Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer

Anneli Ågren,[1] Ishi Buffam,[2,4] Martin Berggren,[1] Kevin Bishop,[3] Mats Jansson,[1] and Hjalmar Laudon[2]

[1] The character and quantity of dissolved organic carbon (DOC) were studied in nine small boreal streams and adjacent soils during two years, with focus on the spring snowmelt period. The streams cover a forest-wetland gradient, spanning from 0% to 69% wetland coverage. Lower values of the absorbance ratio measured at 254 nm and 365 nm (A_{254}/A_{365}), in both soil plots and streams, indicated that wetland-derived DOC had higher average molecular weight than forest DOC. Higher $SUVA_{254}$ (DOC specific ultraviolet absorption at 254 nm) in wetland runoff indicated more aromatic DOC from wetlands than forests. During low flow, the stream DOC character was sensitive to the forest-wetland proportion of the catchment, and when wetland coverage exceeded 10%, the streams appeared to be dominated by wetland-derived DOC. During the spring snowmelt period, the character changed to lower molecular weight and more aliphatic DOC, particularly in streams with a high proportion of forest in the catchment. The forested soil solutions had higher A_{254}/A_{365} in the surface horizons that were hydrologically activated during the high flow events, while wetland soil solution had relatively low A_{254}/A_{365} at all depths. Consequently forest soils contributed more to stream DOC concentration during snowmelt that during winter low flow.

1. Introduction

[2] The landscape is composed of a heterogeneous mosaic of different geology, soils and vegetation, causing variations in stream chemistry [*Humborg et al.*, 2004; *Hutchins et al.*, 1999]. The chemistry of streams embedded in the boreal landscape is determined by stream size, catchment characteristics, season and flow [*Ågren et al.*, 2007; *Buffam et al.*, 2007]. Major sources of dissolved organic carbon (DOC) in these systems are wetlands [*Creed et al.*, 2003; *Hope et al.*, 1994; *Mulholland*, 2003], together with the upper organic horizons of the riparian forest zone [*Bishop et al.*, 2004; *Findlay et al.*, 2001] as well as the organic layers of podzol profiles in coniferous stands [*Kortelainen and Saukkonen*, 1998; *Mattsson et al.*, 2003]. Differences in flowpaths between wetlands and

forests have recently been shown to cause different stream hydrochemical responses as runoff changes, e.g., during snow melt when the contribution of DOC from forest soils increases relative to that from wetlands [*Ågren et al.*, 2007; *Laudon et al.*, 2004b].

[3] Based on the importance of DOC in freshwaters, it is of fundamental interest to better understand the spatial and temporal variation of both the concentration and characteristics of DOC [*Hornberger et al.*, 1994; *Laudon et al.*, 2004a]. Many studies have shown how DOC concentrations are affected by flow events [*Boyer et al.*, 1997; *Butturini et al.*, 2006; *Evans et al.*, 1999]. Fewer studies have, however, investigated changes in the properties of the organic carbon during high flow [*Hood et al.*, 2006; *Hruska et al.*, 2001], or interannual variations in the DOC character. As different sources of DOC in catchment soils can have different chemical characteristics, a shift in the character of stream water DOC can provide important information about which parts of the catchment become hydrologically connected to the stream at different stages of the hydrograph [*Hood et al.*, 2006].

[4] Absorbance analysis is a standard, readily available analysis that provides important information about the bulk properties of DOC [*McKnight et al.*, 1997; *Weishaar et al.*, 2003]. Absorbance spectra tend to change with increased average molecular weight of DOC [*Butler and Ladd*, 1969;

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[1]Department of Ecology and Environmental Science, Umeå University, Umeå, Sweden.
[2]Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå, Sweden.
[3]Department of Environmental Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden.
[4]Now at Ecosystem and Landscape Ecology Laboratory, Department of Zoology, University of Wisconsin, Madison, USA.
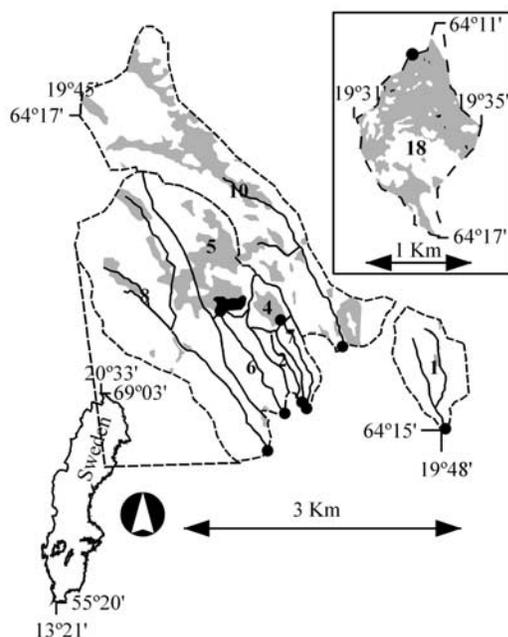
Figure 1. Location of the studied catchments in the Krycklan watershed. White areas are forested areas, gray areas are wetlands, and the lakes are in black. The solid lines show streams; catchment boundaries are dashed lines, and the black dots show sampling sites. Catchment 18 is situated 10 km southwest of the other catchments. The forest soil profiles are sampled in C2 and the wetland soil profile in C4.

De Haan and Deboer, 1987]. A steep slope of UV-absorption spectrograms indicates low average molecular weight of the DOC compounds [*Dahlén et al.*, 1996; *Strome and Miller*, 1978]. Different spectral slopes (using different wavelength intervals) or absorbance ratios can be calculated to show this. One simple characteristic is the A_{254}/A_{365} ratio which is negatively correlated to the molecular weight of DOC [*Dahlén et al.*, 1996; *De Haan*, 1993]. Low molecular weight (LMW) and high molecular weight (HMW) fractions of organic substances have different biogeochemical properties [*Kramer et al.*, 1990]. LMW compounds are for example generally considered to be better substrates for bacteria than more complex HMW compounds [*Tranvik and Jørgensen*, 1995]. In boreal Sweden, the geographic region of this study, bacterial productivity has been found to be positively correlated to A_{254}/A_{365} [*Berggren et al.*, 2007]. Carbon-specific ultraviolet absorbance at 254 nm

per DOC (SUVA$_{254}$) is also commonly used to assess the composition of DOC in stream water [*Rostan and Cellot*, 1995]. A higher value of SUVA$_{254}$ indicates higher contents of aromatic carbon [*Fu et al.*, 2006; *Weishaar et al.*, 2003] which, in general, has lower bioavailability compared to aliphatic compounds [*Perdue*, 1998].

[5] The dynamics of the DOC concentration during different runoff stages is largely known, but to better understand the dynamics of the character of DOC, and how these are connected to soil-stream interface characteristics, nine small boreal streams were studied in conjunction with detailed soil water investigations in two of the catchments. The DOC characteristics, A_{254}/A_{365} and SUVA$_{254}$, as well as DOC concentrations were analyzed during winter low flow, spring snowmelt period, and summer low flow in 2004 and 2005. The objectives were to investigate how the DOC character and quantity were expressed (1) in streams draining catchments with different proportions between forests and mires, and (2) as a response to changes in the hydrological conditions.

2. Material and Methods

2.1. Study Sites

[6] Nine small streams in the Vindeln experimental forests (64°, 16′N, 19° 46′E) were chosen: eight in the Krycklan catchment and one draining the adjacent (10 km southwest) Degerö Stormyr catchment (Figure 1). Catchment areas range from 14 to 312 ha and stream orders from one to two (Table 1). The land cover of the catchments is composed of forests (31%–100%) and *Sphagnum*-dominated peat wetlands (0%–69%; categorized as acid, oligotrophic and minerogenic [*Granberg et al.*, 1999]). In addition, a small humic lake covers 5% of catchment C5 (Stortjärnen Outlet, Figure 1). The stream from the adjacent Degerö Stormyr peatland (C18) was included to increase the range of wetland coverage (from 40% in C4 to 69% at C18). The streams were divided into 3 groups based on their wetland coverage; forest dominated streams (0–9% wetland coverage), mixed streams (10–39% wetland coverage) and wetland dominated streams (≥40% wetland coverage) (Table 1). The forests are dominated by Scots Pine (*Pinus sylvestris*) in dry upslope areas and Norway Spruce (*Picea abies*) in lower, wetter areas. Dominant quaternary deposits are glacial tills (9–94%), peat (0–69%) and thin soils (6–32%). Some catchments are nested; C2 and C4 drain into C7, and C5 into C6. Mean annual air temperature is 1.3°C, the annual precipitation 600 mm and 35% of the precipitation falls as snow during 5 months of winter (December–April) [*Ottosson Löfvenius et al.*, 2003]. During the 2 month snow melt period, with the peak around the first of

Table 1. Characteristics of the Nine Catchments

Catchment No.	Site Name	Category	Stream Order	Area (ha)	Water (%)	Forest (%)	Wetland (%)
C1	Risbäcken	Forest	1	66	0.0	99	1
C2	Västrabäcken	Forest	1	14	0.0	100	0
C4	Kallkällsmyren	Wetland	1	19	0.0	60	40
C5[a]	Stortjärnen Outlet	Mixed	1	95	4.7	59	36
C6	Stortjärnbäcken	Mixed	1	140	3.1	73	24
C7[a]	Kallkällsbäcken	Mixed	2	50	0.0	85	15
C8	Fulbäcken	Mixed	2	248	0.0	89	11
C10	Stormyrbäcken	Mixed	2	294	0.0	74	26
C18	Degerö stormyr	Wetland	1	312	0.2	31	69

[a]In order to only include independent catchments, these catchments were excluded from the regression analysis.
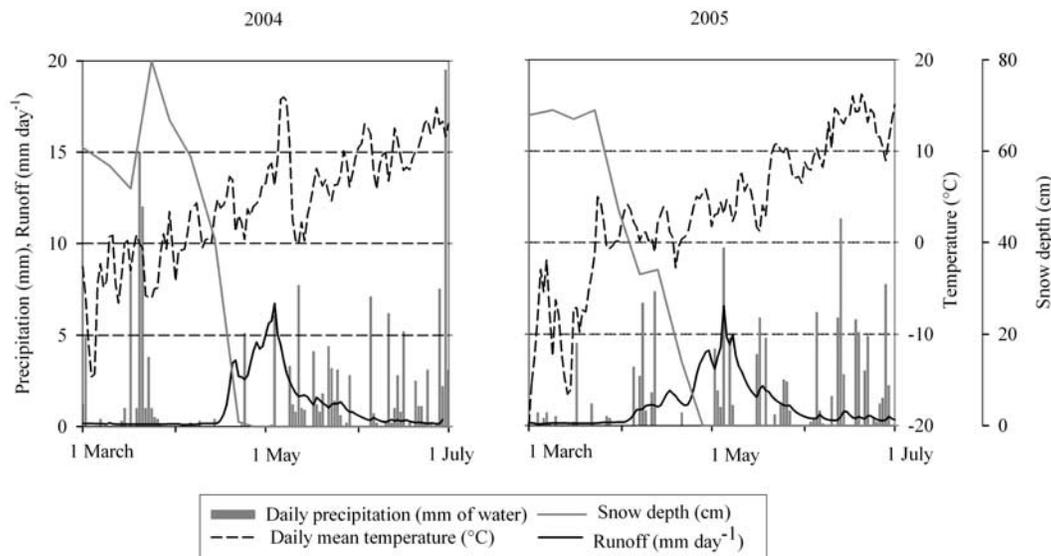
Figure 2. The black solid line shows the runoff (mm day^{-1}), the gray solid line shows the snow depth (cm), the dotted line is the mean daily temperature ($^\circ$C), and the bars show daily precipitation (mm of water). The meteorological data are from the climate reference monitoring station at Svartberget, situated in the Krycklan catchment.

May, ca. 40% of the annual runoff occurs, making the spring snowmelt period the major annual hydrological event [*Buffam et al.*, 2007]. The snowmelt is driven by changes in temperature with occasional boosts from rain (Figure 2). In this region, spring is usually the season with least precipitation [*Vedin et al.*, 1995].

2.2. Sampling and Calculations

[7] During the period from 1 March–30 June 2004, 22 stream water samples were collected in each stream. During the same period in 2005, 19 stream water samples were collected in each stream. The sampling intensity varied according to the runoff, with weekly sampling during the stable base-flow situations before spring snowmelt period, every second day during the peak of the spring snowmelt period and every third to fourth day on the receding limb of the spring snowmelt period, proceeding into summer low flow. Samples were collected in acid washed 250-mL high-density polyethylene bottles after multiple rinses with stream water. Samples were kept cool and dark until processing. Samples for absorbance were filtered through a 0.45 μm MCE filter (Millipore) and the absorbance measurements were conducted within 24 hours of the sampling. Absorbance spectra were measured on room-temperature samples in 1 cm quartz cuvettes using a Hewlett Packard 8452A diode array spectrophotometer. Deionized water was used as a blank. The absorption coefficient was calculated from absorbance as follows:

$$A_\lambda = a_\lambda/d \qquad (1)$$

where:

A_λ absorption coefficient (m^{-1}) at wavelength λ nm
a_λ absorbance unitless (AU) at wavelength λ nm
d pathlength (m)

[8] The ratio between absorption coefficients at 254 nm and 365 nm (A_{254}/A_{365}) was calculated for each sample. In order to validate the choice of this simplified absorbance index, A_{254}/A_{365} was compared to the spectral slopes (S) of Ln-transformed spectrograms between 250 nm and 400 nm. S showed the same pattern as A_{254}/A_{365} ratio and the two were strongly correlated ($r^2 = 0.83$, $n = 1863$, $p < 0.01$).

[9] During 2004, samples for DOC were filtered using a 0.45 μm MCE filter (Millipore), while samples were not filtered during 2005. The DOC samples were frozen until analysis with Shimadzu TOC-V$_{CPH}$ analyzer. No measurable difference (using a paired sample t-test ($p = 0.016$ $n = 44$)) in the concentration of organic carbon due to filtering was found. Particulate organic carbon concentrations are usually negligible relative to the dissolved fraction in Swedish boreal surface waters [*Ivarsson and Jansson*, 1995; *Laudon and Bishop*, 1999]. SUVA$_{254}$ (specific ultraviolet absorbance at the wavelength 254 nm) was calculated as: A_{254} (m^{-1})/DOC (mg C L^{-1}).

[10] Specific runoff (runoff per time unit and area) at C7 was used to estimate the runoff in all catchments, assuming that specific runoff was the same in all catchments. The assumption that specific runoff was the same in all catchments introduced potential errors. The intersite differences in annual runoff (e.g., due to differences in subcatchment evapotranspiration) has been calculated to be ±12% (based on discrete discharge measurements at the other sites, which were compared to the continuous measurements at C7) [*Ågren et al.*, 2007]. An additional uncertainty due to intersite differences in flow regime ("flashiness") has been calculated to a maximum error of ±12% during the spring [*Ågren et al.*, 2007].

[11] Forest soil solution depth profiles were sampled at 4 sites (K4, K6, K9 and S22; in the Västrabäcken catchment (C2) (Figure 1)) using suction lysimeters (Suction Cup SKP 100 from Umwelt-Monitoring Systeme). K4, K6 and K9 are situated in the riparian zone (approximately 2 m from the
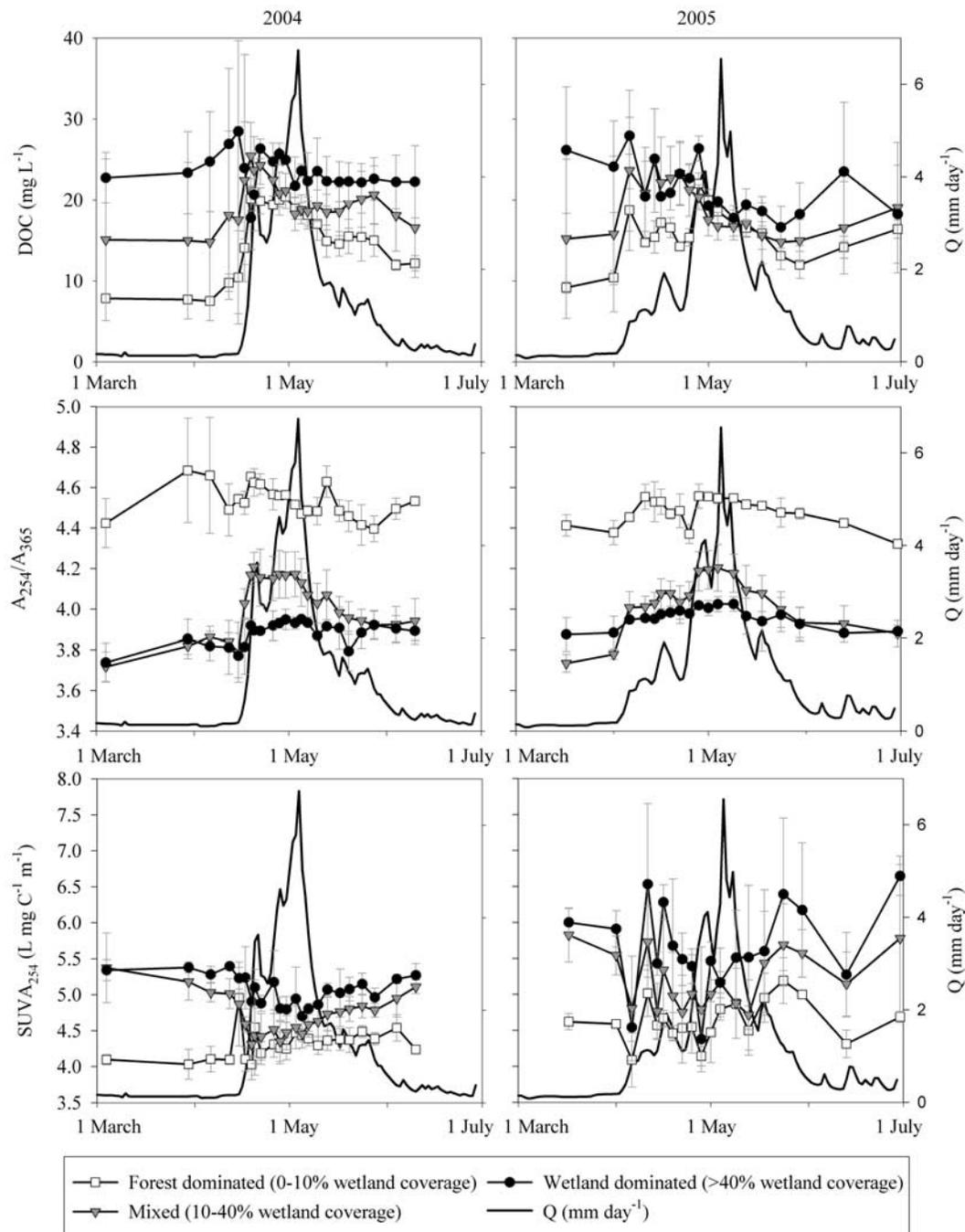
Figure 3. The daily variation in runoff and the average DOC, A_{254}/A_{365}, and SUVA$_{254}$ for catchments with different proportions of forest coverage. (Forest dominated: C2 and C1. Wetland dominated: C4 and C18. Mixed: C5, C6, C7, C8, and C10.) Error bars denote SD between the streams.

stream channel) of C2, and S22 more upslope in the forest soil (22 m from the stream channel). A 345 kPa vacuum was applied to lysimeters one day prior to sampling and the initial volume was discarded before collecting samples for analysis. K4 and K6 were sampled at 10, 25, 40, 60, and 80 cm depths on 10 September 2003, 8 June 2004, 13 July 2004, 1 September 2004, 17 August 2005, and 12 October 2005. K9 was sampled on 6 April 2004, 20 April 2004, 7 May 2004, 9 June 2004, and 12 October 2005 at the depths of 10, 25, 35, 45, 55 and 65 cm. S22 was only sampled once, in 9 June 2004, at 6, 12, 20, 35, 50, 75 and 90 cm depths.

Because of the single sampling occasion of S22 we verified that the samples were representative, by comparing them with analyses made in 1997–98. From this comparison, the absorbance ratio in the soil solution at S22 was found to be within the same range, except the sample from 75 cm which was excluded as an outlier.

[12] The wetland soil profile was sampled at the mire of the Kallkällsmyren catchment (C4) (Figure 1). Samples were collected at depths of 75, 100, 125, 150, 175, 200, 225, 300, and 350 cm, using nested wetland wells with
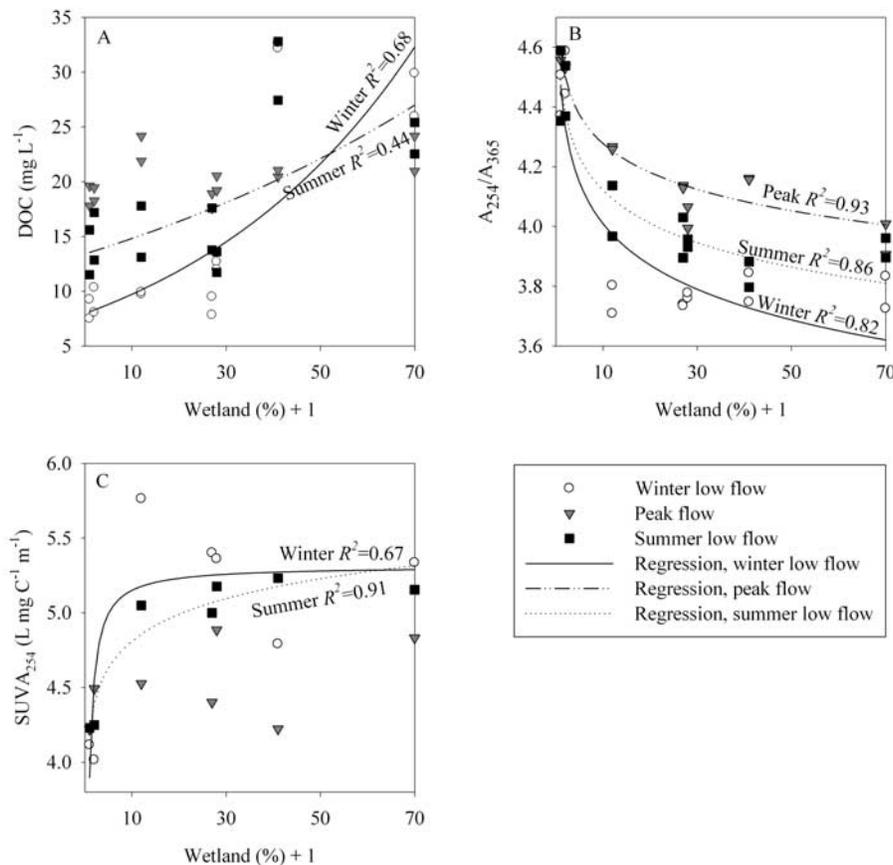
Figure 4. The relationship of wetland coverage (%) to (a) stream DOC concentration, (b) A_{254}/A_{365}, and (c) $SUVA_{254}$ for winter low flow (average of measurements during March), peak of spring snowmelt period (average of measurements when $Q > 3$ mm day^{-1}), and early summer low flow (average of measurements 10–30 June). The regressions are made on seven independent catchments. DOC and A_{254}/A_{365} are averages for the two years, and SUVA is taken from 2004 (see Table 2 for descriptors of the regressions). Some regression models require positive values; therefore, the wetland percentage was transformed (+1) to avoid catchments with 0% wetland in the analysis.

closed bottoms, perforated at the lower 10 cm [*Petrone et al.*, 2007]. The water from the wells was extracted by a peristaltic pump. The first samples were discarded (two times the stored volume in each tube). The wetland profile was sampled on 5 occasions during the 2004 spring snowmelt period; on 5, 19, and 27 April, 8 and 30. The samples were filtered before analysis (0.45 μm MCE filter (Millipore)).

[13] The function ''curvefit'' in SPSS 14.0 was used to assess the relationship between DOC concentration and wetland coverage, as well as between measures of DOC character and wetland coverage, during different flow situations. The procedure applied 11 different models and the model that gave the highest r^2 was chosen if significant (with exception of the cubic curve). Some models require positive values, therefore the wetland percentage was transformed (+1) to avoid a catchment with 0% wetland, i.e., 1% was added to all wetland percentages.

[14] The form (narrow ellipse or circle), rotational patterns (clockwise or anticlockwise) and trends (increasing or decreasing during the first half) of hysteresis loops can provide further information about storm flow hydrochemistry [*Butturini et al.*, 2006; *Evans and Davies*, 1998]. In order to further investigate the variation in quantity and character of the DOC during spring snowmelt period, we

plotted the concentration of DOC, A_{254}/A_{365} and $SUVA_{254}$ versus runoff during spring snowmelt period (1 March– 10 June) of 2004 (Figure 5) and 2005. Three representative sites are presented: the forest dominated C2 (0% wetland), the wetland dominated C18 (69% wetland) and the mixed C10 (26% wetland). The other sites (not shown) fell into the general pattern described in the results.

3. Results

[15] During low flow, especially winter low flow, the DOC concentrations were higher in the wetland dominated streams (above 20 mg L^{-1}) compared to the forest dominated streams (below 10 mg L^{-1}) (Figure 3). Concurrent with the increase of flow during the spring snowmelt period the DOC concentration decreased in the wetland streams, whereas DOC increased in the forested and mixed streams to levels more or less the same for all streams (15–20 mg L^{-1}). The DOC character (indicated by A_{254}/A_{365} and $SUVA_{254}$) was different in forest and wetland dominated streams (Figure 3). The forest streams had a high A_{254}/A_{365} at base flow, which increased somewhat during peak flow (Figures 3 and 4). In the wetland stream A_{254}/A_{365} was low at base flow and increased during the spring snowmelt period. The

Table 2. Descriptors of the Regressions in Figure 4

Variable	Runoff Situation	Function	Equation	a	b	p	r^2	n
DOC	Winter low flow	Exponential	$y = ae^{bx}$	7.96	0.02	0.000	0.68	14
	Spring snowmelt	*Nonsignificant*						
	Summer low flow	Exponential	$y = ae^{bx}$	13.40	0.01	0.010	0.44	14
A_{254}/A_{365}	Winter low flow	Logarithmic	$y = a + b \ln x$	4.47	−0.20	0.000	0.82	14
	Spring snowmelt	Logarithmic	$y = a + b \ln x$	4.60	−0.14	0.000	0.93	14
	Summer low flow	Logarithmic	$y = a + b \ln x$	4.49	−0.16	0.000	0.86	14
$SUVA_{254}$	Winter low flow	S	$y = e^{(a+b/x)}$	1.67	−0.31	0.025	0.67	7
	Spring snowmelt	*Nonsignificant*						
	Summer low flow	Logarithmic	$y = a + b \ln x$	4.21	0.26	0.001	0.91	7

mixed streams showed a much larger response with respect to A_{254}/A_{365}, which shifted to ward the forested streams values during the spring snowmelt period. The major change in A_{254}/A_{365} occurred when runoff reached 3 mm day^{-1} (Figure 3), which happened during the first week of the snowmelt in 2004, and one month after the onset of the spring snowmelt period in 2005. $SUVA_{254}$ showed the opposite pattern, being low in forest streams and higher when the wetland coverage increased. However, $SUVA_{254}$ did not paint as clear a picture as A_{254}/A_{365}, especially not during 2005.

[16] Further exploration with regression analysis (Figure 4, Table 2) showed that wetland coverage could explain much of the spatial variation in the DOC concentration in the streams during winter low flow, but not during the peak of the spring snowmelt period (Figure 4a). In early summer there was a weak relationship between DOC concentration and wetland coverage, due to large interannual variation. In 2004 there was an exponential relationship ($r^2 = 0.73$, $p = 0.003$, $n = 7$), but in 2005 the regression was not significant. A_{254}/A_{365} decreased sharply with wetland coverage, indicated by the logarithmic regressions (Figure 4b, Table 2). There were also seasonal variations in A_{254}/A_{365}. The lowest values were found at winter low flow and the highest at peak flow. $SUVA_{254}$ increased rapidly with wetland coverage during both winter and summer low flow (Figure 4c). $SUVA_{254}$ was best described with an S-function of wetland coverage during winter low flow. During the peak of the spring snowmelt period, wetland coverage was not a significant parameter for $SUVA_{254}$.

[17] The forested and the mixed catchments (exemplified by C2 and C10, respectively; Figure 5) demonstrated similar patterns during the spring snowmelt with respect to hysteresis. The DOC concentrations increased and showed a clear clockwise hysteresis loop during the two studied years in both C2 and C10 (Figure 5 only show the data from 2004, the results from 2005 are discussed in the text). A_{254}/A_{365} also increased, especially at C10. The ratio A_{254}/A_{365} was higher on the rising limb than on the falling limb in 2004, and the major shift occurred during the first week of snow melt. In 2005, A_{254}/A_{365} in C2 and C10 increased but with more unclear/counterclockwise rotational patterns, i.e., the difference between the rising and the falling limb of the hydrograph was small. $SUVA_{254}$ decreased during the first week of snow melt 2004, creating a counterclockwise loop. In 2005, $SUVA_{254}$ decreased and showed a number of intertwined loops.

[18] In wetland dominated catchments (exemplified by C18), the pattern was different (Figure 5). During 2004, the DOC concentration increased from 25 to 35 mg L^{-1} during the winter low flow in March. After the onset of snowmelt the DOC concentration decreased rapidly, forming a counterclockwise loop over time. In 2005 DOC concentrations also decreased but the loop was clockwise. The A_{254}/A_{365} was lower in C18 compared to C2 and C10 and A_{254}/A_{365} was more or less stable in 2004. In 2005 A_{254}/A_{365} increased from 3.8 to 4.2 in C18, but there was no difference between the rising and the falling limb. $SUVA_{254}$ decreased, but showed no clear rotational pattern.

[19] The DOC character was different in forest and wetland soil water (Figure 6). The riparian forest soil water had a higher A_{254}/A_{365} and lower $SUVA_{254}$ than the wetland profile. A_{254}/A_{365} increased upward in the soil profile in both wetland (Figure 6a) and forest soil waters (Figure 6b) but the increase was more pronounced in the latter, where A_{254}/A_{365} increased by more than 1.5 units within 80 cm depth in the riparian zone. In the wetland, A_{254}/A_{365} increased less than 1 unit in 3 m. In the upslope S22-profile (not shown) A_{254}/A_{365} was 2.5 from 90 to 50 cm depth, and then increased to 4.5 near the surface, at 6–12 cm depth. $SUVA_{254}$ (not shown) decreased to ward the top of the soil in the wetland profile. This was the opposite of A_{254}/A_{365}. In the riparian forest profile the $SUVA_{254}$ was more or less stable at about 3.7 L mg C^{-1} m^{-1} while the wetland $SUVA_{254}$ was higher (3.7–4.5 L mg C^{-1} m^{-1}), indicating a more aromatic material in the wetland soil.

4. Discussion

[20] The spatial variation in DOC concentration and character was dependent on the forest-wetland proportion of the catchment (Figure 4). In wetland dominated streams, DOC concentrations and $SUVA_{254}$ were high, while A_{254}/A_{365} was low (Figures 3 and 4). This result is in agreement with previous studies showing that the highest DOC concentrations are found in waters draining wetlands [*Hope et al.*, 1994; *Mulholland*, 2003], and that carbon leaching from peat is more aromatic compared to forest drainage carbon [*Kalbitz et al.*, 2003; *Tipping et al.*, 1999]. In the forest dominated streams, DOC concentrations were lower and the DOC had high A_{254}/A_{365} and low $SUVA_{254}$, indicating more low molecular weight [*Dahlén et al.*, 1996; *De Haan*, 1993; *Strome and Miller*, 1978] and more aliphatic DOC [*Fu et al.*, 2006; *Weishaar et al.*, 2003]. In the soil water profiles, A_{254}/A_{365} increased toward the surface of the soils in both the riparian soil water profiles and the wetland soil water profile (Figure 6). A special feature of the sampled wetland was the preferential flow layer between 2 and 2.5 m depth, that corresponds to a layer of higher hydraulic conductivity [*Laudon et al.*, 2007], possibly including pipeflow. Inflow-
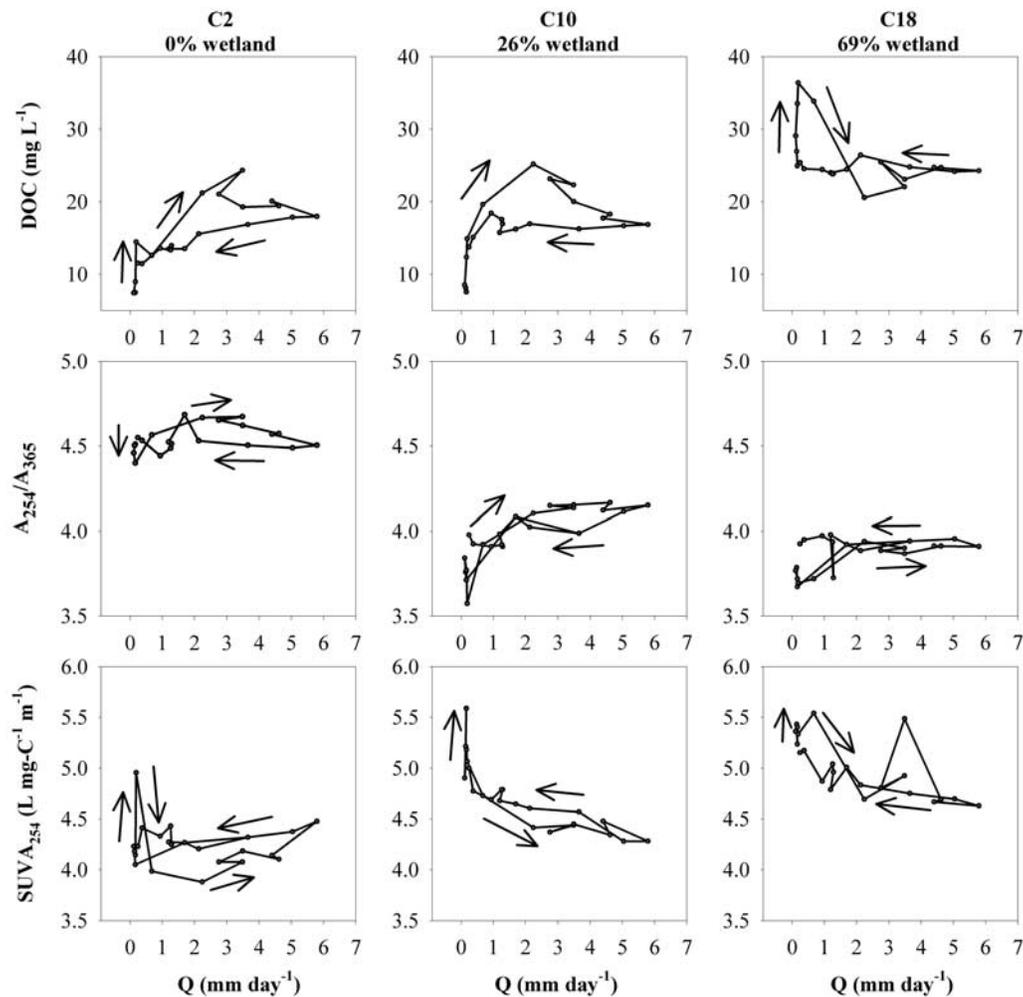
Figure 5. Concentration of DOC (mg L^{-1}), A_{254}/A_{365}, and SUVA$_{254}$ (L mg$-C^{-1}$ m^{-1}) versus runoff (mm day^{-1}) during the spring snowmelt period of 2004 (1 March−10 June) for three representative catchments with wetland coverages of 0% (C2), 26% (C10), and 69% (C18). Arrows indicate progression of time.

ing surface water and/or groundwater from the surrounding area is thought to have increased A_{254}/A_{365} in this layer in excess of what would be expected for a typical peat profile at this depth. Values of A_{254}/A_{365} in forest and mire dominated streams corresponded well with those of the sections of the soil profiles that represented major flow paths (Figures 6 and 7). An interesting result was how sensitive the DOC character in the streams was to the forest-wetland proportion, in particular during winter low flow. If the wetland cover was more than 10% (Figures 4b and 4c), the DOC character was similar to the most wetland dominated streams, suggesting that wetlands are a major source of stream organic carbon during this period.

[21] The DOC character also changed with runoff (Figures 3 and 4), especially in the wetland dominated and mixed streams. The DOC at snowmelt was apparently of lower molecular weight [Dahlén et al., 1996; De Haan, 1993; Strome and Miller, 1978] and more aliphatic [Fu et al., 2006; Weishaar et al., 2003] than at low flow. Other DOC characteristics have previously been studied in the investigated area. Contrary to the variations we found, Hruska et al.

[2001] did not find any variation in organic acid dissociation properties or site density (amount of carboxylic functional groups per milligram organic carbon), between forest and wetlands or between winter low flow and snowmelt. However, carboxylic acidity has been found to be surprisingly uniform among aquatic samples [Shuman, 1990].

[22] The temporal changes in A_{254}/A_{365} in the streams indicated flow dependent variations in DOC sources. The A_{254}/A_{365} increased up ward in all soil profiles and, hence, a rise in the water table increases A_{254}/A_{365} in the streams. Another important factor is that the relative importance of wetlands and forests to the DOC concentration change during spring snowmelt period. During snowmelt, the surface of the wetlands are frozen and the DOC from wetlands is diluted by low DOC snow melt water (Figures 3 and 7) [Laudon et al., 2004a, 2007]. However, in the forest streams, the DOC levels increased following the water table rise of the riparian zone [Bishop et al., 2004; Findlay et al., 2001; Hinton et al., 1998], also supported by the absorbance data in the riparian soil water profile (C2) (Figure 6b). The
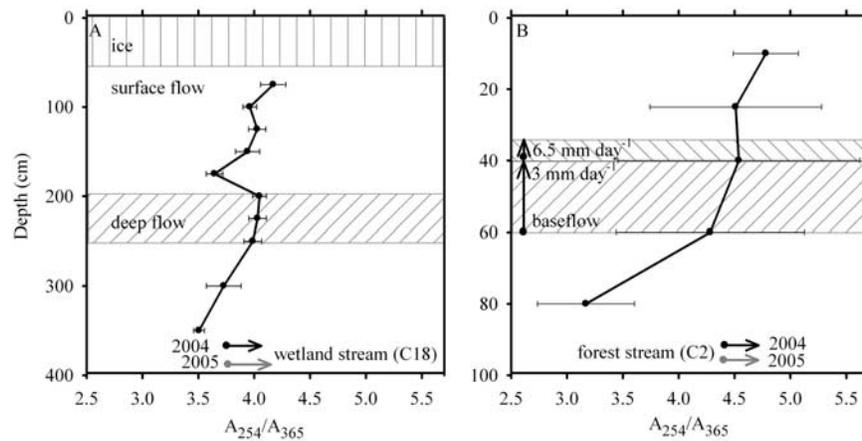
Figure 6. (a) Depth profile of A_{254}/A_{365} in a wetland, with major flow paths (deep, surface, and over ice) indicated after *Laudon et al.* [2007] and *Petrone et al.* [2007]. Error bars denote the temporal variation (SD) between six sampling occasions. (b) shows the depth profile of A_{254}/A_{365} in riparian soil water of a forested catchment. The curve shows the average of the three profiles in the riparian zone from different occasions. Error bars includes both temporal and spatial variation (SD). The horizontal arrows indicate the change in A_{254}/A_{365} from winter low flow to spring snowmelt high flow in (a) a wetland stream and (b) a forested stream. The vertical arrows in (b) show the groundwater level in riparian zone profile K9 corresponding to a range of stream flow values [*Laudon et al.*, 2004b].
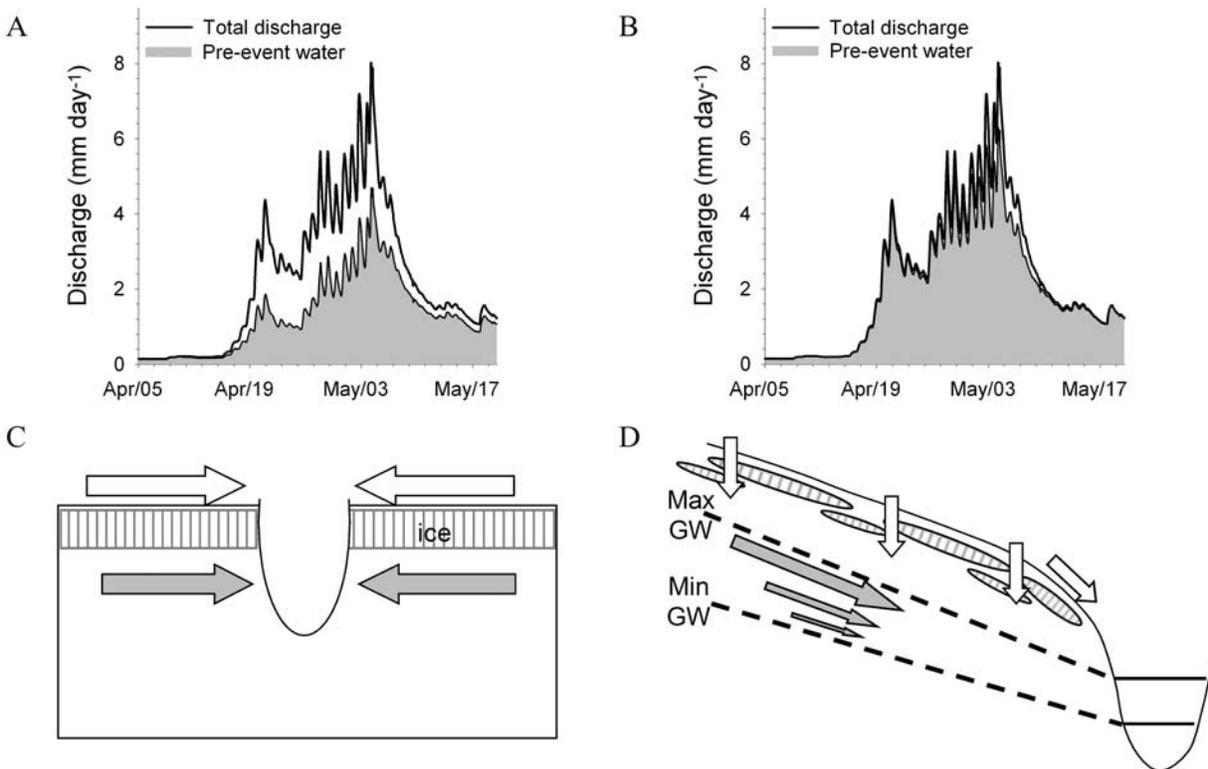

Figure 7. The hydrological mechanisms believed to explain intersite variation in the partitioning of water during the spring snowmelt period (modified from *Laudon et al.* [2007]). The stream spring hydrograph from (a) the wetland catchment C4 has similar proportions of event and preevent water, while the hydrograph from (b) the forested catchment C2 is dominated by preevent water. In (c) the wetland, a large proportion of snow melt waters cannot infiltrate the soil because of impermeable soil frost (hatched area) and instead of run off as overland flow or through preferential flow pathways (e.g., deep flow as shown in Figure 6). In (d) the forest, snow melt waters are able to infiltrate through the topsoil because of discontinuous soil frost (hatched ovals), raising the groundwater level into soil horizons of higher hydrologic conductivity, which results in more rapid lateral flow of preevent water.

change in A_{254}/A_{365} in the forest stream, from 4.3 to 4.7 between base flow and spring snowmelt period, corresponded to the change in A_{254}/A_{365} in the riparian soil profile from approximately 60 cm depth to 20 cm depth. These depths corresponded to the depths of the water table at winter low flow and spring peak flow. In the upper layers (6–12 cm depth) of the upslope soil profile S22 A_{254}/A_{365} was 4.5, indicating this layer as a possible source of DOC for the stream water. However, these layers are not hydrologically connected as the ground water level in S22 during peak flow is at 20 cm depth [Bishop et al., 2004].

[23] The similarity in DOC character between streams of mixed and wetland dominated catchments at winter base flow agrees with previous results from the region, demonstrating that wetlands represent a major source of DOC in winter [Buffam et al., 2007]. During spring snowmelt period, the relative importance of the forest sources increased due to the dilution of DOC in wetland areas [Hayashi et al., 2004; Schiff et al., 1998], in combination with an increase in DOC concentration in forested areas by activation of the riparian zone [Kendall et al., 1999]. Consequently, in the mixed streams, the A_{254}/A_{365} and $SUVA_{254}$ shifted toward values closer to those of forest streams during spring snowmelt period. Activation of the riparian zone could potentially have explained part of the change in DOC character in the wetland dominated stream C18 which had 31% forest coverage. However, the stream in C18 has no stream length in forested areas (the forested area is upslope of the wetland), thus the "riparian zone activation" is not applicable to the wetland site the way it is to the mixed sites. The increases in A_{254}/A_{365} in the wetland dominated stream were also consistent with the variation in the wetland soil profile, i.e., increasing contributions of water from higher in the profile where A_{254}/A_{365} was slightly higher.

[24] The major shift in DOC character during snowmelt occurred when runoff changed from winter low flow to at least 3 mm day^{-1}. A further increase in runoff brought little increase in groundwater levels due to the higher hydraulic conductivity in the shallower soil horizons. Thus more new soil DOC sources were activated per unit increase in runoff at the onset of snow melt (Figure 6b) which could explain the major shift in character at runoff up to 3 mm day^{-1}. This is in agreement with results from a previous investigation by Laudon et al. [2007] where oxygen-18 analyses were used to demonstrate the effect of soil frost on the partitioning of event and preevent water during snow melt in boreal regions. Stream monitoring as well as isotopic and hydrometric measurements from wetland and forest soil solution, enabled the development of a conceptual framework that could explain the variation in hydrological pathways (Figure 7). The principles behind different runoff generation processes in different landscape elements provide an understanding that is important when explaining the spatial variation in temporal dynamics in biogeochemistry, for example DOC characteristics, during the snow melt period. The vastly dominating fraction of preevent water in the forest stream is explained by infiltration of melt water in the forest soil, which leads to rising of the groundwater table resulting in increased lateral flow due to the increasing hydraulic conductivity toward the soil surface in glacial till soils. This leads to mobilization of previously stored water in the soil (with a DOC concentration and character determined by its vertical location in the soil horizon).

[25] The clockwise hysteresis pattern during the spring snowmelt period (Figure 5) could have been a result of different mechanisms; (1) flushing of a finite source [Boyer et al., 1997; Weiler and McDonnell, 2006], (2) different DOC sources during rising and falling limb, i.e., from near stream to more upslope sources [Hood et al., 2006; Kendall et al., 1999], or (3) changes in relative specific DOC export between forest and wetlands [Ågren et al., 2007; Laudon et al., 2004a]. The upslope more layer (S22) was not likely a significant source of DOC to stream runoff in these catchments, as they are not hydrologically connected to the streams [Bishop et al., 2004], as explained above, ruling out explanation (2). As the forest streams contain no wetlands but have the most pronounced hysteresis effect, this refutes (3) for these sites and leaves flushing of a finite leachable DOC pool in the riparian zone (1) the most plausible mechanism for the observed hysteresis effect in DOC and A_{254}/A_{365}.

[26] In conjunction with the mechanism for the forested streams described above, the clockwise hysteresis pattern for the mixed streams could further be explained by changes in specific DOC export between forest and wetlands (3). The declining DOC concentration for wetland areas resulting from overland flow during the spring snowmelt period (Figure 7) and the increase in DOC from the forested areas change the proportion of water from the two sources in the mixed streams during the shift from low flow to spring snowmelt period. Thus the higher A_{254}/A_{365} on the rising limb and peak flow in the mixed streams could be an effect of more forest derived DOC compared to the falling limb in combination with the flushing of a finite source, as discussed above.

[27] The rotational pattern of the hysteresis curves differed between the two years, further pointing to the importance of the intensity of snow melt. In 2004 the start of the spring snowmelt period was abrupt, resulting in a dramatic, rapid shift in the DOC character. In contrast, spring snowmelt runoff of 2005 (Figure 3) did not reach 3 mm day^{-1} until a month into the spring snowmelt period. Hence a less pronounced flushing effect was detected and the shift in DOC character was more gradual during this latter year.

[28] The decrease in $SUVA_{254}$ during snowmelt of 2004 indicates that a more aliphatic and bioavailable DOC [Fu et al., 2006; Perdue, 1998; Tranvik and Jørgensen, 1995; Weishaar et al., 2003] was exported during the spring snowmelt period. The result is in contrast to the investigation by Schuster et al. [2008] who found that the DOC in streamwater in northeastern USA became more aromatic with increasing discharge during snowmelt. The decrease in $SUVA_{254}$ in our system can be explained by the variation in the soil sources. The water-soluble organic carbon in forest soils is more leachable and aliphatic near the soil surface, with stability increasing with soil depth [Van Miegroet et al., 2005]. A similar vertical pattern was found in the wetland soil profile where $SUVA_{254}$ decreased toward the surface of the mire. It should be noted though, that $SUVA_{254}$ did not paint the same clear picture as the absorbance ratio and the levels in the streams did not always correspond to the levels in the soils. This is something that warrants further investigation.

[29] The change in DOC character during the spring snowmelt period brings implications for the export of bioavailable DOC. Different source pools vary in their degree of microbial processing prior to entry in the stream, and as a result their bioavailability can be expected to differ [*Buffam et al.*, 2001; *Kalbitz et al.*, 2003]. The importance of source variability was demonstrated by other studies in these streams which showed that the bacterial production (during 7-day-dark bioassays) was explained by both the quantity and quality (A_{254}/A_{365}) of the DOC. The DOC from forested catchments stimulated bacterial production much more than DOC from mire dominated catchments [*Ågren et al.*, 2008; *Berggren et al.*, 2007]. The increase in A_{254}/A_{365} in the streams during the spring snowmelt period was reflected in the bacterial production which also increased. This effect is contrary to what has been shown for temperate and tropical climates, where hydrological pulses usually have no or negative effects on the bioavailability of organic carbon in receiving lakes and rivers [*Farjalla et al.*, 2006; *Hood et al.*, 2006; *Kritzberg et al.*, 2004; *Leff and Meyer*, 1991; *Volk et al.*, 1997].

[30] Based on our results, we suggest that differences in DOC character were driven by variation in the hydrological pathways as well as catchment characteristics. DOC in wetland streams was more aromatic and had a higher molecular weight than the DOC in forest streams, a difference that largely could be explained by the DOC composition of the soil water that become hydrologically connected to the streams at different stages of the hydrograph.

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A. Ågren, M. Berggren, and M. Jansson, Department of Ecology and Environmental Science, Umeå University, SE-901 87 Umeå, Sweden. (anneli.agren@emg.umu.se)

K. Bishop, Department of Environmental Assessment, Swedish University of Agricultural Sciences, P.O. Box 7050, SE-750 07 Uppsala, Sweden.

I. Buffam, Ecosystem and Landscape Ecology Laboratory, Department of Zoology, University of Wisconsin, Madison, WI 53706, USA.

H. Laudon, Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, SE-901 83 Umeå, Sweden.