

Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling

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ABSTRACT

We bring together three decades of research from a boreal catchment to facilitate an improved mechanistic understanding of surface water dissolved organic carbon (DOC) regulation across multiple scales. The Krycklan Catchment Study encompasses 15 monitored nested research catchments, ranging from 3 to 6900 ha in size, as well as a set of monitored transects of forested and wetland soils. We show that in small homogenous catchments, hydrological functioning provides a first order control on the temporal variability of stream water DOC. In larger, more heterogeneous catchments, stream water DOC dynamics are regulated by the combined effect of hydrological mechanisms and the proportion of major landscape elements, such as wetland and forested areas. As a consequence, streams with heterogeneous catchments undergo a temporal switch in the DOC source. In a typical boreal catchment covered by 10–20% wetlands, DOC originates predominantly from wetland sources during low flow conditions.

During high flow, the major source of DOC is from forested areas of the catchment. We demonstrate that by connecting knowledge about DOC sources in the landscape with detailed hydrological process understanding, an improved representation of stream water DOC regulation can be provided. The purpose of this study is to serve as a framework for appreciating the role of regulating mechanisms, connectivity and scaling for understanding the pattern and dynamics of surface water DOC across complex landscapes. The results from this study suggest that the sensitivity of stream water DOC in the boreal landscape ultimately depends on changes within individual landscape elements, the proportion and connectivity of these affected landscape elements, and how these changes are propagated downstream.

Key words: dissolved organic carbon; scaling; connectivity; boreal forest; Krycklan catchment; hydrology.

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Author Contributions: H.L. wrote the manuscript with active contributions from all co-authors. Data from this study has been collected over close to 30 years and would not have been possible without the important work by K.B., S.K., I.B., M.B., and H.L. The conceptual and more mechanistic modeling approach has been developed by H.L. together with all co-authors.

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INTRODUCTION

Increasing dissolved organic carbon (DOC) concentrations and fluxes in surface waters observed in large areas of the northern hemisphere have recently resulted in large research efforts to better

understand the causes and effects of stream water DOC dynamics. An important reason for this increasing interest arises from the fact that DOC plays an integral role in the biogeochemistry and ecology of surface waters across most forested regions of the world. DOC affects the food-web structure in lakes (Jansson and others 2007), exerts control on the acid-base chemistry of soil and surface waters (Hruska and others 2003) and influences metal export and speciation in streams and rivers (Shafer and others 1997). Surface water DOC also has an important role in catchment carbon budgets (Cole and others 2007; Nilsson and others 2008).

Several mechanisms have been postulated for explaining the increasing DOC concentration and export, including declining S deposition (De Wit and others 2007; Monteith and others 2007; Haaland and others 2010), land management use (Findlay and others 2001; Wilson and Xenopoulos 2008; Laudon and others 2009), and variability in climate (Erlandsson and others 2008; Sarkkola and others 2009). In a majority of recent reports in the scientific literature the observations and trend analysis have, for obvious reasons, been made on catchments used for environmental monitoring motivated by the fact that this is where most long-term data sets are available. A limitation of many of these monitoring catchments is that they were not designed for process-based research and instead drain large complex heterogeneous catchments systems. This design often limits the analyses to statistical approaches which provide little guidance into the mechanistic regulation of surface water DOC.

Most research on understanding the processes that regulate surface water DOC includes studying stream and lake water concentrations and fluxes with some attempts to regress patterns and dynamics to various landscape characteristics (reviewed in Mulholland 2003). Some previous work on regulation mechanisms has been based on single, small, well-characterized research catchments (Hinton and others 1998; Billett and others 2006; Petrone and others 2006; Eimers and others 2008a) or larger meso- and macro-scale basins (Ågren and others 2007b; Clair and others 2008), whereas others attempted to include a range of different scales and landscape characteristics in the analyses (Gergel and others 1999; Canham and others 2004; Frost and others 2006; Ågren and others 2007a; Clark and others 2010). In most of these previous attempts the role of catchment sources of organic carbon has been emphasized. For example, multiple studies have demonstrated the role of wetlands for controlling surface water DOC (Dillon and

Molot 1997; Creed and others 2003; Laudon and others 2004a; Creed and others 2008), whereas others have discussed the importance of organic-rich riparian soils (Hinton and others 1998; Findlay and others 2001; McGlynn and McDonnell 2003; Bishop and others 2004). However, a factor often neglected in most previous attempts to understand the regulation of DOC is the transport mechanism and hydrological connectivity between the organic matter sources and the surface water draining the catchment. The water flow paths in the catchment determine the areas that may be activated during runoff events and are therefore of fundamental importance for deciphering patterns and dynamics of DOC in the landscape. Hence, the understanding of the regulating mechanisms of surface water DOC will remain limited without a proper mechanistic understanding of soil-surface water hydrology, hydrological pathways, and catchment hydrology.

Many early concepts of stream water DOC regulation were developed in the temperate forest biome where streams, rivers, and lakes are characterized by low to moderate DOC concentrations. In the last decade, an increased focus has been paid to the boreal forest biome where surface water DOC concentrations often are substantially higher. The total soil carbon stock is also approximately six times the size when compared to the temperate biome (Pregitzer and Euskirchen 2004) emphasizing the importance of the boreal forest region from a global carbon cycling perspective. Also, most climate change scenarios predict that the most severe climate effects will be in higher latitudes suggesting that the boreal region will be affected more strongly than other forested regions of the world (IPCC 2007).

To move beyond the present perception of DOC regulation, we combine a process-based understanding of hydrological pathways and catchment hydrology with that of soil-stream water DOC regulation on a landscape scale using a uniquely well-studied boreal research catchment. The objective of this study is to bring together three decades of research from the Svartberget/Krycklan research catchment to provide an improved mechanistic understanding of the regulating processes of surface water DOC across spatial and temporal scales. By doing so the goal is not only to provide a basis for how this specific catchment is functioning but also to present a conceptual framework that can be used in other regions to better appreciate the role of regulating mechanisms, connectivity, and scaling for understanding the pattern and dynamics of surface water DOC across heterogeneous landscapes.

THE KRYCKLAN CATCHMENT STUDY

The field data originate from the interdisciplinary Krycklan Catchment Study (KCS) at the Svartberget long-term ecological research site (LTER) (64°23' N, 19°78' E), approximately 50 km northwest of Umeå, Sweden (Figure 1). The upper part of the study area, the Svartberget catchment, was established in 1980 and has since included three sub-catchments [Västrabäcken, catchment 2 (C2); Kallkälsmýren, catchment 4 (C4); and Kallkälsbäcken, catchment 7 (C7)]. In 2002, research at the 50 ha Svartberget catchment was expanded to include 15 partly nested sub-catchments in the 6900 ha Krycklan catchment (including C2, C4, and C7; see Figure 1, Table 1).

The climate, monitored since 1980 as part of the Svartberget LTER, in the center of the Krycklan catchment (Figure 1), is characterized by long winters and short summers. The mean annual precipitation and temperature (1980–2008) are 612 mm, and +1.7°C, respectively, with an average runoff of 312 mm. Approximately, 50% of the annual precipitation falls as snow and the average January temperature is –10°C. Snow covers the ground for 168 days on average, from the end of October to the beginning of May (1980–2007). Snow depth varies between 43 and 113 cm (1980–2007) and soil frost between 2.5 and 79 cm (1993–2007) depth at reference plots in the catchment.

Snowmelt generally started between mid- and late-April, following a period of 5–6 months of

permanent snow cover. Winter baseflow preceding the spring flood was on average 0.15 mm day⁻¹ and generally constituted the lowest observed annual flow, except some exceptional drought periods during summer. Spring flood runoff peak, which normally is the largest annually occurring runoff event, varied between 8 and 12 mm day⁻¹ and generally happened between the end of April and mid-May. The 4–6-week long snowmelt period contributed between 40 and 60% of the annual runoff.

The upper parts of the Krycklan catchment are mainly forested with Norway spruce (*Picea abies*) in low-lying areas and Scots pine (*Pinus sylvestris*) in upslope areas with large patches of mires and smaller lakes interspersed in the landscape. In the lower part of the catchment, Norway spruce and Scots pine are still the dominant tree species, but deciduous trees (*Alnus glutinosa* and *Betula pendula*) and shrubs become more common along the stream channels. Wetlands cover on average 8% of the Krycklan catchment, but occupy over 40% of some small first-order catchments in the upper reaches. The bedrock consists of svecofennian rocks with 94% metasediments/metagraywacke, 4% acid and intermediate metavolcanic rocks, and 3% basic metavolcanic rocks. Approximately 50% of the Krycklan catchment area is below the highest postglacial coastline (HC). The glacial till in the upper part of the catchment therefore gives way to sorted sediments consisting mainly of sand and silt

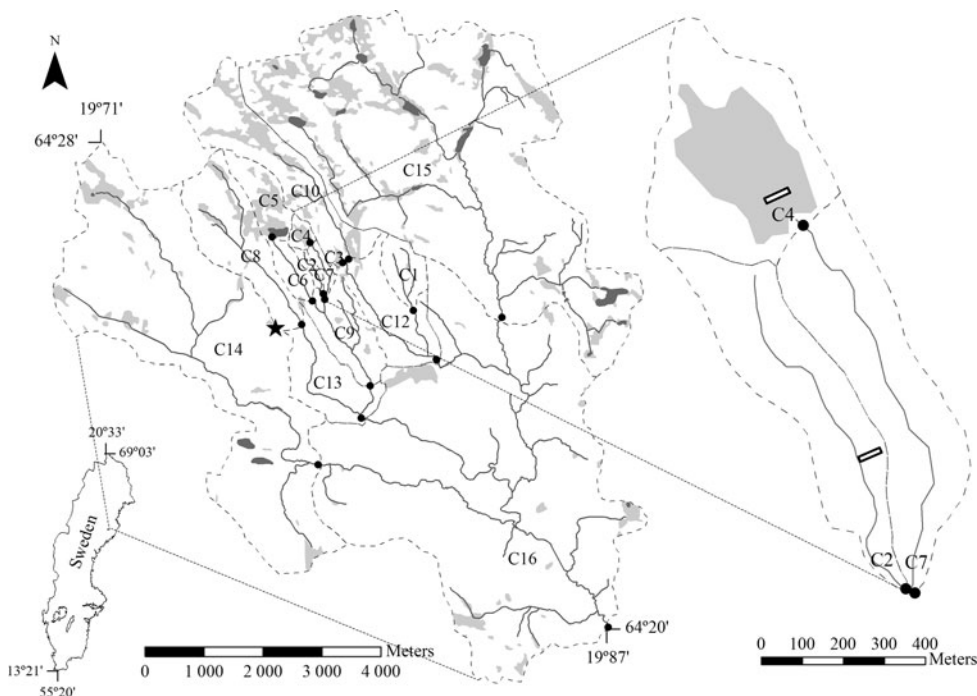


Figure 1. The Krycklan catchment with an insert of Sweden (left) and the Svartberget catchment (right) with the most intensive soil and stream monitoring locations. The full lines denote streams, hatched lines are catchment boundaries, gray shaded areas are mires, the star is the long-term climate station, and the elongated open squares are locations of soil monitoring.

Table 1. Basic Catchment Characteristics for the 15 Catchments

Site no	Forest (%)	Wetland (%)	Lake (%)	Arable land (%)	Area (km ²)
C1	98	2	0	0	0.48
C2	100	0	0	0	0.12
C3	24	76	0	0	0.04
C4	58	42	0	0	0.18
C5	55	40	5	0	0.65
C6	72	25	3	0	1.10
C7	84	16	0	0	0.47
C8	88	12	0	0	2.30
C9	85	13	1	1	2.88
C10	75	25	0	0	3.36
C12	83	17	0	0	5.44
C13	89	9	1	1	7.00
C14	91	5	0	4	14.10
C15	83	14	2	1	20.13
C16	88	8	1	3	68.91

toward the catchment outlet. Small areas of agricultural fields are found in the lower part of the catchment but make up less than 1% of the total catchment area. More details of the 15 study catchments are presented in Table 1 as well as in Cory and others (2006), Buffam and others (2007), and Ågren and others (2007a).

Field Methods

Discharge has continuously been monitored all-year around at C7 since 1980, using a 90° V-notch weir located inside a heated housing. In the remaining 14 streams continuous measurements of discharge have been conducted during the snow-free period. At all sites discharge has been computed on an hourly basis from water level measurements (using pressure transducers connected to Campbell Scientific data loggers, USA or duplicate WT-HR capacitive water height data loggers, TruTrack Inc., New Zealand) behind thin plate, V-notch weirs in the smaller streams and at road culverts or well defined natural stream sections in the larger streams. Rating curves have been derived based on discharge measurements using salt dilution or time-volume methods ($n > 850$). Data from C7, scaled for differences in catchment area, have been used to compile continuous discharge records for both winter baseflow and the snowmelt period for all streams. Data from the remaining sites have been used to estimate uncertainty in transferring area specific discharge from C7 to the remaining sites (see Ågren and others 2007a for a summary of this analysis). The inter-site differences in specific discharge as estimated based on the 850 discrete discharge measurements at the 15 sites and

compared to the continuous discharge data from site 7 show that the absolute value of bias was less than 12%. Furthermore as demonstrated by Buffam and others (2007) the flow at the 15 sites were generally synchronous, with maximum discharge during snowmelt at all sites occurring during a single 72-h period.

The stream water sampling program prior to 2002 has been year-round sampling based on a weekly frequency at catchments C2, C4, and C7, with more intensive sampling during some snowmelt and rain events. Since 2002, the sampling program has been based on fortnightly samples at all 15 catchments prior to, and after the snowmelt period, and then every second to third day during the spring until the flow receded to levels close to baseflow. During stable winter conditions the sampling is conducted on a monthly basis.

Detailed soil water measurements have been conducted since 1996 in two of the catchments: in the forest-dominated catchment (C2) and in the wetland-dominated catchment (C4). In C2, soil water samples were collected from three soil profiles located along a transect 4, 12, and 22 m from the stream approximately monthly during the snow-free period (Cory and others 2007). The soil transect is aligned to follow the assumed lateral flow paths of the groundwater toward the stream based on the groundwater slope and local hillslope topography (Seibert and others 2003). The riparian soil profile closest to the stream, S04, is dominated by organic material. The upslope location, S22, is located in a typical podzolic soil with a 10–15 cm organic layer overlying the mineral soil. The soil profile S12 is between the riparian and the upslope location in an organic-rich mineral soil. Each soil

profile consists of ceramic suction lysimeters (P80), as well as time domain reflectometry probes (TDR) and thermistors connected to a Campbell Scientific data logger (CR10) to measure soil water content and soil temperatures at six soil depths between 5 and 90 cm. Groundwater levels have also been measured continuously using pressure transducers connected to a CR10 in shallow groundwater wells perforated along their full length and extending approximately 1 m below the soil surface.

Soil measurements in the wetland-dominated catchment (C4) have been conducted using 12 nested wells extending to different depths in the wetland, ranging from 25 to 350 cm below the ground surface (Petronne and others 2007). The wells have a closed bottom and are perforated over the lowest 10 cm. Samples from each well (if the water at the sampling depth was unfrozen) have been collected several times per year since 1996 including winter baseflow and spring flood peak flows.

Laboratory Methods

Samples for DOC analyses were frozen immediately after collection. Analyses during pre-1995 were analyzed using a Dohrmann Carbon Analyzer although later samples were analyzed using a Shimadzu TOC-5000. In total over 6000 stream water samples and close to 2000 soil water samples have been analyzed from the Krycklan catchment. To avoid potential bias in the DOC results before and after the change in the carbon analyzer, only data from post-1996 was used in this study. A comparison of 72 samples ranging from 4 to 43 mg l⁻¹, including all seasons, catchment types, and hydrological flow conditions for both TOC and DOC (filtered through 0.45 µm filters), show that the particulate fraction of TOC on average is less than 0.6% ($r^2 = 0.99$, $P < 0.0001$; root mean square error (RMSE) 3%). These analyses suggest that measurements of TOC and DOC essentially are the same. In this study, we use the term DOC. The oxygen-18 data used in this study have been described elsewhere by Laudon and others (2007) and is used here only to help provide a mechanistic explanation to the DOC pattern.

LANDSCAPE ANALYSES

The watershed delineation and catchment characteristics were based on a combination of gridded digital elevation model (DEM) using light detection and ranging (LIDAR) measurements, soil maps, and field observations. The point density of the

LIDAR measurements was 3.3–10.2 m⁻². Based on the LIDAR data two DEMs were constructed with a 0.5 and 5 m resolution, respectively. Built-in hydrological algorithms in ArcGIS 9.3 were applied to remove sinks and delineate watersheds based on the 5 m DEM. Questionable sections were corrected using the 0.5 m DEM. Manual corrections of the water divide were also carried out in some areas using a professional cartographer and field surveys. Additional manual adjustments to the DEMs were done where bridges and road culverts obstructed the flow algorithm. A stream network was derived from the corrected 5 m DEM using the “channel network” module in the open source SAGA GIS program (Böhner and others 2008; Conrad 2007) with an initiation threshold area of 5 ha calculated based on a multiple-flow-direction algorithm (Seibert and McGlynn 2007). To exclude intermittent streams from the analysis, only those streams that were also shown on a digital land-cover map were kept (1:100 000) (Lantmateriet, Gävle, Sweden).

In this study, we defined baseflow and high flow as the 10 percentile lowest and highest discharge conditions, respectively. Baseflow is hence defined as discharge lower than 0.15 mm day⁻¹, whereas high flow defines conditions with discharge exceeding 5.5 mm day⁻¹. The terms forested and wetland dominated, as well as mixed catchment streams, was used in this work. We defined forest- and wetland-dominated catchment streams as those draining an area with less than 5% or more than 25% wetland cover. Consequently, mixed catchment streams are defined as those that drain catchments covered with between 5 and 25% wetlands. This can be compared to the average wetland, or open mire areas, in Sweden of 12% (Nilsson and others 2001).

CALCULATIONS

To test if the DOC concentration in downstream locations could be calculated as a proportional combination of the dominant landscape features we applied a two-component mixing model using the concentrations from the two most well-studied catchments C2 and C4, as representatives for forest and wetland covered catchment, respectively. The area covered by arable land and lakes, covering less than 3 and 1% of the catchments, respectively, were excluded from the analyses. The mixing model was applied to the downstream catchments C7, C13, and C16, in proportion to their forest/wetland percentage coverage.

A wetland to forest DOC export ratio was calculated for each sampling date largely following the

method described by Berggren and others (2009). In short, the ratio was calculated by first extrapolating the linear relationship between stream DOC and wetland coverage to 100% wetland (=0% forest) and 0% wetland (=100% forest) for each sampling point, and then dividing the two obtained end-point DOC values with each other. Assuming the same specific discharge from all catchments, the ratio of DOC between two catchment types is identical to the ratio of DOC export at a given moment. Flow rates in the lower range of base flow (0.01–0.1 mm day⁻¹ at C7) were excluded from the calculation because flow sometimes ceased from the smallest streams and, thus, the assumption of constant specific discharge could not be justified during extreme low flow. In total 138 occasions of concurrent sampling of all 15 streams where included in the analysis.

RESULTS AND DISCUSSION

Spatial variability in DOC concentrations across the 15 streams was high at baseflow (range 2–41 mg l⁻¹ across all catchments) with the highest concentrations in the wetland-dominated catchment streams and lowest in the larger downstream sites. Intermediate baseflow DOC conditions were found in all small- and medium-sized mixed and forested catchment streams. Average baseflow concentration (<0.15 mm day⁻¹) was positively correlated with percentage wetland in the catchment ($r^2 = 0.83$, $P < 0.001$, $n = 15$). DOC concentrations became more similar across the entire catchment during high flow (>5.5 mm day⁻¹), although the mean DOC concentration increased from 13 to 18 mg l⁻¹ (range 10–37 mg l⁻¹ across all catchments). During high flow no significant correlation between wetland percentage and DOC were found ($r^2 = 0.18$, $P = 0.09$, $n = 15$).

The dynamics of DOC concentrations during high flow depended on catchment characteristics and size (Figure 2). The small forested sites (C1 and C2) had an average DOC concentration during baseflow of around 10 mg l⁻¹ but increased during high flow to an average of 210% of their baseflow values. In contrast, the wetland-dominated sites (C3 and C4) had a high baseflow average DOC concentration (35–39 mg l⁻¹) which declined during the snowmelt to an average of 60% of their baseflow values. The small lake outlet (C5) remained at a high, but constant, concentration around 20 mg l⁻¹. The smaller mixed streams (<10 km²) had a pattern in-between the forested- and wetland-dominated catchments with somewhat higher baseflow DOC compared to the

forested sites but with a less pronounced increase during high flow (60% average increase). For the three largest (>10 km²) catchments (C14, C15, and C16) baseflow DOC decreased somewhat with size (Figure 2). The average increase during high flow for these largest streams was similar to the small mixed streams (70% average increase).

To interpret the stream water DOC pattern we incorporated the information of hydrological pathways of the catchment soils, based on the hydrometric and isotopic information presented previously by Rodhe (1987), Bishop (1991), and Laudon and others (2004b, 2007). The contrasting hydrological functioning of wetland and forest catchments is exemplified in C2 and C4 by the spring flood, which is the largest recurring event of the year and constitutes 40–60% of the annual runoff (Bishop and Pettersson 1996; Buffam and others 2008). In the forested catchment, C2, the isotopic ($\delta^{18}\text{O}$) composition in the soil transect showed a small temporal variability in the upper 50 cm of the soil which was largest further away from the stream (Figure 3A). In the near-stream zone, and at greater soil depth (>60 cm depth), the $\delta^{18}\text{O}$ was less affected, demonstrating that the event water progressively moved toward the stream, but never reached the deeper soil layers (Laudon and others 2004b). In the wetland-dominated catchment, C4, the precipitation water

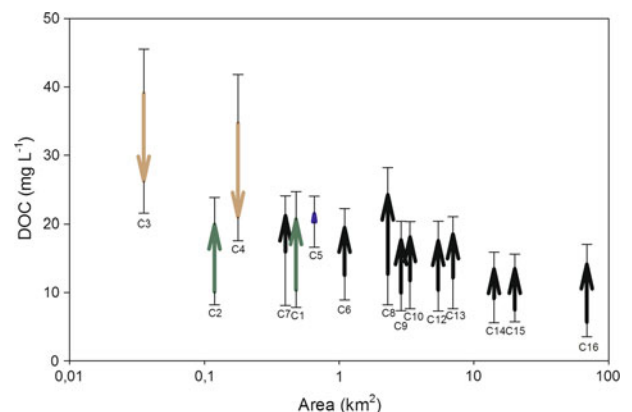


Figure 2. Average variability in DOC concentration for the 15 catchments from baseflow to high flow (2003–2008). The tail and head of arrows are average baseflow (<0.15 mm day⁻¹) and high flow (>5.5 mm day⁻¹) concentrations, respectively. The whiskers denote the standard deviation of average concentrations. Light brown arrows are wetland-dominated catchments (C3 and C4), green arrows are the forest-dominated catchments (C1 and C2), and blue arrow is the lake outlet (C5), whereas the black arrows denote mixed catchments (Color figure online).

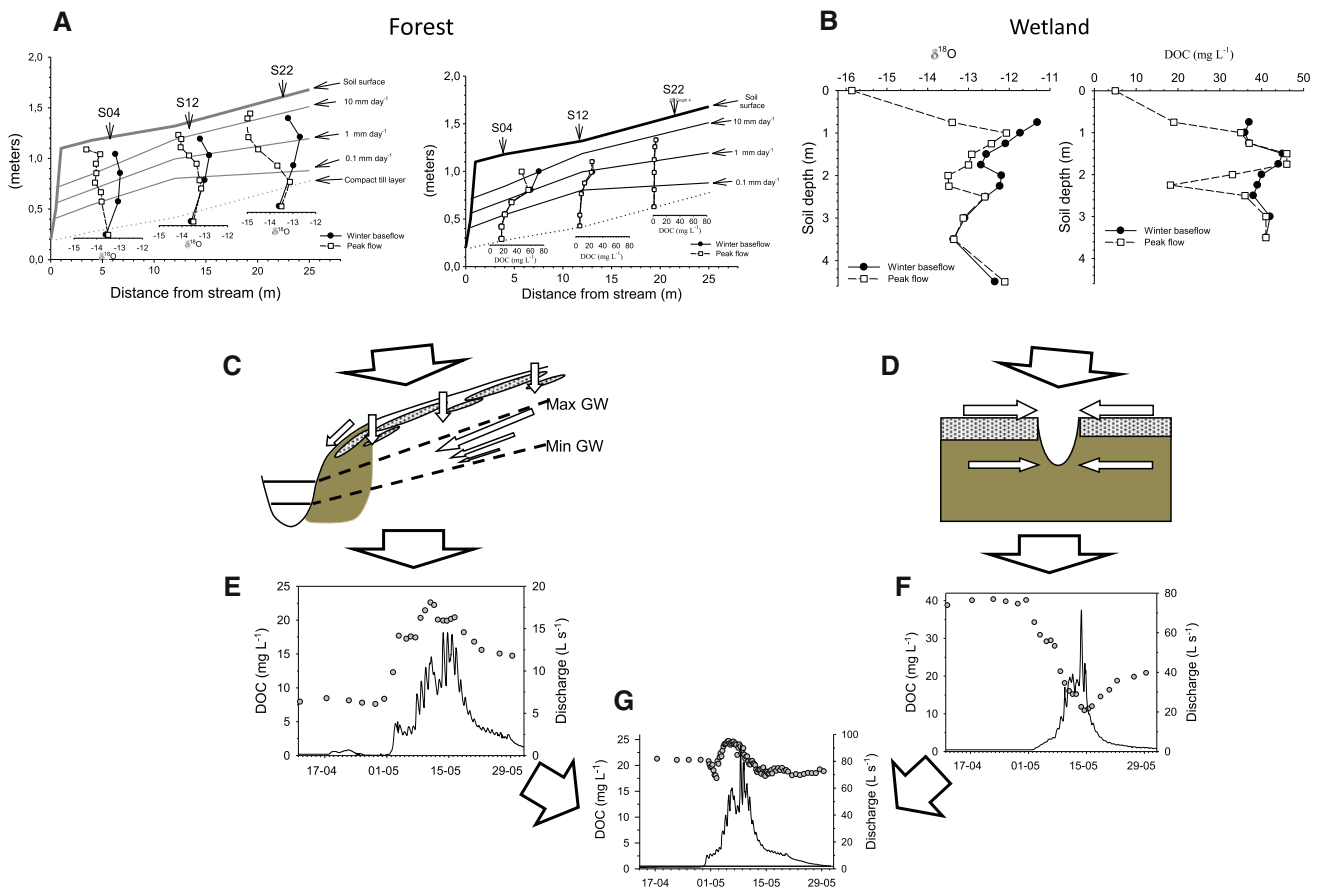


Figure 3. Isotopic composition (*left*) and DOC concentrations (*right*) in the soil profile of the forested catchment C2 (**A**) and wetland-dominated C4 (**B**) at winter baseflow and peak flow, respectively. In the forested transect (**A**) the near-horizontal lines denote the corresponding groundwater levels for different specific discharges. In the wetland site (**B**) the entire soil is saturated, but frozen during base flow, which explains the lack of data points in the uppermost soil during winter. In the central panes the mechanistic explanation from **A** and **B** are described conceptually for the forested (**C**) and wetland (**D**) soils, respectively. The *open arrows* illustrate the dominant hydrological flow paths, the *dotted sections* denote soil frost and the *solid color* is organic soils. Panels **E** and **F** show examples of the resulting stream DOC concentrations (points) during the spring flood hydrograph (*solid line*) for forest (C2)- and wetland-dominated stream (C4), respectively. The downstream effect in a mixed catchment (**G**) is consequence of the contributing landscapes in **E** and **F**, as exemplified from catchment C7.

affected the isotopic composition at two levels in the mire; as overland flow and through a section of the mire at 200–250 cm depth (Figure 3B). The preferential flow pathway at approximately 200 cm depth in the wetland is caused by a layer of relatively high hydrological conductivity; likely a result of successive stages of the wetland development (Sirin and others 1998). Overland flow, which quantitatively is the most important flow pathway, is especially pronounced during the spring when solid ice formation on the wetland inhibits infiltration (Laudon and others 2007), also occurs at high flow during summer and autumn conditions due to saturation excess (Bishop 1991). Laudon and others (2007) demonstrated that the contrasting hydrological pathways in C2 and C4, at least

during the spring flood, could be extrapolated to the entire Krycklan landscape scale, where the separation of event and pre-event water to a large extent was determined by the proportion of wetland and forest in the catchments.

In the small forest-dominated catchment streams the DOC concentration is almost entirely controlled by the soil/stream water interface in the riparian zone. High DOC concentrations in the riparian soils, compared to low concentrations in the upslope hillslopes, can in combination with the hydrological flow pathways explain most of the temporal variability that is observed in the stream water. This large increase in DOC in the riparian zone is not caused by a recent build up of organic carbon, but is a common geomorphologic feature in

this landscape, developed since the last glaciation by lateral water movement toward the stream causing waterlogged conditions (Lyon and others 2011). The role of the riparian zone for controlling stream DOC has previously been demonstrated both qualitatively (Bishop and others 2004) and quantitatively (Köhler and others 2008; Köhler and others 2009) in the C2 catchment. Recently, a more stringent mathematical formulation has been presented demonstrating the role of the riparian zone for regulating stream water DOC both in C2 (Seibert and others 2009) and across the entire Krycklan catchment (Grabs 2010). A major reason for the strong agreement between riparian soils and stream water DOC is the hydrological connectivity between soil/groundwater and stream water. A typical feature of till soils in this glaciated landscape is that the saturated hydraulic conductivities increase toward the soil surface (Lundin 1982; Rodhe 1989) and has been termed the transmissivity feedback mechanism of runoff generation (Bishop and others 2004). This results in an exponentially increasing stream discharge for every incremental increase in groundwater level. Combining previous findings about hydrological pathways with what is known about sources and dynamics of DOC, it is evident that although the upslope hillslope areas with low DOC content ($1\text{--}3\text{ mg l}^{-1}$) provide the majority of the water to the stream because of the extensive (90–95%) areal coverage, it is the last few meters of organic-rich riparian (DOC ranging $10\text{--}60\text{ mg l}^{-1}$) soil that determine the stream water DOC. As a consequence, the temporal dynamics of stream water DOC is regulated by the varying groundwater level that activates different riparian soil profiles with increasing soil DOC concentrations toward the soil surface (Figure 3A).

In contrast to the forested catchment streams, DOC dynamics of wetland-dominated streams (again exemplified by C4) have high concentrations at baseflow, followed by a decline during peak runoff (Figure 3F). During baseflow conditions the high stream water DOC concentrations are derived from drainage of the catotelm (Yurova and others 2008). At the rising stage of the hydrograph the declining DOC concentrations result from dilution caused by event water running off as overland flow and through a pathway at approximately 200 cm depth in this wetland. As discussed above, these mechanisms are clearly manifested by the isotopic data suggesting a rapid transfer of event water via preferential pathways on top and through the wetland (Figure 3B).

The small heterogeneous, or mixed, catchments display DOC dynamics in-between the for-

ested- and wetland-dominated catchment streams. Baseflow DOC is generally intermediate and the temporal response during the spring flood is often less pronounced (Figure 2). One example of this is catchment C7 that is downstream of C2 and C4, where baseflow DOC is approximately 20 mg l^{-1} and remains rather constant during the spring freshet (Figure 3G). Again this different response can be explained by the mixing of DOC from two dominating, but contrasting, features of the boreal landscape: forests and wetlands. The larger mixed streams, although experiencing a response similar to that of the smaller mixed streams during spring flood, also have a tendency for decreasing baseflow DOC with catchment size (Figure 2). Similar patterns have been seen in other similarly sized boreal and temperate stream networks (Temnerud and others 2010; Likens and Buso 2006). Two alternative mechanisms have been proposed to explain this decreasing baseflow concentration in Krycklan, based on isotopic and biogeochemical information. The first is that the declining DOC concentration is caused by increased deep groundwater inflow and longer average residence time of water in the larger catchments, a mechanism supported by isotopic composition (Laudon and others 2007; Lyon and others 2010) and higher base cation concentrations (Buffam and others 2008; Klaminder and others 2011). The other proposed mechanism is that the soils change in character in the lower part of the catchment, from unsorted till in the upper reaches to sorted fine sediments further down (Ågren and others 2007a).

Applying the two-component mixing model based on the small, but contrasting, first-order streams C2 and C4 to a number of downstream locations gave a RMSE of 3.1 ($r^2 = 0.65$; $P < 0.001$; $n = 150$) for C7 and 3.2 mg l^{-1} ($r^2 = 0.64$; $P < 0.001$; $n = 150$) for C13 (Figure 4). For both of these streams, which are underlain by unsorted till, the mixing model worked generally well with a slight over-prediction at low concentrations followed by a slight under-prediction at high concentrations. This suggests that as long as the basic catchment characteristics downstream remain similar to those upstream, the proportion of forest and wetlands can explain much of the downstream variability in DOC despite a difference of over 30 times in size. In contrast, applying the mixing model to the outlet of the catchment (C16) results in an over-prediction at both high and low concentrations with a RMSE of 7.5 mg l^{-1} ($r^2 = 0.68$; $P < 0.001$; $n = 150$). One possible explanation for this is that in the catchment C16 up to 50% is underlain by fine sediments with a higher specific

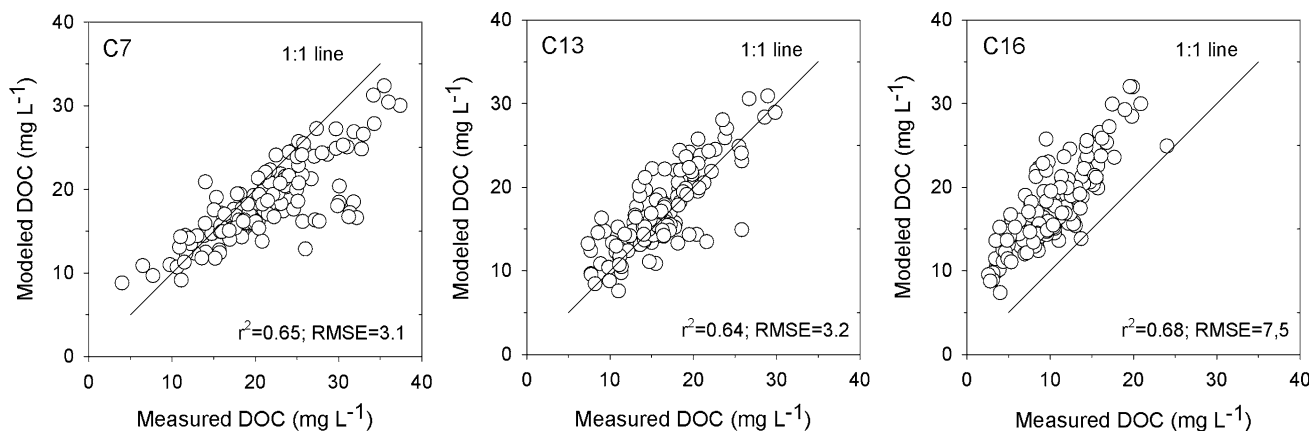


Figure 4. Applying the simple mixing model based on the forested catchment (C2) and wetland-dominated catchment (C4) of the three downstream locations C7 (left), C13 (mid), and C16 (right), respectively. Root mean square of errors (RMSE) are given in the figure, $n = 150$ for each stream.

surface area suggesting that the change in soil type from the unsorted till in the upper reaches, as proposed by Ågren and others (2007a), could be an important factor explaining the significant decreasing downstream DOC concentration. The lower DOC values at base flow (Figure 2) at site C16 are also indicative of a more efficient DOC removal via sorption and/or degradation processes. Differences in the riparian soil conditions, with a lower build up of organic carbon in the silty area where the stream is meandering could possibly also partly explain this pattern (Grabs 2010).

Another consequence of the contrasting behavior of the forested- and the wetland-dominated catchment streams is that there is a switch in the sources of DOC for the mixed catchment streams when moving from baseflow to peak flow. This is exemplified by a strong negative relationship between the wetland/forest DOC export ratio and specific discharge ($r^2 = 0.79$, $n = 138$, $P < 0.001$; Figure 5A), with values ranging from 1 to 10. By multiplying this ratio with different wetland/forest proportions, we could calculate the relative amounts of stream DOC coming from the two sources at different flow conditions and for streams with variable degrees of forest/wetland coverage (Figure 5B). During baseflow, there was an average ratio between DOC export of wetlands and forests of approximately 10. With increasing discharge this ratio approached 1, suggesting that the areal export during high flow is similar for wetlands and forested areas. As a result, mixed landscapes which cover most of the subcatchments in Krycklan, as well as in the boreal region in general, are dominated by DOC from wetlands at baseflow (when wetlands export several times more DOC) and forest sources at high flow conditions (when forest

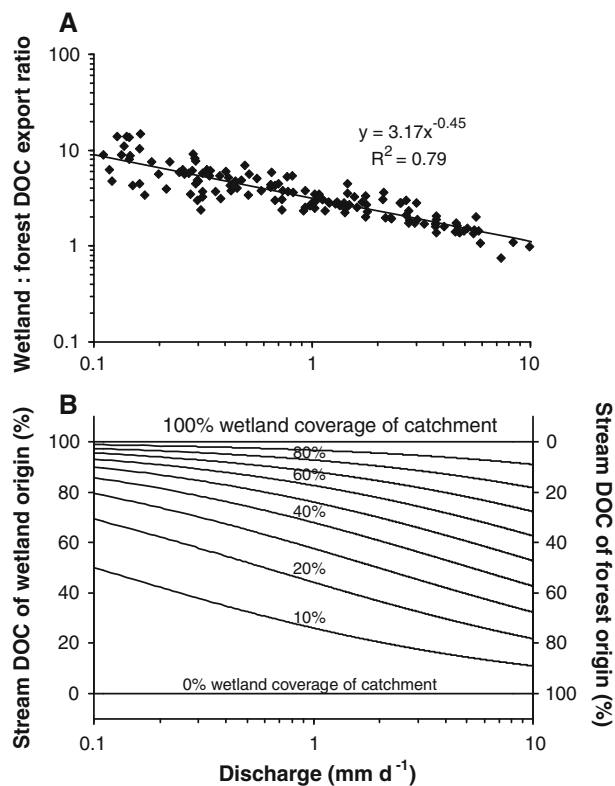


Figure 5. **A** The relationship between wetland/forest DOC export ratio and discharge ($y = 3.17x^{-0.46}$, $R^2 = 0.79$, $n = 138$, $P < 0.001$). The figure is based on 138 sampling dates between 2003 and 2008 and each ratio is calculated using data from all 15 streams. **B** The relative contribution of DOC from the two sources forests and mires (calculated from **A**) at different specific discharges and in streams draining catchments with different wetland coverages.

and wetlands have similar export rates but the dominating areal cover of forest makes forest a bigger net source). One important implication of

this source switch is that it can help explain the dynamics of carbon quality. As the DOC quality varies to a large extent depending on its terrestrial origin in terms of bioavailability (Berggren and others 2007; Ågren and others 2008) and proportion of low molecular weight organic carbon (Berggren and others 2010), this source switching results in the quality of DOC in mixed streams switching from old recalcitrant DOC originating from wetlands at low flow to more highly biodegradable DOC from the riparian soils in forested catchments during high flow (Berggren and others 2009). The source switching of DOC origin is not only relevant for variability in carbon quality downstream, but also for other constituents associated with DOC such as metals and organic contaminants (Bergknut and others 2010a). The assumption used of uniform area specific discharge will likely not alter the mixing ratios substantially as there is a large synchronicity between sites (Buffam and others 2007). If the mixing ratio will be affected by the above assumption, it will likely further emphasize the dominance of wetland sources at low flow as the specific discharge in general is higher from wetland areas during base-flow. However, to better distinguish between eventual areal variation in specific discharge and how this influences the export model will be an important question to pursue in the future.

In this study, we have used the mapped areal extent of forest and wetlands to quantify the role of different catchment sources of DOC. As the importance of wetlands probably is not only dependent on the areal coverage, but also on hydrological connectivity and position within the catchment, a valuable step forward of this study would be to analyze how the actual wetland location in relation to the hydrological functioning of the catchment affects the DOC dynamics. This is, for example, clear in C4 where the wetland covers approximately 40% of the catchment, but its location forces essentially all of the catchment's flowing water to pass through the wetland immediately before entering the stream (see Figure 1). If we, instead of using the simple mixing proportional relationship between wetland and forest (Figure 4), assume that C4 represents a 100% wetland end-member the mixing relationship at C7 would improve with RMSE dropping from 3.1 to 2.7 mg l⁻¹ (and r^2 increasing from 0.65 to 0.75). However, a more complex approach may be warranted for other wetlands. For instance, although it is reasonable to assume that the role of wetlands increases in proportion to the upslope area draining through large valley bottom wetlands, that

approach is likely to overestimate the influence of wetlands at other locations including narrow fringe wetlands where the DOC pool can more easily become exhausted. Few studies have examined the role of landscape position on watershed-stream DOC connectivity, and these have had inconclusive results. Gergel and others (1999) found that the influence of wetlands on stream DOC was actually clearer at the scale of whole watersheds than when only buffers immediately surrounding the streams were considered, but that study did not explicitly account for hydrologic flowpaths within the watersheds. Creed and others (2003) found a strong relationship between stream DOC and wetland area in watershed, but this relationship was not further improved by accounting for the hydrological connectivity of wetlands to the stream network. Different methods for incorporating hydrology and landscape position in analysis of watershed-stream hydrochemical connectivity have been proposed by Creed and others (2003) and Baker and others (2006). Research is ongoing to explore the utility of these approaches at the Krycklan Catchment Study, but requires further evaluation before coming into practical use.

How generalizable are the DOC patterns and processes that we have presented for the Krycklan Catchment to other regions? The pattern of increasing DOC in forest streams during snowmelt and other high flow events is commonly observed in northern latitudes (for example, Hornberger and others 1994; Hinton and others 1997; Ågren and others 2010), and generally attributed to the intersection of rising water tables with organic-rich surficial soils, particularly in the near-stream zone (for example, Bishop and others 1995; Hinton and others 1998; Grabs 2010). The temporal pattern of DOC in wetland streams has not been as thoroughly studied, but the pattern of DOC dilution during snowmelt as observed in Krycklan has also been noted in other northern/boreal regions, including Nova Scotia, Canada (Gorham and others 1998), Ontario, Canada (Hinton and others 1997; Eimers and others 2008a, b), and Wisconsin, USA (Gergel and others 1999). In studies in Ontario the dilution was attributed primarily to hydrological flushing of riparian peat resulting in a depleted DOC reservoir during periods of sustained high flow (Schiff and others 1998), whereas in Krycklan this mechanism likely plays a role but there is also a substantial contribution of dilute snowmelt flow over surficial ice in wetlands with little peat contact on the way to the streams (Laudon and others 2007). Based on the apparently common contrast between forest streams and wetland streams in

DOC response to snowmelt, we believe that the pattern of shift from more wetland to more forest-derived DOC likely applies to a large proportion of the boreal forest zone, and some of the north temperate zone which has a similar landscape to the boreal and experiences an annual snowmelt event. This implies a shift in stream dissolved organic matter chemical character and bioavailability (Ågren and others 2008; Berggren and others 2009) during high flow events in mixed boreal landscapes, as well as a spatial “evening out” of DOC concentration. In terms of the general applicability of the upstream–downstream DOC decrease observed in Krycklan, there are few studies for comparison which have a high enough spatial density of DOC measurements extending up into headwaters, though Likens and Buso (2006) and Temnerud and others (2010) did find similar patterns in snapshot surveys in New Hampshire, USA and Sweden, respectively. We hesitate to speculate as to the generalizability of this pattern as there are many proposed mechanisms for the upstream–downstream trend (Likens and Buso 2006; Buffam and others 2008), not all which would generalize to most northern/boreal catchments. However, the conceptual framework laid out in this article could prove useful for considering a broad range of watershed types across different biomes, and is not limited to those exhibiting similar DOC patterns as those found in the Krycklan catchment.

The implication of this conceptual framework is not only limited to deciphering the spatial and temporal variability of DOC, but can also help explain patterns and dynamics of other solutes in the landscape. Incorporating this approach on other research efforts in the Krycklan catchment on the quality and bioavailability of DOC (Ågren and others 2008; Berggren and others 2007, 2009); DIC dynamics (Wallin and others 2010); acid–base chemistry (Buffam and others 2007, 2008; Laudon and Buffam 2008), aluminum (Cory and others 2006, 2009), iron and manganese (Björkvald and others 2008), selenium (Lidman and others 2011), persistent organic pollutants (Bergknut and others 2010b) as well as inorganic and organic sulfur (Björkvald and others 2009; Giesler and others 2009) can improve our mechanistic understanding on the role of processes, connectivity and scaling of both natural and anthropogenic constituents in surface waters.

In summary, this study provides a conceptual framework for understanding natural variability of DOC export and associated dynamics of nutrients, metals, and other contaminants from heterogeneous boreal landscapes. This is not only important for understanding the past and present conditions

but even more so as climate is moving outside the envelope that has dominated since the last glaciation. An important consequence of this study is that the impact of environmental change on DOC in boreal catchments will not solely depend on the driver of change, but also on multiple effects depending on, for example, hydrological, morphological, geological, and vegetation characteristics of the catchment. Many heterogeneous catchments may respond in a seemingly unpredictable manner as the effects in some instances will cancel out, although they may amplify in others. Ultimately, the outcome of environmental change on DOC in heterogeneous boreal landscapes will depend on how individual landscape elements are affected, the proportion and connectivity of these landscape elements, and how these changes are propagated downstream.

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