than in the earlier part of the record. The drop in the flashy spring DOC from the upper soil layers suggests that stream DOC is driven more by intermittent rainfall flushing the top or subsurface layers than prolonged soil inundation from rising groundwater levels. This can further explain our observed reduction in the amplitude of spring [DOC] variability in the late period in contrast to early period of record where there was higher variability (Fig. 5). The increase in soil [DOC] in October shown in S4_{45} lysimeter might have driven C2 stream [DOC] toward significant increases that we observed in November. The increases in stream water [DOC] during snowmelt, especially in April where we observed a monotonic increase, can be under the control of riparian processes in the forest dominated catchment (˚Agren et al., 2010).

We observed significant increasing trends in soil solution [DOC] in lysimeters at depths of 55–65 cm. The upward swing in the riparian DOC at this depth and corresponding increase in stream baseflow DOC (Fig. 7) is an indication of more contribution of riparian deep-soil layer to stream [DOC]. This suggests an increasing influence of temperature on riparian soil processes (Winterdahl et al., 2011a). The temperature effect might explain why we also observed significant increasing trend in soil solution and stream water [DOC] in April (Table 1 and 2).

However, gap exists in quantifying the absolute contribution of each riparian layer so as to ascertain how riparian systems influence adjacent stream [DOC] both laterally and vertically down the soil profile. Since our study period is characterized by a series of contrasting wet- dry year regimes, the onset of wetter years that followed some of
the driest year on record might have set the stage for the increasing trend and variability in stream [DOC] that we observed. Prolonged wet periods in the riparian soil lead to statistically significant increases in soil water [DOC] (Köhler et al., 2009). Our result therefore showed that dry-wet cycle has pronounced effects on [DOC] in intermittent C2 stream, which might be more susceptible to drought conditions. However, rewetting of soils and flushing of accumulated DOC in the subsequent wetter year might lead to a significant increase in the overall [DOC] trend at C2. Though increases in air temperate and associated increases in evapotranspiration might plausibly indicate drier soils in the future, this needs to be investigated further to complement the earlier modelling concept of riparian flow-concentration integration (Seibert et al., 2009; Winterdahl et al., 2011a, b).

4.3 Trends and variations in deposition, climate and stream DOC concentration

Our study site is located in a region that has only been minimally impacted by anthropogenic acid deposition as only episodic acidification during spring snowmelt and autumn episodes has previously been reported (Bishop et al., 1990, 2000; Laudon et al., 1999; Laudon and Hemond, 2002). Svartberget has not been regarded as an acidified catchment since stream pH must have dropped by at least 0.4 units for a site to be classified as acidified (Fölster et al., 2007; SEPA, 2007). Furthermore most of the recovery from anthropogenic acidification in the area occurred already in the early 1990’s when the large decline in acid deposition occurred (Laudon and Bishop 2002). Therefore, the acidification recovery hypothesis of Monteith et al. (2007) might contribute in part but is not likely to be a dominant controlling factor of the long-term stream [DOC] pattern that is observed in the Svartberget streams.

While no detectable overall monotonic trend in precipitation and runoff were observed (Fig. 2), significant trends existed for individual months (Table 2). Runoff showed a significant increase in March and declined in May. This suggests earlier snow melt in recent years. Temperature and moisture are important drivers of autumn DOC (Preston et al., 2011). The significant monotonic increase in [DOC] that we observed in autumn
can therefore be attributed to biological controls as the microbial enzymatic activities that convert humified organic matter to leachable organic carbon is more favorable under this condition. This suggests that DOC production is becoming more dependent on runoff and antecedent soil temperature, as temperature showed significant increase in preceding August and September (Table 2). The significant increase in autumn [DOC] at the upland forest site can also be explained as forests are expected to have permeable soils and high rates of evapotranspiration. However, it is not fully clear what is simultaneously driving the autumn increase in [DOC] in mire dominated C4 in our study site despite its contrasting autumn DOC dilution mechanism. Our observed increase in autumn is in agreement with some other studies carried out elsewhere using similar small headwater catchments (e.g. de Wit et al., 2007; Preston et al., 2011). However, the dominant drivers of the biogeochemical processes behind the autumnal increase might be different. De Wit et al. (2007) attributed the response of autumn DOC in a Norwegian catchment to the effect of reduction in acid deposition. Preston et al. (2011) attributed the autumnal increase in DOC over their 29 yr record in south-Central Ontario catchment to hydrologic and temperature change. They observed that stream [DOC] was negatively correlated with autumn runoff and precipitation. The significant trend in autumnal DOC might therefore result from little loss to degradation (either microbially or photolytically) in the streams (Köhler et al., 2002).

4.4 Linkage between deposition, stream DOC and other chemical parameters

We cannot totally rule out the subtle effect of catchment recovery from acidification as depicted in its stream water chemistry where we observed increase in pH in spring and a decline in sulfate. This is consistent with previous work by Laudon and Bishop (2002) and Laudon and Hemond (2002) on the episodic acidification in the catchment. The pulse of stream acidity during snowmelt regimes is as a result of depositions on snowpack during winter and washed down to streams during spring melts. Winter sulfate lowers acid neutralizing capacity and will cause pH to decrease. Therefore, catchment recovery from acidification can increase stream [DOC] (Monteith et al., 2007). However,
deposition in our site is low and is even further declining (Fig. 3). Declines in stream base cation concentration in response to reductions in acid deposition have been reported (e.g. Watmough and Dillon, 2001; Watmough et al., 2005). General declining trajectories of stream base cation concentration in our site (Fig. 4) as well suggest the acidification recovery effect. Alkalinity is a conservative parameter that is not influenced by temperature. Therefore, the decline in sulfate and base cation during other times of the year which is not accompanied by a change in pH and alkalinity is also consistent with a change (recovery from non-acidified state) driven by declining sulfate deposition. This would be consistent with the classic inorganic model of acidifications (e.g. Galloway et al., 1983) where the decline in anionic deposition leads to a reduction in co-transport of base cations.

Calcium has been identified as one of the base cations that is most at risk of depletion in boreal catchments (Thiffault et al., 2011). Calcium is declining in Canadian boreal streams (Watmough and Dillon, 2003; Watmough et al., 2005). Therefore, significant decline in calcium (both overall and monthly) in our catchment can be attributed to depleting soil reserves in the catchment as a result of continuous leaching and/or intermittent drought like conditions induced by several dry-wet years in our study. Declining soil water calcium can reduce DOC adsorption in mineral soils through a cation bridging mechanism and as a result contribute to long term increasing DOC trends in streams draining upland catchments (Kerr and Eimers, 2012). This is because sorption equilibrium is an important mechanism controlling DOC at the soil-water interface. Stores of calcium can increase at the same time as runoff concentrations decrease if there are less counter ions to desorb and transport calcium ions to the stream. Significant declines in potassium in the spring can be as a result of low capacity of the catchment soil to retain potassium ions leached from the plant residues (Thiffault et al., 2011). Our results showed that sodium had no significant monotonic trend on either monthly (except June) or overall. It has been shown that sodium has little or no effect on the DOC adsorption (Kerr and Eimers, 2012) as divalent cations (e.g. calcium) are
more important in cation bridge formation than sodium which is monovalent (Munch et al., 2002).

We observed a declining trend in stream conductivity and a significant increase in pH especially in winter to spring months (Table 2). Reducing ionic strength that resulted from such monotonic decline in the conductivity can be explained by the decrease in both sulfate and calcium during the same period. Changes in ionic strength at the soil-water interface can influence the configuration of DOC molecules (Vermöhlen et al., 2000) and might suggest that winter and spring are becoming more favorable for production of soluble DOC. This might explain why there was no detectable [DOC] trend in those seasons unlike autumn, despite the increasing trend in absorbance (Table 2).

Atmospheric deposition of trace metals decreases significantly in Sweden toward the northern part of the country (Huser et al., 2011) where our study catchment is located. We expected that most metals should increase with DOC at least in autumn (except iron) but we observed the opposite. Though the declining trend that we observed in zinc is understandable as the element has weak binding capacity with organic matter (Hernandez et al., 2006; Huser et al., 2012) and its deposition is generally declining in Northern Sweden (Huser et al., 2011). However, stream copper concentration showed similar declining trend on both overall and seasonal basis despite their stronger affinity to DOC. The significant declining trend in copper that we observed can be attributed more to regional controls such as non-alkaline nature of soils in the northern boreal catchments (Huser et al., 2011) as pH increase was not significant in most months. However, the interpretation of copper behavior appeared to be more complicated than the complexation hypothesis stated above, as seasonal declining trend was observed in January, March, and June when there was corresponding increase in pH. The recent study by Huser et al. (2011) reported a similar declining pattern in copper trend across the gradient of Sweden. Landre et al. (2009) also noted that little or no relationships existed between copper chemistry and DOC, suggesting that there are more subtle processes in copper biogeochemistry in headwater catchments that are yet to be understood. Simultaneous monotonic increase in DOC and iron in autumn is a strong
indication of co-precipitation of iron with DOC in the form of organo-metal complexes and/or adsorption that provide stability for colloidal iron species in the catchment. This is because polyvalent cations such as aluminum or iron might play a significant role in influencing the mobility of DOC in organo-mineral soils (Jansen et al., 2005; Kothawala et al., 2009).

Since base cations (except sodium) and trace metals (except iron) are generally on the declining trend despite the relatively undisturbed state of our catchment, future climate and forest management might shift the trend in a more complicated direction; an indication of catchment sensitivity to disturbance. The overall pattern of relationships shown from the PCA suggested that complex interactions existed in stream chemical parameters. If base cations are close together on PCA axes, this would have suggested a strong geochemical weathering signal. Clustering of zinc, copper and iron together suggest a stronger geochemical signals but their orthogonal projection to the first axis is an indication of other factors superimposed on the geochemical weathering. However, closeness of temperature and iron to the centre of the axes is an indication that some information is carried on other axes. This makes the interpretation of stream chemical parameters by PCA alone difficult unless complemented by other analyses such as end member mixing analysis. While, this presents a preliminary attempt in understanding the long-term pattern of deposition chemistry and water quality from available long term series in the Krycklan study catchment, possible future work would include end member mixing analysis in the catchment coupled with the application of ensembles of process based models to further understand the present dynamics and/or project possible future conditions of the catchment. Our expectation is that these will complement some other studies on metal biogeochemistry in the catchment (e.g. Lidman et al., 2011; Klaminder et al., 2011b) so as to quantify and reduce the uncertainties that can be associated with future projections under plausible climate change and forest management scenarios in the Krycklan study catchment.
Acknowledgement. We thank Ida Taberman for managing the Krycklan water quality database and other that has helped out in the field and in the laboratory. This study could not have been carried out without the Svarterget/Krycklan data collection that over the years have been funded by Swedish science council, Formas, SKB, Kempe foundation, Mistra, VR and SLU. This project is part of two larger Forest water programs, ForWater and Future Forests studying the effect of climate and forest managements on forest water quality.

References


Table 1. The significance of monthly and overall Mann-Kendall trend statistics for climate, runoff, in-stream chemical parameters, base cations as well as trace metals in Svartberget catchment relative to stream [DOC]. Except stream [DOC] that were available in the three headwater streams (C2, C4 and C7), other chemical parameters (and runoff) were available from C7. The values in italics represent statistically significant declines and the values in bold represent statistically significant monotonic increasing trend.

<table>
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<tr>
<th>Group</th>
<th>Parameter</th>
<th>Data Period</th>
<th>Mean Jan</th>
<th>Mean Feb</th>
<th>Mean Mar</th>
<th>Mean Apr</th>
<th>Mean May</th>
<th>Mean Jun</th>
<th>Mean Jul</th>
<th>Mean Aug</th>
<th>Mean Sep</th>
<th>Mean Oct</th>
<th>Mean Nov</th>
<th>Mean Dec</th>
<th>Mean Overall</th>
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Table 2. The significance of monthly and long term MKT statistics from riparian soil transect lysimeter (S4) at various soil depths near C2 stream (approximately 4 m). Symbol † denotes that lysimeter at 10 cm depth was excluded from the MKT test due to low statistical power. The values in italics represented significant decline and bold highlight represent significant monotonic increasing trend.

<table>
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<th>Group</th>
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<td></td>
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<td>C7 stream [DOC]</td>
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<td>S4 (65 cm depth)</td>
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Fig. 1. Map of Svartberget catchment.
Fig. 2. (a) Pattern and non-homogeneity of air temperature series with the long term trend and Sen's Slope estimate as summarized in Table 2 and (b) plot of change in growing season length (days) at $T > 5$°C and corresponding change in growing degree days above 5 degree. Long term average growing season length changed from 140 days (1981–1999) to 156 days (2000–2008). There are significant monotonic increases in both growing season length ($MK = 2.26, p < 0.05$) and change in degree days above 5 degree ($MK = 2.90, p < 0.05$).
**Fig. 3.** Temporal variations and trend in long term climate data in Svartberget catchment showing a non-significant monotonic trend in the long term precipitation and runoff series in C7.
Fig. 4. Long term pattern and the significance of trend in the annual depositional fluxes of Calcium (a), Magnesium (b), Sodium (c), Sulfate (d) as well as dissolved inorganic nitrogen (e).
Fig. 5. Long term series of stream [DOC] in (a) forest dominated C2 stream (b) mire drained C4 stream and (c) C7 draining both forest and mire landscape elements.
Fig. 6. Long term pattern of runoff control on stream DOC concentration in C2, C4 and C7 catchments.
Fig. 7. Riparian soil S4 profile and C7 stream [DOC], riparian soil solution [DOC] is shown at depths of 41–42 cm (a), 35–45 cm (b) and 55–65 cm (c).
Fig. 8. Long term pattern of flow weighted concentration of stream DOC (a), Sulfate (b), Base cations (c) and (d), Chloride (e) and stream alkalinity (f).
Fig. 9. Long term series of absorbance at 420 nm in C7.
Fig. 10. Principal component analysis (on correlations) showing the overall pattern of relationships in the C7 long term chemical parameters used in this study.