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Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements

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[1] Large spatial and temporal variations in stream total organic carbon (TOC) concentration and export occurred during an 11-year observation period (1993–2003) in a boreal headwater catchment. TOC flux and concentration patterns from mire- and forest-dominated subcatchments differed (mean annual flux 8.2 g m^{-2} a^{-1} versus 5.8 g m^{-2} a^{-1}). Temporal variations in stream TOC concentrations in both landscape types were primarily driven by variations in streamflow, with the mire stream generally diluting by half with increased runoff during spring flood and TOC from the forested landscape increasing during runoff peaks irrespective of season. Average TOC concentration in the mire stream in the snow-free season increased with increased seasonal precipitation from around 20 to 40 mg L^{-1} but then dropped to around 35 mg L^{-1} during very wet years. Average snow-free season TOC concentration at the forested site remained stable when summer precipitation was below average but then increased from 10 to around 25 mg L^{-1} during exceptionally wet years. For both the forested subcatchment and the whole catchment, TOC concentrations increased during the warm summer months during wet years, but no such increase occurred during dry years. Interannual variations in TOC flux were primarily driven by variations during the snow-free period. Wet years decreased the relative TOC export from the mire and favored the relative export of TOC from areas dominated by forest, an observation that also held true on a larger scale when similar landscape types were considered. Predicted climate change in rainfall and temperature patterns will affect the amount and character of TOC exported downstream from boreal landscapes with a mix of forest and mire.

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1. Introduction

[2] The short- and long-term dynamics of organic carbon in soils and streams are important for the transport of metals [*Gorham et al.*, 1998; *Tipping and Hurley*, 1992], acidity [*LaZerte*, 1993; *Köhler et al.*, 2002b], iron and phosphorous dynamics [*Dillon and Molot*, 1997a], biological carbon turnover in aquatic ecosystems [e.g., *Stepanauskas et al.*, 2000; *Karlsson et al.*, 2003], and base cation export [*Lydersen*, 1995; *Gorham et al.*, 1998]. Highly variable dissolved organic carbon (DOC) concentrations are responsible for most of the observed variations in pH, pCO_2 and buffering capacity in many pristine boreal streams in catchments with base poor bedrock such as granites, gneiss or schist [*Kahl et al.*, 1989; *Bishop et al.*, 1994; *Jansson and Ivarsson*, 1994; *Kortelainen*, 1993; *Laudon and Bishop*, 1999; *Algesten et al.*, 2004]. Changes in DOC concentrations in streams and surface waters due to climate change, land use, or pollution may lead to important changes in surface water chemistry with profound consequences for biota [*Schindler*, 1997]. Moreover, organic matter concentration is an important factor for drinking water quality both from an esthetic point of view and owing to the possible formation of harmful oxidation products during water treatment [e.g., *Chow et al.*, 2003].

[3] There is a large variability of stream DOC concentrations in both space and time in the boreal zone. Spatial variation of at least an order of magnitude is observed for neighboring headwater catchments [*Temnerud and Bishop*, 2005; *Buffam et al.*, 2007], and temporal changes of over 100% occur, often associated with drought, rainfall or snowmelt. Precipitation and streamflow [e.g., *Bishop et*

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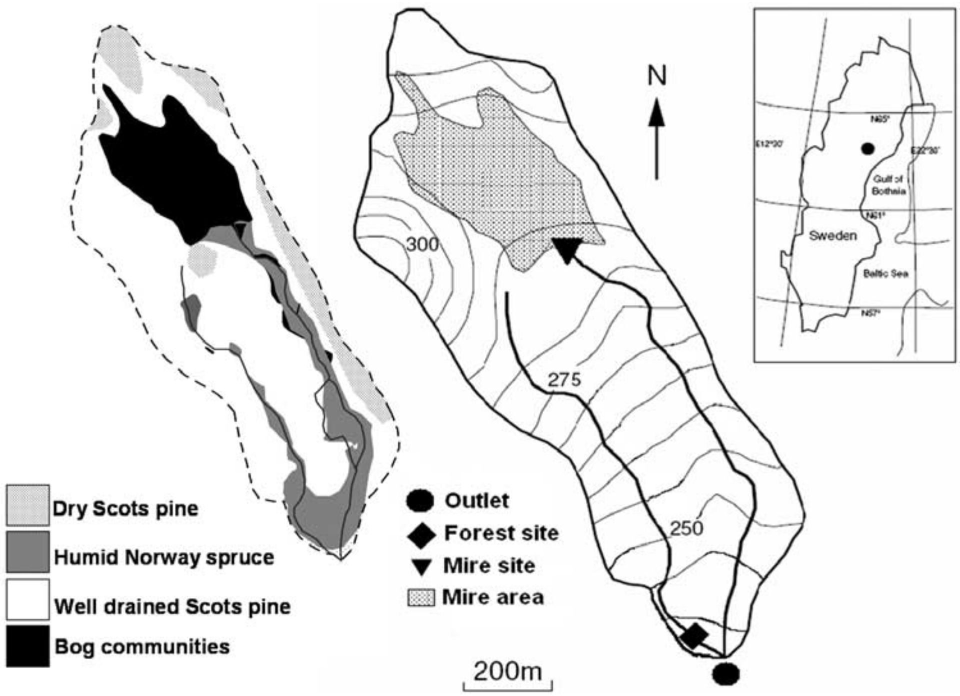

Figure 1. (left) Detailed vegetation map. (right) Map of Sweden with location of the Nyänget catchment, as well as a topographic-hydrographic map with stream sampling sites: headwater mire (triangle), headwater forested (diamond), and catchment outlet (circle).

al., 1990; *Hemond*, 1990; *Mulholland et al.*, 1990; *Grieve*, 1991; *Easthouse et al.*, 1992; *Schiff et al.*, 1997] as well as season and temperature [*Vance and David*, 1991; *LaZerte*, 1993; *Christ and David*, 1996a; *Gorham et al.*, 1998] all influence DOC concentrations and fluxes. Recently, decadal-scale temporal trends of increasing organic carbon concentrations in surface waters in Scandinavia and the UK have been documented [*Freeman et al.*, 2001; *Evans et al.*, 2005; *Worrall and Burt*, 2004; *Vuorenmaa et al.*, 2006]. In some cases these trends have been used to predict future DOC concentrations under climate scenarios [*Worrall and Burt*, 2005].

[4] Many studies are focused on understanding the observed long-term trends in varying and sometimes heterogeneous landscapes. The study of interannual dynamics and the possibility of varying signals from distinct landscape elements merit more attention. While larger catchments typically drain catchments of mixed landscapes, headwater catchments can present an opportunity to examine catchment-stream coupling in relatively homogeneous landscapes. This is important since different landscape elements may respond differently to basic environmental factors such as changing temperature or precipitation. Patterns of TOC concentrations frequently exhibit a seasonality over the course of a year at a given stream site but also may vary between years, as a result of variation in climate parameters. In order to identify important patterns and drivers influencing TOC at relevant temporal scales, long-term studies of between-year variation are required which also incorporate information about shorter-term within-year variations in TOC. Except for annual fluxes, which represent lumped data, much of the existing literature is focused on understanding episode driven TOC values that are the result of very distinct antecedent conditions at a particular site in a specific landscape. In boreal landscapes a characteristic hydraulic regime with high flow during spring flood and heavy autumn rains is common. Here we present an 11-year-long time series, encompassing a range of extreme climatic situations, of total organic carbon (TOC) concentration and flux from neighboring boreal mire and forest subcatchments, together with the patterns in a larger catchment downstream that includes both landscape elements. We analyze averages as well as variance of TOC values during different seasons and climatic situations in these two landscape elements. We argue that this type of analysis provides for an improved understanding of how intra-annual and interannual variability respond to variations in temperature and hydrologic inputs.

[5] The objectives of this study are to (1) define temporal variations (monthly, seasonal, and interannual timescales) in stream TOC concentrations and fluxes in two contrasting landscapes typical of the boreal zone, (2) examine the observed variations in relation to variations in climate, and (3) examine the effect of mixing headwaters with homogeneous landscape elements to simulate TOC temporal patterns in larger streams with heterogeneous landscape.

2. Materials and Methods

2.1. Site Description

[6] The study was conducted on the 50 ha Nyänget catchment in the Vindeln Experimental Forests (64°14′N, 19°46′E), 60 km northwest of Umeå, Sweden (Figure 1). The eastern tributary, the mire stream, originates in an 8 ha mire within a 19 ha subcatchment and then flows approximately 1 km to the catchment outlet. The western tributary

drains a 13 ha forested catchment (forest sampling site) and then joins the eastern tributary just above the outlet of the catchment (outlet sampling site). The water sampled at the outlet is thus a mixture of the water draining the forested subcatchment, the water from the mire sampling site and additional water originating from forested area downstream of the mire. These three sampling places will be referred to as "mire," "forest," and "outlet" in the following. Aside from the 8 ha mire, the Nyänget catchment is forested with 80-year-old Norway Spruce (*Picea abies*) in wetter areas and Scots pine (*Pinus sylvestris*) on drier soils. On the drier soils the field layer is a pine heath consisting primarily of heather (*Calluna vulgaris*) and lingonberries (*Vaccinium vitis-idaea*), while the wetter forested soils have a field layer primarily of blueberries (*Vaccinium myrtillus*), with *Sphagnum spp.* mosses on the mire and riparian wetlands. Like many other streams in the region the two tributaries were deepened to improve forest drainage, in this case during the 1920s. There are, however, no drainage ditches extending into the mire itself. Annual mean temperature (1981 to 2000) is 1°C, with an average air temperature in January and June of −11°C and 12°C, respectively. Precipitation was measured daily approximately 1 km from the outlet sampling location. Mean annual precipitation is 646 mm with an average runoff of 323 mm, giving rise to an estimated mean annual evapotranspiration of 323 mm for the whole catchment. The catchment was snow covered 171 days per year, on average, during the months December to May [*Ottosson Löfvenius et al.*, 2003].

[7] Typical Podzols on glacial till formed from biotite plagioclase schist (quartz, feldspar, hornblende, and biotite) and orthogneiss (quartz, biotite, amphiboles, and pyroxenes) cover most of the catchment, except for the fibric Histosols in the mire above the mire stream sampling location and the riparian wetlands where histic Gleysols occur. The forest upland soils in the area roughly correspond to the areal distribution of Scots pine in Figure 1. They are ferric Podzols with a sandy texture that blend into humic Podzols with a loamy texture when approaching the streams. The intermittently water logged riparian wetlands closer to the streams are covered by Norway spruce (see Figure 1) on histic Gleysols. These soils have a coarse and fibrous organic top layer of around 20 cm thickness followed by a moist and temporarily water logged peaty horizons of around 10 cm thickness which is underlain by a grey sandy loam. More information may be found in the work of *Bishop et al.* [1990] and *Cory et al.* [2007].

2.2. Stream Water Sampling

[8] Hourly streamflow was calculated from continuous height measurements made at the V notch weirs at the outlet, forested and mire stream using Campbell Scientific data loggers equipped with pressure transducers. Over 50 calibrations of each of the weirs have been conducted using salt dilution and bucket measurements. The outlet weir is located in a heated building. At the forested and mire stream, discharge was not measured continuously during winter months, and there are some gaps in the snow-free period for the years 1993–1995. Discharge was calculated for the missing periods by calibrating the relationship between manual weekly stage readings at the forested and mire stream to the continuous discharge at the heated dam house at the outlet. Hourly flow was averaged to give mean daily flow throughout the entire record for each site. The associated error is estimated to be below 5% [*Laudon et al.*, 2007].

[9] Approximately 1500 stream water TOC samples were collected during the 11-year period. TOC samples were collected at the outlet, forested and mire stream weirs (Figure 1). The weekly or biweekly sampling regime was augmented with additional samples taken during high flow snowmelt periods, and some rain driven episodes. Weekly sampling began in 1993 at the forested and mire stream, and one and a half years later at the outlet. For 1993 and 1994 carbon export at the outlet was estimated from the export data from an extra sampling site 10 m upstream from the outlet but downstream of the mire stream (Figure 1). A linear regression of the measured TOC at the extra sampling site and that at the outlet reveals a very strong relationship ($Outlet_{TOC} = 0.99Extra_{TOC} + 1.2$; $R^2 = 0.93$ n = 73 $\sigma_{TOC} = 1.9$). Data for 1995 through 2003 revealed that the calculated TOC fluxes from the extra site are very closely related to those measured at the outlet. This was verified using data from the outlet minus that from the forested site ($Outlet_{TOCFLUX} = 1.04Extra_{TOCFLUX} + 0.15$; $R^2 = 0.98$ n = 7 $\sigma_{TOCFLUX} = 0.64$). Samples for TOC analyses were frozen immediately after collection. TOC analyses during the early period (1993–1994) were analyzed using a Dohrmann Carbon Analyzer while samples after 1995 were analyzed using a TOC-5000 Shimadzu. *Peltzer et al.* [1996] could not find any systematic difference when comparing both techniques when samples were properly diluted. Numerous comparisons over the years indicate that at these sites DOC represents more than 90% of TOC during all flow conditions. However, as the samples used in this study were unfiltered we use the term Total Organic Carbon (TOC) throughout the text.

2.3. Data Analysis

[10] For data presentation and basic statistical analysis, the TOC concentration and flux data were aggregated to give monthly values (mean and total for concentration and flux, respectively). For the purposes of flux calculations, daily TOC concentration was constructed through linear interpolation of TOC between the sampling occasions. Total export was estimated by multiplying these daily TOC values with average daily discharge. In an alternative approach, we also calculated volume-weighted TOC flux according to the following equation:

$$TOC_{flux} = \frac{\sum_{i=1}^{total\ days\ in\ seasons} q_i}{\sum_{j=1}^{days\ with\ sampling} q_j} \sum_{j=1}^{days\ with\ sampling} \left(TOC_j * q_j\right). \quad (1)$$

[11] The reported monthly mean TOC concentrations were not weighted by stream discharge or in any other way. In most graphs and tables the data have been divided into three characteristic periods (seasons): snow cover (December through March), snowmelt (April and May) and snow free (June through November). Student's t-test (SPSS for Windows v 14.0) was used to compare monthly and seasonal TOC concentration averages between groups of wet (above average precipitation) and dry (below average precipitation) years. To account for multiple comparisons at

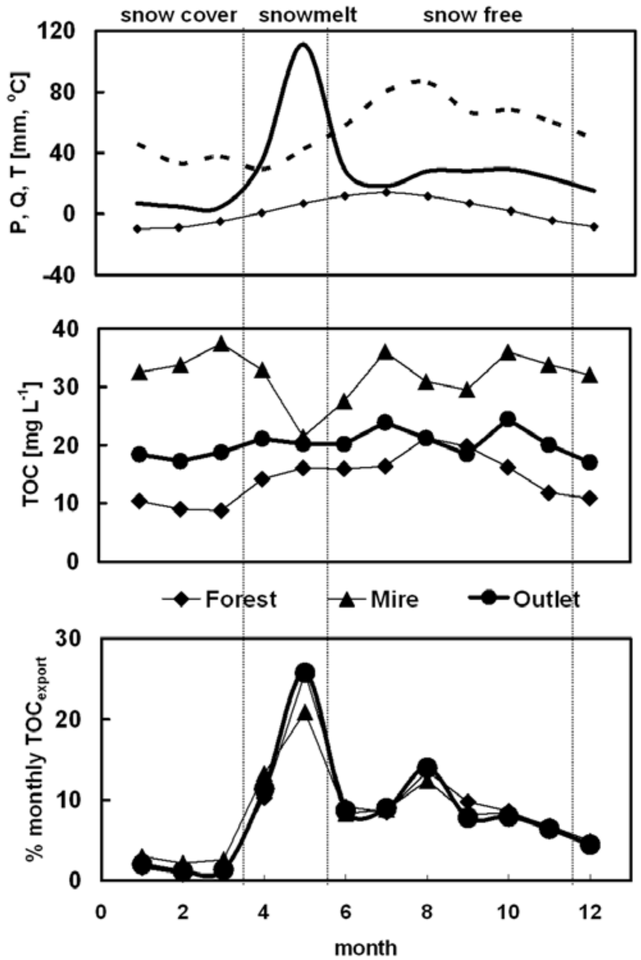

Figure 2. (top) Long-term (1983–2003) mean monthly climate variables: air temperature (diamonds), flow (black line), and precipitation (dashed line). (middle) Long-term (1993–2003) monthly average total organic carbon (TOC) in the forest, mire site, and outlet. (bottom) Mean percentage of annual TOC export occurring in each month for the three studied catchments.

each site (N = 15 including 12 months and 3 seasons), a Bonferroni multiple t-test correction was applied to give a total Type 1 error probability of $\alpha = 0.05$ for each site.

[12] Linear regression analysis (Microsoft Excel 2003) was used to examine linear correlations between mean monthly TOC concentrations and mean monthly soil water temperature or total monthly precipitation. For this analysis, soil temperature during the snow-free period at 30 cm depth in the organic horizon of the riparian zone 4 m from the stream within the forested catchment was calculated according to equation (2), which uses measured daily air temperature as the sole variable input parameter:

$$T_i^{soil} = a\frac{\sum_{i-1}^{i-15} T_i^{soil}}{14} + b\frac{\sum_{i-7}^{i-21} T_i^{air}}{14}. \quad (2)$$

This relationship best mimics the amplitude and shift of soil versus air temperature and was fitted using available in situ temperature probe readings during the snow-free period for the years 1996 through 2001 using the SOLVER function in Microsoft Excel 2003, minimizing the sum of errors between the measured and estimated values according to equation (2) during the observation period. The average error in prediction using the best fit parameters a = 0.743 and b = 0.158 is 0.6°C for an observed range of 0 to 9°C.

3. Results

[13] The average (1981–2003) monthly temperature, precipitation, and flow at the outlet are displayed in Figure 2 (top). The average air temperatures remain below freezing until April. Snowmelt occurs in April and May leading to the highest monthly flows. On average 40% of the annual flow occurs during these two months. Temperatures and monthly precipitation amount increase through the late spring and summer, with temperature peaking in July and precipitation in August. In autumn temperatures decrease while autumn rains typically maintain streamflow at a moderately high level. While spring flood occurs predictably as an extended 4–6 week event in April–May, the timing and intensity of summer and autumn rains vary substantially from year to year. For 10 of the 11 years, the days on which stream TOC sampling occurred accounted for at least 9% of the time and 15% of the total annual water export at each site.

[14] The 11 years sampled (Table 1) encompass the hydrological range experienced during the period for which climate data exists at this site (1981–2003). During this 23-year record, the three driest years with respect to precipitation were 1994, 1997, and 2002 (446–514 mm) while the three wettest years were 1982 (1019 mm), 1998 (847 mm) and 2000 (828 mm). The highest annual runoff values at the outlet were recorded in 1998 (497 mm), 2000 (576 mm) and 2001 (523 mm) while the lowest were recorded in 1996 (128 mm), 2002 (212 mm) and 1997 (212 mm). Thus, the 11-year TOC sampling period generally represents the climatic extremes experienced during the past 23 years, except for the highest precipitation year which occurred in 1982.

[15] The long-term average monthly TOC concentrations in the forested stream start at around 10 mg L^{-1} during the snow cover season, then increase during the snowmelt period and throughout the summer, peaking in August at 19 mg L^{-1} (Figure 2). During autumn the concentrations decrease again. In the mire stream average monthly TOC concentrations are much higher, around 35 mg L^{-1} during the snow cover period, but dilute strongly during the snowmelt period to around 20 mg L^{-1}. During the snow-free period, TOC concentrations increase again, but with a tendency for lower concentrations during August and September, coinciding with the late summer/autumn rains. The pattern at the catchment outlet shows less variation in average monthly TOC, with a concentration (17–24 mg L^{-1}) intermediate between those of the two subcatchments (Figure 2).

[16] The long-term pattern in average monthly fluxes of TOC from the three catchments resemble one another, and generally follow the annual hydrograph (Figure 2). On average around 35% of the TOC is exported during snowmelt, another 55% during the snow-free period and only

Table 1. Average Annual Climate Data, Annual and Snow-Free Season Volume-Weighted TOC Export, and Annual TOC Concentration for the Three Sampling Sites on the Nyänget Catchment[a]

Year	Q (mm)	Q* (mm)	P (mm)	P* (mm)	Tair (°C)	Tair* (°C)	Forest ($mg\ L^{-1}$) TOC	Mire ($mg\ L^{-1}$) TOC	Outlet ($mg\ L^{-1}$) TOC	$Forest_{total}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export	$Forest_{snow\ free}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export	$Mire_{total}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export	$Mire_{snow\ free}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export	$Outlet_{total}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export	$Outlet_{snow\ free}$ ($g\ m^{-2}\ a^{-1}$) TOC-Export
1993	418	240	711	474	1.6	5.6	15.4	31.0	22.5	8.2 (8)	5.2 (5.1)	10.3 (9.5)	7.2 (6.6)	11 (10.2)	7.4 (6.9)
1994	262	48	446	238	1.2	7.2	10.6	24.2	15.4	2.9 (2.9)	0.7 (0.6)	4.9 (4.9)	1 (0.9)	4.6 (4.3)	0.8 (0.8)
1995	291	75	550	265	1.9	7.2	11.7	29.3	16.8	4.7 (4.6)	1.8 (1.6)	7 (6.4)	2.3 (1.9)	6.4 (6.2)	1.9 (1.7)
1996	128	80	553	390	1.2	7.1	14.4	41.8	25.3	2.3 (2)	1.5 (1.3)	4.8 (4.3)	3.2 (2.9)	4.1 (3.2)	2.5 (2.1)
1997	212	50	514	307	2.5	8.4	13.9	36.2	21.5	3.1 (2.7)	0.8 (0.7)	4.8 (5.7)	1.5 (1.5)	4.1 (4.1)	1.1 (1.1)
1998	508	286	847	579	1.5	6.8	20.0	37.8	25.1	11.9 (12.4)	8.7 (8.8)	12.6 (13.8)	7.5 (8)	12.1 (12.4)	8.2 (8.1)
1999	257	56	549	268	2.2	8.8	13.4	22.3	15.7	3.3 (3.4)	0.7 (0.7)	4.6 (5.1)	1.1 (1)	4.1 (4.2)	0.9 (0.9)
2000	558	286	828	523	3.3	8.7	14.5	35.3	20.3	10.4 (10.1)	6.4 (6.3)	12.4 (13.7)	6.7 (7.4)	13.2 (12.8)	8.1 (7.9)
2001	523	329	825	570	1.8	8.3	20.1	31.2	23.7	10.9 (11)	7.6 (7.7)	15.1 (17.1)	11.1 (12.7)	13.9 (12.7)	9.8 (8.9)
2002	212	39	470	278	2.5	7.6	11.7	25.5	15.7	3.1 (2.4)	0.5 (0.5)	6.5 (4.2)	1.4 (1.1)	5.6 (3.6)	1.2 (0.8)
2003	232	130	597	412	2.6	8.1	12.8	35.8	24.4	3.2 (3.2)	1.8 (1.9)	7.5 (6.1)	4.9 (4.2)	9.3 (5.9)	5.9 (3.6)
Average	351	147	626	391	1.9	7.6	14.4	31.9	20.6	5.8 (5.7)	3.2 (3.2)	8.2 (8.3)	4.3 (4.4)	8 (7.2)	4.4 (3.9)
SD	155	114	149	129	0.7	1.0	3.1	6.2	4.0	3.7 (3.9)	3.1 (3.1)	3.8 (4.5)	3.4 (3.8)	3.9 (4)	3.5 (3.4)

[a]Values in parentheses are calculated according to equation (1). Q* is the amount of flow measured at the outlet occurring during the snow-free period June to November. P* is the amount of precipitation occurring during the snow-free period June to November. Tair* is air temperature measured during the snow-free period June to november.

around 10% during the snow cover period. The maximum average monthly export occurs in May during snowmelt, with April also above average reflecting the early portion of the spring flood. An additional peak in average monthly export occurs in August, coinciding with the maximum average monthly precipitation.

[17] The annual average area normalized export (±standard deviation) of TOC during the period 1993–2003 at the outlet is 8.0 ± 3.9 $g\ m^{-2}\ a^{-1}$ (Table 1). Area normalized export from the forested stream is lower (5.8 ± 3.7 $g\ m^{-2}\ a^{-1}$), while area normalized export from the mire stream is higher (8.2 ± 3.8 $g\ m^{-2}\ a^{-1}$). Interannual variability in annual (Table 1 and Figure 3) and monthly (Table 2) TOC export is high, with annual fluxes varying by a factor of 6 at the forested stream, and by a factor of 4 at the mire stream and the outlet. The variation in annual export was dominated by the variation in export during the snow-free season (Figure 3). With the exception of one year (1996) with extremely little snow (less than 40% of average), interannual variability in TOC export during snowmelt is low (2.3 ± 0.5 $g\ m^{-2}\ a^{-1}$ for the forested stream, 3.1 ± 1.0 $g\ m^{-2}\ a^{-1}$ for the mire stream) relative to that during the snow-free period (3.2 ± 3.1 $g\ m^{-2}\ a^{-1}$ for the forested stream, 4.4 ± 3.4 $g\ m^{-2}\ a^{-1}$ for the mire stream). Variation at the outlet stream generally follows the patterns observed in the two subcatchments, with intermediate fluxes (Figure 3).

[18] TOC export during snowmelt was linearly related to the amount of water present in the catchment in the form of snow during the preceding winter and snow/rain during snowmelt, for both the forested and the mire subcatchment (Figure 4). Linear regressions are included in Figure 4 for the snowmelt season (solid line, forested site–$R^2 = 0.73$; dashed line, mire site–$R^2 = 0.65$) and the data for which P > 350 mm during the snow-free season (solid line, forested site–$R^2 = 0.98$; dashed line, mire site–$R^2 = 0.77$), while a horizontal line approximating the relationships during the snow-free season for P < 350 mm has been added to guide the reader's eye. During snowmelt the mire mobilizes on average one and a half times as much carbon per m^2 of catchment as the forested catchment. This is in line with the annual averages of surface normalized TOC export (Table 1).

[19] During the snow-free season, the relationship between precipitation and TOC export was nonlinear for both subcatchments. TOC export was low and independent of precipitation amount for years in which snow-free season precipitation was below around 350 mm. Above this threshold, TOC export is linearly related to snow-free season precipitation amount and the slope of TOC export versus precipitation was steeper during the snow-free season than the winter for the mire and particularly the forested subcatchment (Figure 4).

[20] During the 11-year record there were four years with higher than average TOC export in all of the subcatchments (Table 1). These years also all had snow-free season precipitation of >450 mm and total annual precipitation >700 mm, both of which are above the long-term (1983–2003) average for respective period (413 mm, 626 mm). In the remaining text we refer to these 4 years (1993, 1998, 2000 and 2001) as wet years, while the other 7 years with below average snow-free season precipitation are referred to as dry years. During dry years, the mass of TOC exported per millimeter of precipitation during the snow-

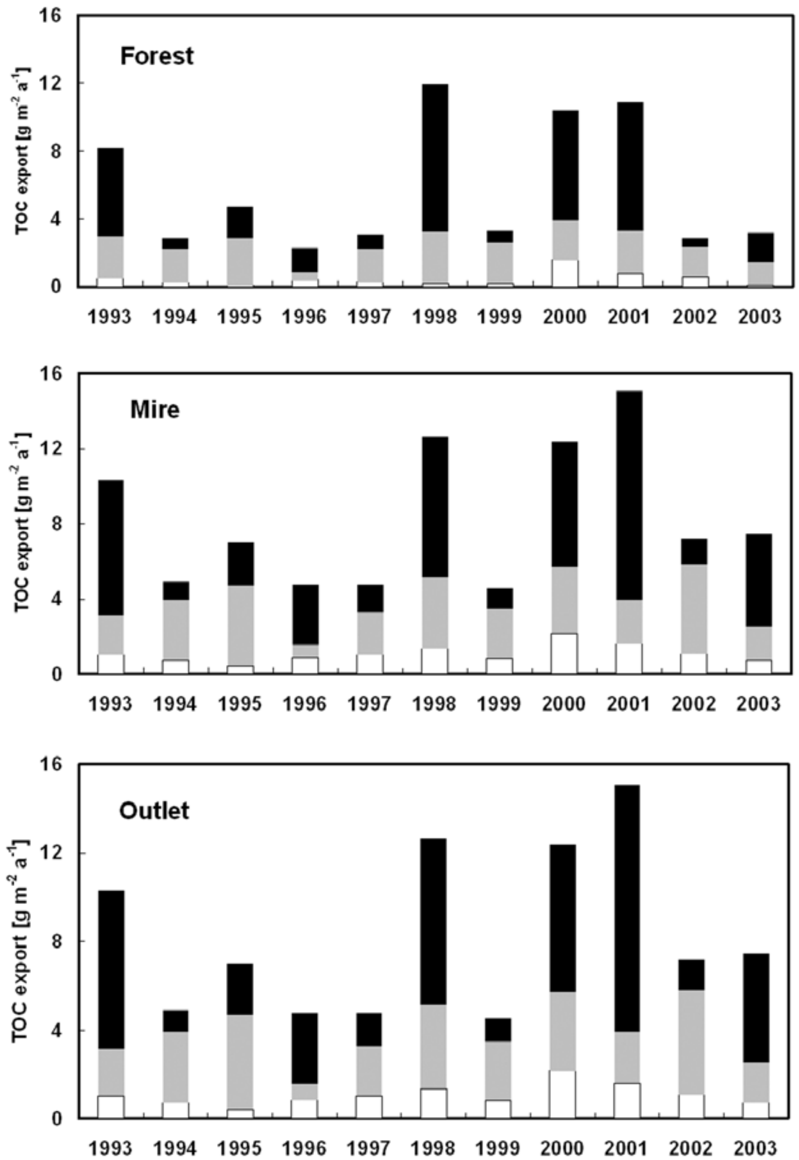

Figure 3. Annual TOC export in the forest, mire site, and outlet for the period 1993–2003, with each year divided into snow cover (white), snowmelt (grey), and snow-free (black) periods.

free season was lower than that recorded for the snowmelt season, where much of the precipitation translates directly into runoff (compare black labeled data points to the white data points for P < 350 mm in Figure 4). Only during wet years with snow-free season precipitation above ca 350 mm, was the mass of TOC exported per millimeter of precipitation equal to or exceeding that during the snowmelt period in both the mire and the forested catchment. In the wet years the water exported as stream runoff was on average 4 times higher than during dry years, for all sites (Table 1). During these same wet years, the forested catchment exported on average 6.3 times more C and the mire catchment 3.7 times more TOC than during the dry years.

[21] The average TOC concentration varied as a function of precipitation during the snow-free season, for both mire and forested subcatchments (Figure 5). In the forested subcatchment TOC averaged around 12 mg L^{-1} during dry years, while during wet years the average was linearly correlated with precipitation, up to 26 mg L^{-1} during 1998. In the mire site, TOC concentrations averaged around 35 mg L^{-1} during all but the driest snow-free seasons. During dry snow-free seasons (<350 mm precipitation), TOC in the mire site was lower, averaging for instance 21 mg L^{-1} during 1994. The nonlinear relationships implied by the data in Figure 5 are highlighted with a solid line for the forested site and a dashed line for the mire site and follow the regression line in the range P >350 mm for the forested site with R^2 of 0.97 and P <350 mm for the mire site with R^2 of 0.83.

[22] In dry years, the monthly average TOC concentrations at the forested site decreased after snowmelt (Figure 6a), while the opposite was true for the mire site (Figure 6b). This translated into relatively constant average monthly TOC throughout the dry years at the outlet (Figure 6c). During

Table 2. Long-Term Monthly Averages for Climate Parameters, as Well as Monthly Means and Coefficients of Variation for TOC Fluxes and Concentrations for the Three Sampling Sites on the Nyänget Catchment[a]

	$Forest_{total}$ (g m^{-2} a^{-1})	CV (%)	Forest (mg L^{-1})	CV (%)	$Mire_{total}$ (g m^{-2} a^{-1})	CV (%)	Mire (mg L^{-1})	CV (%)	$Outlet_{total}$ (g m^{-2} a^{-1})	CV (%)	Outlet (mg L^{-1})	CV (%)
Jan	0.09	103	10.4	33	0.25	60	32.5	20	0.16	80	18.4	17
Feb	0.05	101	9.0	23	0.18	61	33.8	21	0.10	60	17.3	21
Mar	0.05	75	8.8	23	0.22	55	37.4	18	0.11	49	18.8	26
Apr	0.60	57	14.2	44	1.10	55	32.9	35	0.91	57	21.1	24
May	1.49	57	16.1	22	1.73	61	21.4	29	2.07	58	20.2	16
Jun	0.53	65	15.9	34	0.69	67	27.5	27	0.70	61	20.2	24
Jul	0.49	93	16.4	39	0.73	76	36.0	27	0.72	84	23.9	32
Aug	0.78	136	21.2	36	1.02	114	30.9	38	1.12	120	21.2	41
Sep	0.56	221	19.8	46	0.68	192	29.5	44	0.63	191	18.4	49
Oct	0.50	134	16.2	45	0.70	99	36.0	35	0.64	103	24.4	34
Nov	0.38	139	11.8	38	0.56	85	33.8	18	0.52	121	20.0	26
Dec	0.26	160	10.9	50	0.40	87	32.0	23	0.36	131	17.0	33

[a]CV, coefficient of variation.

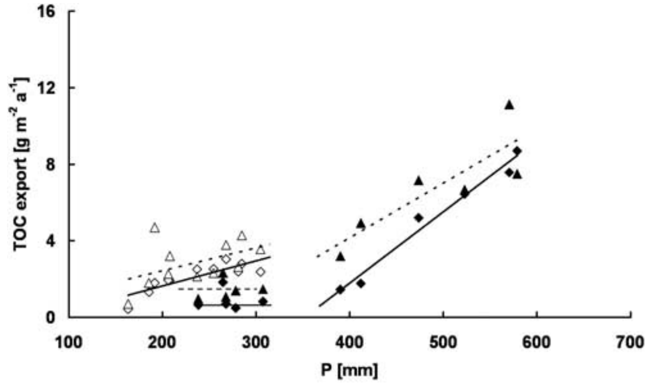

Figure 4. Annual variation in seasonal TOC fluxes for the forested and mire sites. Snowmelt season export (white symbols) is plotted against precipitation during the snowmelt and preceding snow cover season, while snow-free season export (black symbols) is plotted against precipitation during the same snow-free season.

the wet years, average monthly TOC increased during the snow-free season at all three sites, and remained elevated during September and October. At the forested site, the snow-free season had a tendency for higher TOC during wet than dry years, and the individual months of July, August, and December had significantly higher TOC during wet than dry years. In the mire site differences between wet and dry years were not significant for any season or month. At the outlet site, the snow-free season had a tendency for higher TOC during wet than dry years, and the month of August had significantly higher TOC during wet than dry years (Figure 6). During the snow-free season, TOC concentration patterns in the outlet were similar to those of the mire site (Figures 6b and 6c) during dry years, while during wet years the outlet exhibited a seasonal pattern similar to that at the forested site, suggesting a greater contribution from forested areas during wet years.

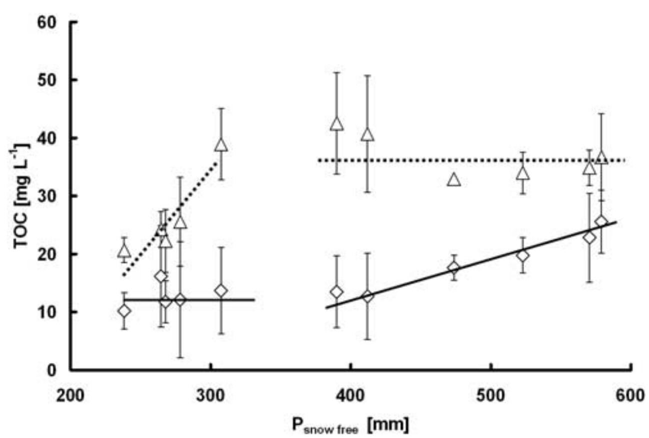

Figure 5. Averages of snow-free season TOC concentration at the forested and mire sites as a function of precipitation during the snow-free season in a given year. Error bars represent standard deviations from averaging individual TOC concentration measurements for the entire snow-free season in a given year.

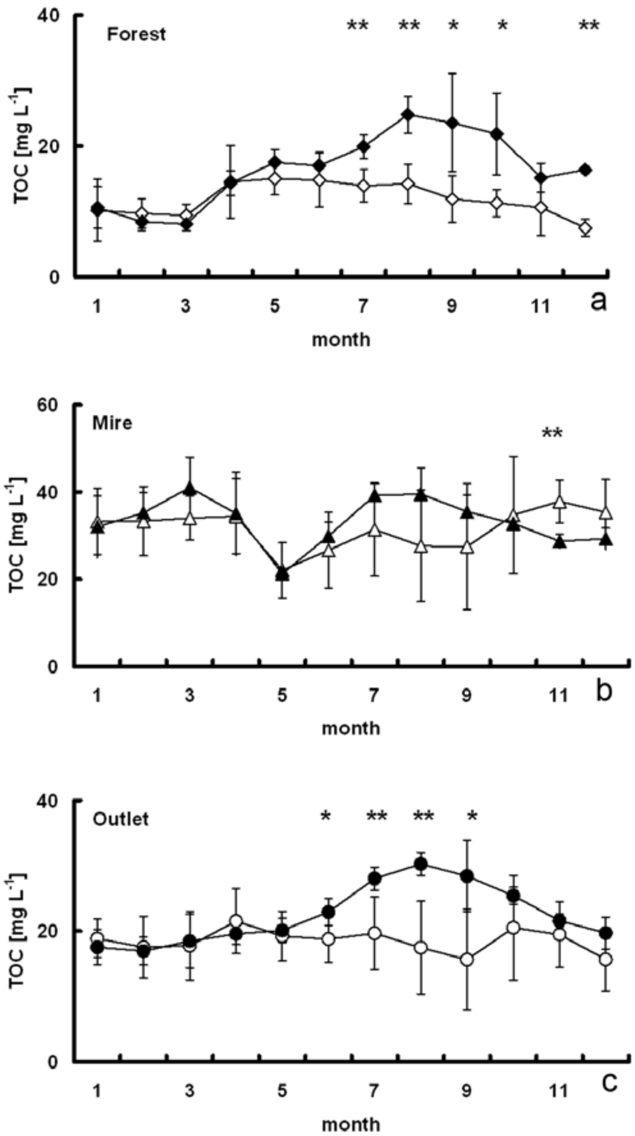

Figure 6. Monthly average TOC concentration for the (a) forested site, (b) mire site, and (c) outlet. White symbols represent the monthly means for seven dry years (1994, 1995, 1996, 1997, 1999, 2002, and 2003), and black symbols represent those for four wet years (1993, 1998, 2000, and 2001). Error bars are standard deviations between the years in each group. Asterisks indicate a significant difference (Student's t-test with Bonferroni correction for multiple comparisons) between wet and dry year TOC concentrations for the given month at the $\alpha = 0.05$ level.

[23] When aggregated as monthly averages, TOC concentrations in the forested stream for the entire period of record had a weak positive linear correlation with the temperature of the soil at 30 cm depth in the riparian zone ($R^2 = 0.15$, $P < 0.001$, $N = 104$). The correlation was much stronger during wet years ($R^2 = 0.64$, $P < 0.001$, $N = 40$) and not significant during dry years ($R^2 = 0.03$, $P = 0.21$, $N = 64$). Similarly, the same analysis using the months of the snow-free season gave a strong positive relationship between TOC and soil temperature during wet years ($R^2 = 0.45$, $P = 0.001$, $N = 22$) and a nonsignificant relationship during dry years ($R^2 = 0.05$, $P = 0.19$, $N = 35$). When the wet years were analyzed individually instead of pooling, relationships between snow-free season monthly temperature and monthly TOC concentration tended to be even stronger (R^2 = 0.55, 0.32, 0.88, 0.64 for the years 1993, 1998, 2000, 2001, respectively).

4. Discussion

[24] Recently, the importance of small catchments for the hydrochemistry of larger streams was emphasized in a 3-year study on temporal and spatial variation of DOC in a mesoscale (67 km^2) boreal catchment [*Ågren et al.*, 2007; *Buffam et al.*, 2007]. *Alexander et al.* [2007] quantified the contribution of nitrogen fluxes from headwater catchments to higher-order streams as up to 70%. A better understanding of the temporal variations of headwater catchments is thus essential for quantifying the potential impact of different human influences on water quality in downstream lakes and rivers. And, while larger catchments typically drain catchments of mixed landscapes, headwater catchments can present an opportunity to examine catchment-stream coupling in relatively homogeneous landscapes.

[25] The two most important boreal landscape elements studied here, forest and mire, behave differently during the different seasons and between wet and dry years. Contrasting behavior in DOC patterns from forested and mire areas in the boreal zone has been previously noted, particularly during the snowmelt-driven spring flood [*Laudon et al.*, 2004a; *Buffam et al.*, 2007]. TOC concentrations and export patterns from mixed catchments are the result of the separate signals from different landscape elements contained therein. In order to identify how a mixed landscape will respond to different drivers of environmental change, such as climate, the response of discrete landscape elements need to be considered separately [*Bishop et al.*, 1994; *Eckhardt and Moore*, 1990; *Hruška et al.*, 2001]. *Eckhardt and Moore* [1990] classified streams into upland and lowland streams and received significantly better relationships between wetland area and DOC in the upland catchments. Similar results in line with this observation were recently obtained by *Billett et al.* [2006]. Downstream sample sites with mixed landscapes may therefore have obscured signals than hamper interpretation of environmental relationships.

[26] The TOC concentrations in the two headwater subcatchments in this study are within the range of earlier studies on the temporal variation of stream and lake organic carbon in the northern hemisphere and especially the boreal region [*Eckhardt and Moore*, 1990; *Kortelainen et al.*, 1997; *Biron et al.*, 1999; *Mulholland*, 2003]. Export of TOC in our study varied from 2–15 g m^{-2} a^{-1}, which is on the lower end of the 8–40 g m^{-2} a^{-1} range reported for peatlands by *Urban et al.* [1989], but typical of the range experienced in boreal streams [*Hope et al.*, 1994; *Mulholland*, 2003, and references therein].

[27] The concentration of TOC from the headwater mire and forested subcatchment respond in opposite ways to snowmelt, with the forested stream increasing its concentration, while the mire stream decreases in concentration. The increase in average TOC concentration in the forested catchment during the snowmelt period is in line with earlier

detailed studies of this and other headwater forested catchments in the region [*Laudon et al.*, 2004a]. Hydrochemical studies in the forested catchment have demonstrated that the TOC increase results from the contribution of soil water stored over winter, while little new snowmelt directly enters the stream during spring flood [*Laudon et al.*, 2004b; *Petrone et al.*, 2007a] and overland flow is minimal or nonexistent [*Nyberg et al.*, 2001]. Soil lysimeter measurements indicate little or no dilution of TOC in the riparian zone soil profile of the forested subcatchment even following spring flood, when the pore water held in those profiles has been exchanged several times over [*Petrone et al.*, 2007a].

[28] During spring flood TOC concentrations at the mire stream typically dilute from about 40 mg L^{-1} to about 20 mg L^{-1}. This is similar to the dilution reported in superficial peat pore waters in the mire site [*Petrone et al.*, 2007b]. This decrease of TOC in the mire during spring flood, and also during prolonged rainy periods in the autumn could be due to a combination of simple dilution or exhaustion of soluble TOC in the peat. *Christ and David* [1996a] observed a fast decrease in leachable DOC during repeated soil extractions. During spring flood the most probable explanation is dilution, since the input of new snowmelt water in the mire stream is on the order of 50% [*Laudon et al.*, 2007], which is similar to the TOC concentration decline during spring flood.

[29] During the snow-free period, the increase in stream TOC concentrations likely indicates the effect of production/biotic activity in the respective catchments with rising temperature [*Christ and David*, 1996b]. The riparian zone of the forested stream functions as a source of TOC [*Cory et al.*, 2007] with peak concentrations in the forested catchment usually occurring in the month of July. This corresponds to the month of peak average precipitation and highest air temperature. *Grieve* [1991] found that 25% of the variance of the DOC variation in soil solution DOC can be explained by the maximum temperature of the previous month.

[30] Annual patterns in TOC flux in this study were primarily driven by variation in stream water flow rather than variation in concentration, as is the case for many other sites and regions [*Urban et al.*, 1989; *Hope et al.*, 1994, and references therein; *Clair and Ehrman*, 1998]. Annual TOC fluxes from the different subcatchments varied by a factor of 6, while the annual mean concentrations varied by a factor of less than 2. In the boreal region of the Northern hemisphere, this annual TOC flux includes a large component during the snowmelt driven spring flood [*Laudon et al.*, 2004a], with additional flux associated with summer and autumn rain events.

[31] Snowmelt related TOC export is very stable at all sites. The strong linear correlation ($R^2 = 0.7–0.8$) between water equivalents in the winter precipitation and TOC export during snowmelt (Figure 4) suggests that the process of carbon mobilization is similar, for example, a limiting kinetic control or limited soil water contribution that are reproducible during the flushing of the melted snow through the soils, during each year and that there is no strong memory effect from the preceding snow-free season conditions. A striking feature in the comparison of the different landscape elements, forest and mire, is the contrast in TOC export between seasons, and the nonlinearity of the response of TOC export to the amount of precipitation during the snow-free period in both the mire and the forested catchments (Figures 3 and 5). A strong dependence of TOC export on amount of precipitation or runoff has been observed in numerous previous studies [e.g., *Eckhardt and Moore*, 1990; *Kortelainen et al.*, 1997; *Urban et al.*, 1989; *Dillon and Molot*, 1997b; *Mulholland*, 2003]. However, in the current study we additionally note the relatively stable snowmelt TOC export contrasting the more variable export during the snow-free season. Interannual variation of concentration in this study during the snow-free period was large, especially in the forested catchment. This variability contributed substantially to the interannual variability in C fluxes the during the snow-free period. This is reflected in the up to 4 times larger coefficient of variation (CV) of TOC export during the snow-free period with respect to the snow cover period in all catchments and a doubling of the CV for TOC concentrations during the snow-free period (Table 2).

[32] The nonlinear response of the snow-free season export from the forested catchment to precipitation in this study can be attributed to several factors. If evapotranspiration is high relative to precipitation, groundwater levels including water levels in the riparian zone remain low and produce little runoff. In contrast, during cold (i.e., little evapotranspiration) or very wet years groundwater level may rise into organic rich soil layers that contribute to streamflow. Prevailing wet conditions may then favor the production of DOC [*Christ and David*, 1996b] and temperature signals directly translate into changes of stream TOC concentrations. This observation is in accordance with an earlier study done by *Eckhardt and Moore* [1990] who reported that the poor relationships observed between stream DOC and percent wetland in lowland catchments may be attributed to the dry summers when the sampling was undertaken.

[33] The slope of the relationship between precipitation and C flux during the wet, snow-free seasons is indicative of the volume-weighted concentration of stream TOC (Figure 4). The increase in TOC concentration during wet snow-free seasons at the forested site in this study (Figure 5) is due to the activation of organic rich soil layers in the riparian zone, as shown by *Bishop et al.* [2004]. This hydrological explanation is sufficient to explain the observed TOC increases, both the overall pattern (Figure 2) and the differences observed between dry and wet years (Figure 6). *Biron et al.* [1999] observed that even moderate year-to-year variations in antecedent moisture conditions may significantly affect the hydrochemistry. Furthermore, *Mitchell et al.* [2006], who also studied a forested landscape, noted that progressive storms had a marked influence on stream DOC concentrations as the watershed wetness increased which is in good accordance with our findings.

[34] Effects of temperature on DOC have been reported by a number of authors [*Christ and David*, 1996a; *Michalzik et al.*, 2003; *Billett et al.*, 2006; *Worrall et al.*, 2006]. Severe droughts in peatlands [*Worrall et al.*, 2006] led to an increase in DOC and *Billett et al.* [2006] could connect higher temperatures with increasing DOC in shallow peat soils. These authors report that a combination of stream temperature, flow and soil DOC explained 55% of the observed variation in the shallow histosols in a small catchment in NE

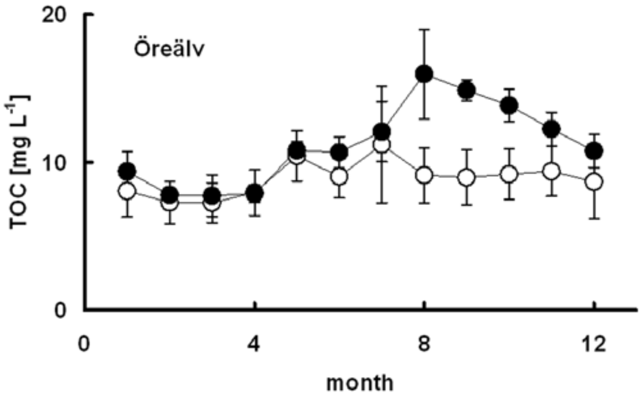

Figure 7. Monthly average TOC concentration for the river Öreälv, the nearest large Environmental Protection Agency monitoring site that has a distribution of landscape types close to that above the outlet of the 50 ha Nyänget catchment. (Öreälv has 2860 km^2 catchment, 81% forested, and 14% mire.) White symbols represent the monthly means for seven dry years, and black symbols represent those for four wet years during 1993–2003 just as in Figure 5. Error bars represent standard deviations between the years in each group.

Scotland. This is why we cannot rule out the impact of increased productivity during the warmer months on TOC concentrations. Production of DOC in soils has been shown to increase with temperature [*Christ and David*, 1996a, 1996b], though this effect on DOC concentrations may be minor relative to other limitations such as sorption kinetics. The elevated concentrations observed in our study at the forested site during wet years may in part result from higher rates of DOC production in superficial soil layers during warm periods. This is supported by the positive correlation between mean monthly soil temperature and mean monthly TOC concentration during wet years (corresponding to flow through upper soil layers), and the lack of consistent significant relationship during dry years (when water tables are restricted to deeper soils). *Michalzik et al.* [2003] found that the supply of the DOC from the surface soil horizon to percolating water depended on the production of easily leached humic material in upper organic horizons, which is a temperature-dependent process. In contrast, *Michalzik et al.* [2003] suggested that fluxes and concentrations in the deeper mineral soil layers were controlled by sorption, thus not temperature dependent.

[35] The importance of considering the response of different landscape elements goes beyond concentration and flux to include quality. While the acid-base character of TOC from the two landscape elements do not differ [*Hruška et al.*, 2001], many other quality parameters of organic carbon such as hydrophobicity, % humic substances, C/N ratio, C/Al ratio and SUVA do depend on landscape type [e.g., *Bishop et al.*, 1994; *Hruška et al.*, 2001; *Temnerud et al.*, 2007]. And, bioavailability of DOC in higher-order boreal streams and downstream lakes is strongly influenced by the character of the incoming organic carbon [e.g., *Jansson et al.*, 1996; *Berggren et al.*, 2007]. DOC from forested areas gives rise to a higher bacterial productivity and efficiency than DOC from mire areas [*Berggren et al.*, 2007]. Forest-derived soil organic carbon in streams has a higher potential for microbial uptake than carbon originating from the mire [*Köhler et al.*, 2002a] and both photodegradation and bacterial degradation influence pH and pCO_2. Our results indicate that wetter conditions lead to increased TOC concentrations in the forested landscape and favor the fraction of carbon that originates from that landscape. This pattern might be an important driver of TOC cycling downstream.

[36] To see if the pattern of influence of wet and dry years that was observed in the study catchment can be generalized to larger scales, we analyzed TOC data from Öreälv, the nearest Swedish EPA river monitoring site that has a distribution of landscapes types close to that of the mixed catchment studied here (81% forested, 14% mire), located around 70km south of the Nyänget research area. Long-term TOC export at this 2860 km^2 river catchment is 3.6 g m^{-2} a^{-1} [*Jonsson et al.*, 2007]. After grouping the same dry and wet years during 1993–2003, a striking similarity between the pattern in the 0.5km^2 Nyänget "outlet site" and that of the 2860 km^2 Öreälv becomes apparent (Figure 7). While the monthly, snow-free TOC concentration hardly changes during dry years, there is a distinct prolonged summer/autumn peak in TOC concentration during wet years in Öreälv just as was observed in the smaller forested catchment. The increase in TOC leads to an average depression in pH in the river of 0.3 pH units during the whole snow-free period and up to 0.5 pH units during august. During these same wet years the concentrations of the elements iron, phosphorous and copper which all are known to be cotransported with TOC are on average 40–50% higher than during the dry years (data from http://www.ma.slu.se). This suggests that understanding the processes occurring in boreal headwater streams provides a critical foundation for addressing environmental issues related to riverine TOC at larger scales.

5. Concluding Remarks

[37] During wet years, the influence of forested areas increased relative to mire areas, in terms of contribution to both export and concentrations of stream TOC. The climate in Sweden is predicted to become warmer and wetter with a higher frequency of precipitation in the coming decades [*Andreasson et al.*, 2004]. Our study shows that in the boreal zone it is critically important to consider both landscape type and the season in which the precipitation falls. Increasing precipitation in catchments with larger mire surfaces will respond with increased TOC export in an approximately linear fashion irrespective of the relative distribution as snow or rain. Catchments with high percentage of forested area on the other hand will respond more strongly if the increased precipitation mainly occurs during the snow-free season.

[38] This study has succeeded in showing that the behavior of headwater streams in a mixed boreal landscape reflects the inputs of two distinct landscape elements. It remains to be seen if the signal from the two landscape elements will be consistently visible downstream in larger catchments, after there has been more in-stream processing and lakes have appeared in the channel network. The nearest large river with similar overall landscape cover

showed strikingly similar intra-annual and interannual patterns in TOC to our study headwater catchment, suggesting that the relationships we have observed may also apply at larger scales.

References

Ågren, A., et al. (2007), Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, *J. Geophys. Res.*, *112*, G03003, doi:10.1029/2006JG000381.

Alexander, R. B., et al. (2007), The role of headwater streams in downstream water quality, *J. Am. Water Resour. Assoc.*, *43*, 41–59.

Algesten, G., et al. (2004), Organic carbon budget for the Gulf of Bothnia, *J. Mar. Syst.*, *63*, 155–161.

Andreasson, J., S. Bergstrom, B. Carlsson, L. P. Graham, and G. Lindstrom (2004), Hydrological change: Climate change impact simulations for Sweden, *Ambio*, *33*(4–5), 228–234.

Berggren, M., H. Laudon, and M. Jansson (2007), Landscape regulation of bacterial growth efficiency in boreal freshwaters, *Global Biogeochem. Cycles*, *21*, GB4002, doi:10.1029/2006GB002844.

Billett, M. F., et al. (2006), Connecting organic carbon in stream water and soils in a peatland catchment, *J. Geophys. Res.*, *111*, G02010, doi:10.1029/2005JG000065.

Biron, P. M., et al. (1999), The effects of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed, *Hydrol. Processes*, *13*, 1541–1555.

Bishop, K. H., et al. (1990), The origins of acid runoff in a hillslope during storm events, *J. Hydrol.*, *116*, 35–61.

Bishop, K., et al. (1994), Identification of the riparian sources of aquatic dissolved organic-carbon, *Environ. Int.*, *20*, 11–19.

Bishop, K., J. Seibert, S. J. Köhler, and H. Laudon (2004), Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry, *Hydrol. Processes*, *18*, 185–189.

Buffam, I., et al. (2007), Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network, *J. Geophys. Res.*, *112*, G01022, doi:10.1029/2006JG000218.

Chow, A. T., et al. (2003), Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils, *Water Res.*, *37*, 4475–4485.

Christ, M. J., and M. B. David (1996a), Dynamics of extractable organic carbon in Spodosol forest floors, *Soil Biol. Biochem.*, *28*, 1171–1179.

Christ, M. J., and M. B. David (1996b), Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol, *Soil Biol. Biochem.*, *28*, 1191–1199.

Clair, T. A., and J. M. Ehrman (1998), Using neural networks to assess the influence of changing seasonal climates in modifying discharge, dissolved organic carbon, and nitrogen export in eastern Canadian rivers, *Water Resour. Res.*, *34*, 447–455.

Cory, N., H. Laudon, S. Köhler, J. Seibert, and K. Bishop (2007), Evolution of soil solution aluminum during transport along a forested boreal hillslope, *J. Geophys. Res.*, *112*, G03014, doi:10.1029/2006JG000387.

Dillon, P. J., and L. A. Molot (1997a), Dissolved organic and inorganic carbon mass balances in central Ontario lakes, *Biogeochemistry*, *36*, 29–42.

Dillon, P. J., and L. A. Molot (1997b), Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments, *Water Resour. Res.*, *33*, 2591–2600.

Easthouse, K. B., et al. (1992), Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, southern Norway, *Water Res.*, *28*(6), 1585–1596.

Eckhardt, B. W., and T. R. Moore (1990), Controls on dissolved organic carbon concentrations in streams, southern Quebec, *Can. J. Fish. Aquat. Sci.*, *47*, 1537–1544.

Evans, C. D., et al. (2005), Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts, *Environ. Pollut.*, *137*, 55–71.

Freeman, C., et al. (2001), Export of organic carbon from peat soils, *Nature*, *412*, 785.

Gorham, E., et al. (1998), The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands, *Wetlands*, *18*(1), 115–132.

Grieve, I. C. (1991), A model of dissolved organic carbon concentrations in soil and stream waters, *Hydrol. Processes*, *5*, 301–307.

Hemond, H. F. (1990), Acid neutralizing capacity, alkalinity, and acid-base status of natural waters containing organic acids, *Environ. Sci. Technol.*, *24*(10), 1486–1489.

Hope, D., et al. (1994), A review of the export of carbon in river water: Fluxes and processes, *Environ. Pollut.*, *84*, 301–324.

Hruška, J., et al. (2001), Acid/base character of organic acids in a boreal stream during snowmelt, *Water Resour. Res.*, *37*, 1043–1056.

Jansson, M., and H. Ivarsson (1994), Causes of acidity in the river Lillån in the coastal zone of central Northern Sweden, *J. Hydrol.*, *160*, 71–87.

Jansson, M., P. Blomqvist, A. Jonsson, and A. K. Bergstrom (1996), Nutrient limitation of bacterioplankton, autotrophic and mixotrophic phytoplankton, and heterotrophic nanoflagellates in Lake Ortrasket, *Limnol. Oceanogr.*, *41*(7), 1552–1559.

Jonsson, A., et al. (2007), Integrating aquatic carbon fluxes in a boreal catchment carbon budget, *J. Hydrol.*, *334*, 141–150.

Kahl, J. S., et al. (1989), The influence of organic acidity on the acid-base chemistry of surface waters in Maine, USA, *Water Air Soil Pollut.*, *46*, 221–233.

Karlsson, J., A. Jonsson, M. Meili, and M. Jansson (2003), Control of zooplankton dependence on allochthonous organic carbon in humic and clear-water lakes in northern Sweden, *Limnol. Oceanogr.*, *48*(1), 269–276.

Köhler, S., et al. (2002a), Photochemical and microbial processing of stream and soilwater dissolved organic matter in a boreal forested catchment in northern Sweden, *Aquat. Sci.*, *64*, 269–281.

Köhler, S., et al. (2002b), Evaluation of different approaches to quantify strong organic acidity and acid-base buffering of organic-rich surface waters in Sweden, *Water Res.*, *36*, 4487–4496.

Kortelainen, P. (1993), Contribution of organic acids to the acidity of Finnish lakes, Ph.D. dissertation thesis, Water and Environ. Res. Inst., Natl. Board of Waters and Environ., Helsinki.

Kortelainen, P., et al. (1997), Leaching of nitrogen from forested catchments in Finland, *Global Biogeochem. Cycles*, *11*, 627–638.

Laudon, H., and K. H. Bishop (1999), Quantifying sources of acid neutralisation capacity depression during spring flood episodes in Northern Sweden, *Environ. Pollut.*, *105*, 427–435.

Laudon, H., et al. (2004a), Seasonal TOC export from seven boreal catchments in northern Sweden, *Aquat. Sci.*, *66*, 223–230.

Laudon, H., J. Seibert, S. Köhler, and K. Bishop (2004b), Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff, *Water Resour. Res.*, *40*, W03102, doi:10.1029/2003WR002455.

Laudon, H., V. Sjoblom, I. Buffam, J. Seibert, and M. Morth (2007), The role of catchment scale and landscape characteristics for runoff generation of boreal streams, *J. Hydrol.*, *344*(3–4), 198–209.

LaZerte, B. D. (1993), The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp, *Biogeochemistry*, *18*, 153–175.

Lydersen, E. (1995), Effects of cold and warm years on the water chemistry at the Birkenes Catchment, Norway, *Water Air Soil Pollut.*, *84*, 3–4.

Michalzik, B., et al. (2003), Modelling the production and transport of dissolved organic carbon in forest soils, *Biogeochemistry*, *66*, 241–264.

Mitchell, M. J., et al. (2006), Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: A combined hydrological, chemical and isotopic approach, *Biogeochemistry*, *78*, 217–246.

Mulholland, P. (2003), Large-scale patterns in dissolved organic carbon concentration, flux, and sources, in *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, pp. 139–159, Elsevier, New York.

Mulholland, P. J., et al. (1990), Hydrogeochemical response of a forested watershed to storms: Effects of preferential flow along shallow and deep pathways, *Water Res.*, *26*(12), 3021–3036.

Nyberg, L., M. Stahli, P. E. Mellander, and K. H. Bishop (2001), Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations, *Hydrol. Processes*, *15*(6), 909–926.

Ottosson Löfvenius, M., et al. (2003), Snow and soil frost depth in two types of shelterwood and a clear-cut area, *Scand. J. Forest Res.*, *18*, 54–63.

Peltzer, E. T., et al. (1996), A comparison of methods for the measurement of dissolved organic carbon in natural waters, *Mar. Chem.*, *54*, 85–96.

Petrone, K., I. Buffam, and H. Laudon (2007a), Hydrologic and biotic control of nitrogen export during snowmelt: A combined conservative and reactive tracer approach, *Water Resour. Res.*, *43*, W06420, doi:10.1029/2006WR005286.

Petrone, K. C., et al. (2007b), The influence of fire and permafrost on subarctic stream chemistry during storms, *Hydrol. Processes*, *21*, 423–434.

Schiff, S. L., et al. (1997), Export of DOC from forested catchments on the Precambrian Shield of central Ontario: Clues from C-13 and C-14, *Biogeochemistry*, *36*, 43–65.

Schindler, D. W. (1997), Climate-induced changes in the dissolved organic carbon budgets of boreal lakes, *Biogeochemistry*, *36*, 9–28.

Stepanauskas, R., H. Laudon, and N. O. G. Jorgensen (2000), High DON bioavailability in boreal streams during a spring flood, *Limnol. Oceanogr.*, *45*, 1298–1307.

Temnerud, J., and K. Bishop (2005), Spatial variation of streamwater chemistry in two Swedish boreal catchments: Implications for environmental assessment, *Environ. Sci. Technol.*, *39*, 1463–1469.

Temnerud, J., J. Seibert, M. Jansson, and K. Bishop (2007), Spatial variation in discharge and concentrations of dissolved organic carbon in a catchment network of boreal streams in northern Sweden, *J. Hydrol.*, *342*(1), 72–87.

Tipping, E., and M. A. Hurley (1992), A unifying model of cation binding by humic substances, *Geochim. Cosmochim. Acta*, *56*, 3627–3641.

Urban, N. R., et al. (1989), Export of dissolved organic carbon and acidity from peatlands, *Water Resour. Res.*, *25*, 1619–1628.

Vance, G. F., and M. B. David (1991), Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest floor, central Maine, USA, *Geochim. Cosmochim. Acta*, *55*, 3611–3625.

Vuorenmaa, J., et al. (2006), Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003, *Sci. Total Environ.*, *365*, 47–65.

Worrall, F., and T. Burt (2004), Time series analysis of long-term river dissolved organic carbon records, *Hydrol. Processes*, *18*, 893–911.

Worrall, F., and T. Burt (2005), Predicting the future DOC flux from upland peat catchments, *J. Hydrol.*, *300*, 126–139.

Worrall, F., T. P. Burt, and J. K. Adamson (2006), Trends in drought frequency: The fate of DOC export from British peatlands, *Clim. Change*, *76*(3–4), 339–359.

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