Key Points:
- Temporal variability in stream [DOC] was strongly related to air temperature
- Temporal variability in DOC character was related to stream discharge
- DOC export rates were among the highest so far presented for Scandinavia

Temporal control on concentration, character, and export of dissolved organic carbon in two hemiboreal headwater streams draining contrasting catchments

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Abstract Although lateral carbon (C) export from terrestrial to aquatic systems is known to be an important component in landscape C balances, most existing global studies are lacking empirical data on the soil C export. In this study, the concentration, character, and export of dissolved organic carbon (DOC) were studied during 2 years in two hemiboreal headwater streams draining catchments with different soil characteristics (mineral versus peat soils). The streams exposed surprisingly similar strong air temperature controls on the temporal variability in DOC concentration in spite of draining such different catchments. The temporal variability in DOC character (determined by absorbance metrics, specific ultraviolet absorbance 254 ($SUVA_{254}$) as a proxy for aromaticity and a254/a365 ratio as a proxy for mean molecular weight) was more complex but related to stream discharge. While the two streams showed similar ranges and patterns in $SUVA_{254}$, we found a significant difference in median a254/a354, suggesting differences in the DOC character. Both streams responded similarly to hydrological changes with higher a254/a365 at higher discharge, although with rather small differences in a254/a365 between base flow and high flow (<0.3). The DOC exports ($9.6-25.2\,g\,C\,m^{-2}\,yr^{-1}$) were among the highest reported so far for Scandinavia and displayed large interannual and intraannual variability mainly driven by irregular precipitation/discharge patterns. Our results show that air temperature and discharge affect the temporal variability in DOC quantity and character in different ways. This will have implications for the design of representative sampling programs, which in turn will affect the reliability of future estimates of landscape C budgets.

1. Introduction

Global estimates of the inland water carbon (C) balance are usually based on various approaches where the terrestrial export of C to aquatic systems is the unknown term that is used to balance a steady state condition [*Cole et al.*, 2007; *Tranvik et al.*, 2009; *Aufdenkampe et al.*, 2011]. The magnitude of these indirect estimates on the global C exports from soils ($2-3\,Gt\,C\,yr^{-1}$) is close to the global terrestrial C uptake [*Randerson et al.*, 2002; *Intergovernmental Panel on Climate Change (IPCC)*, 2013]. However, since the soil C export is indirectly determined, such estimates will be associated with considerable uncertainty derived from the individual uncertainty of all other included components in the aquatic mass balance. Hence, there is an urgent need to produce empirical data on the terrestrial C export in order to improve future global C balance estimates. Also, since the soil C export is highly dynamic, information about temporal variability is required to make such estimates reliable.

Dissolved organic carbon (DOC) is one of the major C components contributing to the total C export from soils to aquatic systems. On a temporal scale, discharge and temperature have been identified as main drivers for DOC concentration variations in streams, either as single-variable control or by a combination of these variables [*Dawson et al.*, 2008; *Raymond and Saiers*, 2010; *Winterdahl et al.*, 2014]. Hydrological dynamics are known to affect the terrestrial-aquatic connectivity and hence the DOC mobility and transport from different source areas within a catchment [*Laudon et al.*, 2011; *Grabs et al.*, 2012]. Temperature has been found to be tightly coupled to the terrestrial production of DOC [*Christ and David*, 1996] but also to affect the solubility of DOC within the soil and hence the mobility [*Jardine et al.*, 1989]. In areas where discharge has been shown to be positively correlated to the temporal variability in stream

DOC concentration, these relationships have been attributed to a thin and shallow organic soil horizon, i.e., a strong DOC concentration gradient in the catchment soil profile decreasing with depth [*Boyer et al.*, 1997; *Hinton et al.*, 1998; *Laudon et al.*, 2011]. At a high groundwater table, DOC is mobilized and exported from the most superficial organic-rich soil layer. In contrast, results showing a strong temperature control on stream DOC concentration with little hydrological influence have been explained by a homogenous soil profile (often peatland dominated areas) with small differences in DOC concentration among different hydrological flow paths [*Schiff et al.*, 1998; *Winterdahl et al.*, 2011, 2014]. To use a paired catchment approach would be an option to better understand differences in the temporal control on stream DOC among these commonly found soil features described above.

In addition to concentration dynamics and the amount of C being exported to aquatic systems, the character of the DOC is central for the processing of C along the aquatic continuum, stretching from the terrestrial-aquatic interface to the ocean [*del Giorgio and Davis*, 2003; *Weyhenmeyer et al.*, 2012]. Whether the C will be mineralized and transferred back to the atmosphere or be buried in lake or ocean sediments will have large-scale implications for landscape C budgets. The bulk DOC pool found in streams is a complex mixture reflecting the different sources within the catchment. Hence, the bioavailability of the stream DOC varies both on a spatial and temporal scale depending on its origin [*Berggren et al.*, 2007, 2009]. Spatial patterns in stream DOC character are often attributed to the distribution and proportion of different land cover elements in the catchment such as forests, mires, and lakes [*Ågren et al.*, 2008; *Temnerud et al.*, 2009]. The temporal variability in DOC character in northern boreal and temperate catchments has been found to be related to variation in hydrology affecting the dominating source areas in the catchment [*Hood et al.*, 2006; *Ågren et al.*, 2008]. These discharge-DOC character relationships have been observed in catchments where hydrology also has a strong influence on the stream DOC concentrations. However, it is less clear if DOC concentration and character dynamics are interrelated and really underlie similar control mechanisms, e.g., through variability in discharge and/or temperature.

Headwater streams typically represent a large portion of the total terrestrial-aquatic interface of the landscape; they are therefore excellent systems for detailed studies on the terrestrial export of solutes, including DOC, to aquatic systems [*Gomi et al.*, 2002; *Alexander et al.*, 2007; *Köhler et al.*, 2008]. Headwater streams typically integrate a larger and more representative landscape unit (catchment) than detailed terrestrial studies conducted at the plot scale but are small enough in size to make land cover-specific studies possible. Such land cover-specific studies can give fundamental insights in how different landscape features may differ in their control on stream DOC quantity and character. Compared to studying larger aquatic systems, the small size of headwater streams is also characterized by short water residence times (hours to days), which make in-stream processes modulating the DOC concentration/character generally being of low importance [*Köhler et al.*, 2002; *Berggren et al.*, 2009].

In this study we investigated the control on temporal variability in concentration, character (using absorbance metrics), and export of DOC for two nearby hemiboreal headwater streams draining catchments with distinctly different land cover (mineral versus peat soils). To our knowledge, such headwater-based boreal studies that combine temporal dynamics of both concentration dynamics, exports, and character of DOC are rare in the literature. The catchments were located in south-western Sweden in an area where the annual precipitation could reach 1400 mm and with a mean annual air temperature (MAT) of $>6°C$, i.e., hydrometeorological conditions that are poorly represented in existing studies of stream DOC from boreal Scandinavia. Based on studies showing differences in the drivers depending on land cover characteristics, we hypothesized that the temporal variability in stream DOC concentration and character is controlled by hydrology in the mineral soil catchment and by air temperature in the peat-dominated catchment. In addition, we quantified the DOC export from both catchments and determined interannual as well as intraannual variability in DOC export rates.

2. Methods

2.1. Site Description

The study was conducted in two nearby headwater streams within the 750 ha Skogaryd research catchment situated in south-western Sweden (58°23′N, 12°09′E) during 2012 and 2013 (Figure 1). The two headwater streams are draining catchments with different dominating soil characteristics (peatland versus forested
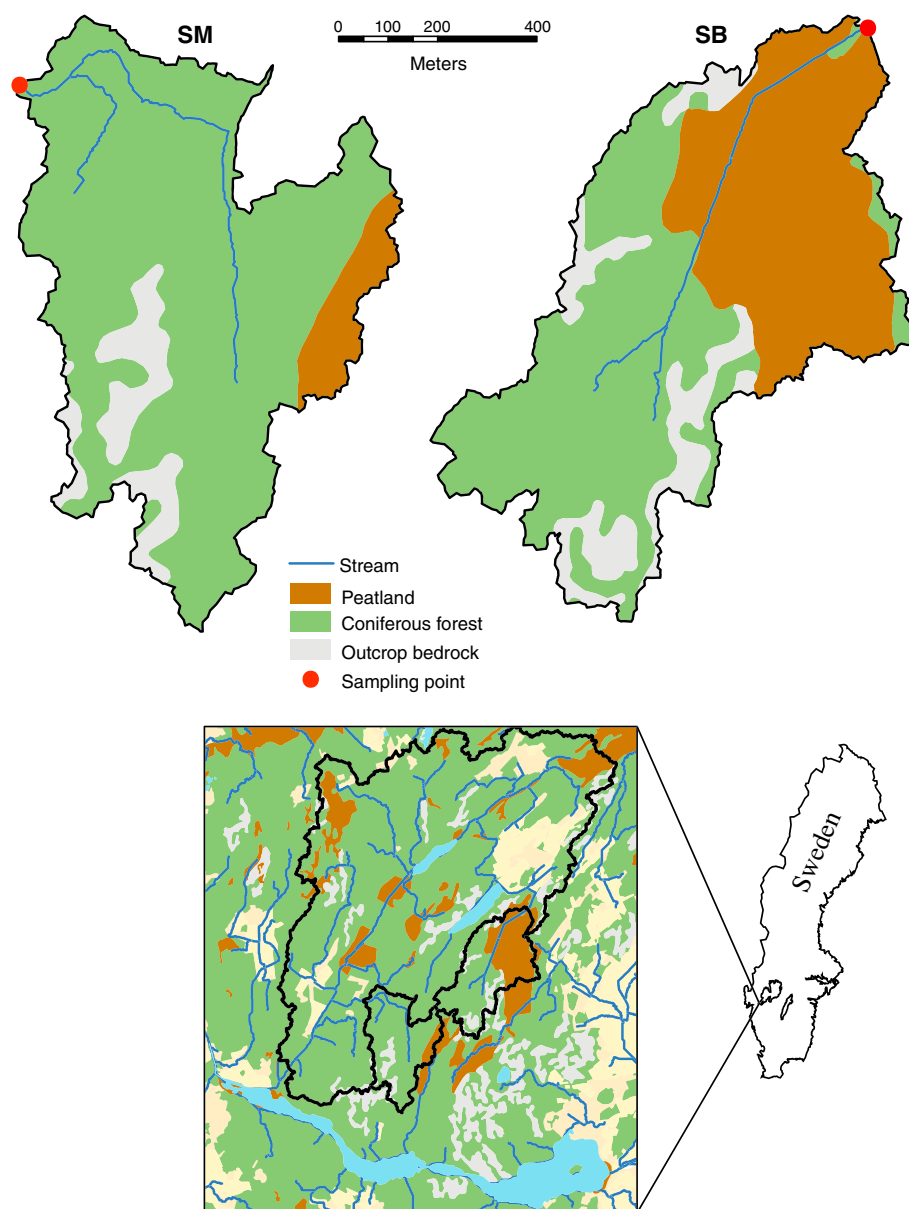
Figure 1. Location of the two hemiboreal catchments (stream mineral, SM and stream bog, SB) located within the Skogaryd research catchment.

mineral soils). Based on the dominating soil conditions, the streams are here denoted stream bog (SB) and stream mineral (SM), respectively. SB is draining a 57 ha large catchment, that is to ~40% dominated by an open minerotrophic fen located toward the catchment outlet. The open fen is mainly covered by mosses (*Sphagnum* sp.), whereas the upstream part of the catchment is mainly covered by coniferous forest. The majority of the soils in the SB catchment consists of peat (<6 m deep) but with areas with postglacial deposits on a shallow bedrock (soil depth, 0.5–1 m) located at higher elevations. The SM is draining a 48 ha catchment, which is to >90% covered by forest. A large part (~50%) of the SM catchment is former agricultural land, which was reforested about 45 years ago and hence on the first stand rotation. The soils in SM are among the most productive for the area [*Shendryk et al.*, 2014] and consist of a mixture of glacial clay and postglacial silt or sand (Swedish Geological Survey). The organic content of the soil in SM is generally >10% in the top 10–20 cm and <7% below 20 cm and with low vertical variability at deeper horizons (O. Karlsson, University of Gothenburg, unpublished data, 2012). The soil in SM is classified as an Umbrisol. Both catchments are underlined by acidic bedrock (granite) covered by a <10 m thick soil layer

but with parts of bare rock outcrops at higher elevations. The main tree species for both catchments are Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). As in the majority of the Scandinavian boreal or hemiboreal regions, both catchments are characterized by man-made ditching conducted 100–150 years ago to improve forest and agricultural productivity.

The mean annual air temperature (MAT) at the closest monitoring station (Vänersborg) situated ~10 km east of the Skogaryd research catchment was 6.7 and 6.9°C for 2012 and 2013, respectively. This was 0.5°C and 0.7°C warmer than the long-term MAT (1961–1990) of 6.2°C according to the Swedish Meteorological and Hydrological Institute (SMHI) [*Raab and Vedin*, 1995]. The annual precipitation in Skogaryd for 2012 and 2013 was 1167 mm and 740 mm, respectively (according to average precipitation data for two SMHI stations situated along a precipitation gradient with a west-east direction, for further information see *Meyer et al.* [2013]). The annual precipitation was 49% higher (2012) and 6% lower (2013) than the long-term (1961–1990) mean annual precipitation, which was estimated to be 785 mm according to the same method described above.

The identification and delineation of the SB and SM headwater catchments were obtained using a high-resolution (2 × 2 m) national digital elevation model (DEM). Land use distribution within each catchment was based on the digital versions of the topographic map (1:50000). Both the DEM and topographic map were provided by the Swedish Land Survey. The hydrology tool box in ArcGis 10.0 (Environmental Systems Research Institute, Redlands, USA) was used for determination of flow direction in each grid cell, flow accumulation, and catchment boundaries.

2.2. Sampling

The two headwater streams were manually sampled biweekly during the ice-free season, from April to December, during the 2 years. Samples were collected without headspace in 250 mL high-density polyethylene bottles. All samples were kept cold and dark during transport to the laboratory. In addition to the manual sampling, the two catchment outlets were instrumented with ISCO 6712 automatic samplers (Teledyne ISCO, USA) programmed to take a daily stream water sample during the 2 week period between the manual samplings. Based on the hydrograph, 3 out of the 14 automatically taken samples were selected (at maximum, mean, and minimum discharges) for further chemical analysis. Manual sampling was conducted at 28 occasions for SB and at 24 occasions for SM. In addition, 87 (SB) and 73 (SM) automatically collected samples were analyzed. Thus, in total, data from 115 and 97 samples were used in the study for SB and SM, respectively. Discharge measurements were made at each catchment outlet for the full years of 2012 and 2013 using installed flumes, where stage height was recorded continuously every 10 min by an ultrasound sensor (710, MJK Automation, Sweden) connected to the ISCO station. Mean daily discharge (Q) was calculated from site-specific stage-height-discharge rating curves ($R^2 > 0.90$), which were based on a series of manual discharge measurements using a handheld Flow Tracker device (SonTek, San Diego, USA). Specific discharge (q) was calculated by normalizing Q to the catchment area in order to make the hydrographs comparable for the two catchments. Daily mean air temperature from the closest monitoring station (Vänersborg, SMHI) situated ~10 km east of the two catchments was used in the analysis.

2.3. Analyses and Calculations

The samples were analyzed for DOC concentration, total iron concentration (Fe), and absorbance in conjunction with other chemical and physical water variables that were not included in this study. Samples were filtered in the laboratory through precombusted glass-fiber Whatman GF/F filters (0.7 μm) prior to analysis for DOC and absorbance. DOC was measured after sample acidification using a Shimadzu total organic carbon (TOC-L) analyzer connected to an ASI-L auto sampler, or by a Sievers 900 TOC analyzer (GE Analytical Instruments, Boulder, USA). Absorbance spectra (200–600 nm, 1 nm resolution) were measured using a 0.5 cm quartz cuvette on a UV-visible spectrophotometer (PerkinElmer Lambda 40, Waltham, USA). Total Fe was measured using a Nexion 300D inductively coupled plasma–mass spectrometry (Perkin Elmer, Waltham, USA). Particulate bound Fe has previously been found to correspond to ~5% of the total Fe in boreal headwaters [*Björkvald et al.*, 2008], headwaters similar to the ones in this study. Hence, we considered total Fe equivalent to dissolved Fe for the streams of this study. The influence of Fe on the absorbance was investigated by conducting a laboratory experiment, where filtered (0.7 μm)

lake water from the Skogaryd catchment with low Fe concentration (Fe $< 1\,\mathrm{mg\,L^{-1}}$; DOC $= 18\,\mathrm{mg\,L^{-1}}$) was spiked with Fe covering a relevant concentration range (1–$5\,\mathrm{mg\,L^{-1}}$; $n = 27$) (Peter et al. in preparation). By using wavelength specific (254 and 365 nm) regression models (absorbance as a function of Fe concentration), we were able to subtract the Fe effect from all included absorbance measurements of the study [*Weishaar et al.*, 2003]. The absorbance data were converted to the decadic form of the absorbance coefficient (α) according to

$$\alpha = \frac{A}{L} \tag{1}$$

where α is expressed in $\mathrm{m^{-1}}$, A is the dimensionless absorbance measure, and L is the path length of the cuvette (0.5 cm). Specific UV absorption (SUVA$_{254}$, $\mathrm{L\,mg\,C^{-1}\,m^{-1}}$) as a proxy for aromaticity was determined by dividing α at 254 nm with the DOC concentration [*Weishaar et al.*, 2003]. In addition, the absorbance ratio of a254/a365 has been shown to be negatively related to the mean molecular weight of the DOC [*De Haan and De Boer*, 1987; *Dahlén et al.*, 1996] and has been used for describing the DOC character in various aquatic systems [*Ågren et al.*, 2008; *Huotari et al.*, 2013; *Müller et al.*, 2014]. The a254/a365 ratio has also been found to be strongly correlated with, and hence show, the same patterns as measures of spectral slope for similar stream systems as presented in this study [*Berggren et al.*, 2007; *Ågren et al.*, 2008].

For the export calculations, daily time series of DOC concentration was constructed by linear interpolation between sampling days in order to capture extreme values. On average, the interpolation time between two sampling days was short, <5 days during the sampling period April–December. Daily DOC concentration for the unsampled period (mid-December–March) was modeled for each of the two streams by using the stream-specific temperature-dependent regression models found in this study (see Figure 4). Annual downstream export of DOC was estimated as the sum of daily export (daily concentrations times mean daily discharge), which was then divided by the area of each catchment to obtain area specific export. Annual flow-weighted concentrations of DOC were obtained by normalizing the annual export to annual runoff. Uncertainty estimates for lateral export of DOC (12% standard deviation) were calculated according to similar studies using Monte Carlo simulations for error propagation and where similar sampling methods, sampling frequency, and analytical and hydrological methods have been used [*Ågren et al.*, 2007; *Nilsson et al.*, 2008].

2.4. Statistical Analyses

In order to explore drivers for the temporal variability in DOC concentration, SUVA$_{254}$ and a254/a365 for the two streams, we used partial least squares regressions (PLS) since it is suitable to use when explanatory variables are interrelated [*Wold et al.*, 2001]. Three PLS models per stream (one for each of the y variables, DOC concentration, SUVA$_{254}$, and a254/a365) were constructed and where a set of specific discharge (q) and air temperature (T) measures were used as explanatory variables. In addition to q and T for the day of sampling, we also investigated the time lag in the terrestrial-aquatic connectivity as well as in the mobilization of soil DOC by incorporating q and T measured x days prior to the sampling day (denoted q_{-x} and T_{-x}). In a similar way, average values of q and T for a certain time period y days prior to the sampling day (denoted $q_{\mathrm{avg}(y)}$ and $T_{\mathrm{avg}(y)}$) were used in the analysis. Eight different T measures and six q measures were chosen to cover relevant time ranges found in the literature [*Fröberg et al.*, 2006; *McGuire and McDonnell*, 2010; *Raymond and Saiers*, 2010]. These were together with the number of the sampling month (4–12) (in total 15 explanatory variables) used in each PLS analysis. The importance of each explanatory variable for the PLS model was determined by the VIP (Variable Importance for the Projection) value. The VIP value was calculated for each explanatory variable by summing the squares of the PLS loading weights, which were weighted by the amount of sum of squares explained in each model component. Explanatory variables with VIP values ≥ 1.0 were considered as important, while variables with VIP values <1.0 were considered unimportant in explaining the variability in each of the three separate models for DOC concentration, SUVA$_{254}$, and a254/a365. Linear regression analysis was used to explore and model simple temporal relationships for the variables that were most strongly related to DOC concentration, SUVA$_{254}$, and a254/a365 according to the PLS. Explanatory variables were logarithmically transformed in the PLS and linear regression analysis if nonnormal distribution was detected. Correlations between different explanatory variables were tested using the nonparametric Spearman's rank correlation test
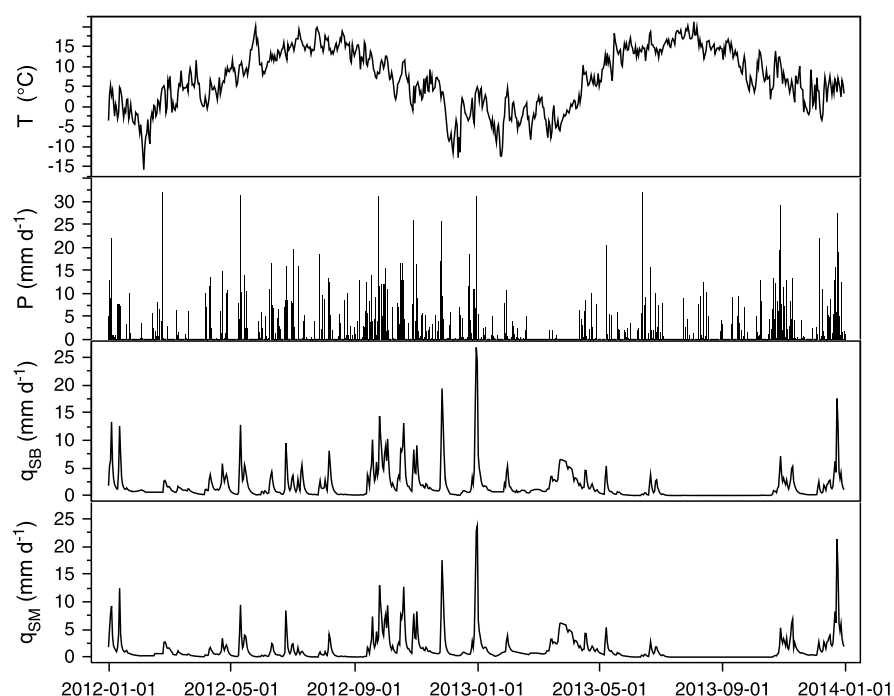
Figure 2. Time series of air temperature (T), precipitation (P), and specific discharge (q) for SB and SM during the study period of 2012–2013. T and P data derive from the closest monitoring station (SMHI, Vänersborg) situated ~10 km east of the catchments.

(Spearman rho). Differences in DOC quantity and character between SB and SM and between the 2 years were tested using the nonparametric Wilcoxon's test. Correlations as well as differences between the streams or between the years were considered significant if $p < 0.05$. The coefficient of variation (CV) was used to describe and compare variability differences between the two streams. JMP 11.0 (SAS Institute Inc., Cary, NC, USA) was used for all statistical analysis except for the PLS analysis where SIMCA-P 13.0 (Umetrics, Umeå, Sweden) was used.

3. Results

3.1. Runoff Patterns

The annual runoff for SB was 792 mm in 2012 and 469 mm in 2013. Specific discharge (q) was ranging from 0 to 26.8 mm d^{-1} (median is 0.8 mm d^{-1}) during the 2 year period (Figure 2). The annual runoff for SM was 583 mm in 2012 and 487 mm in 2013, with q ranging from 0 to 23.7 mm d^{-1} (median is 0.6 mm d^{-1}). The discharge distribution was very similar between the two streams ($\rho = 0.94$, $p < 0.0001$, $n = 730$, Spearman rho). According to frequency analysis (average q for both sites), 58% of the days had a q <1 mm d^{-1}. Despite the few days with $q > 5$ mm d^{-1} (<9% of the entire period), those days accounted for on average 43% of the accumulated discharge. The majority (>70%) of these high-discharge days occurred during autumn and early winter months (September–January).

3.2. DOC Concentrations

SB showed consistently higher DOC concentrations than SM (Wilcoxon's test, $p < 0.0001$). The annual median and annual flow-weighted mean concentrations for SB were 38.8 mg L^{-1} and 30.5 mg L^{-1}, respectively, to be compared with 27.7 mg L^{-1} and 22.0 mg L^{-1} for SM. Both streams had a pronounced intraannual pattern in DOC with maximum monthly mean concentrations occurring during summer months. Using data from both years, maximum DOC concentrations occurred in July for SB and in August for SM (Figure 3). The December DOC concentrations were in both streams similar to the median monthly DOC for April when the sampling program started. The largest interannual variability in DOC concentration between the 2 years was in both streams observed in October after a period of drought. The monthly median DOC concentration for
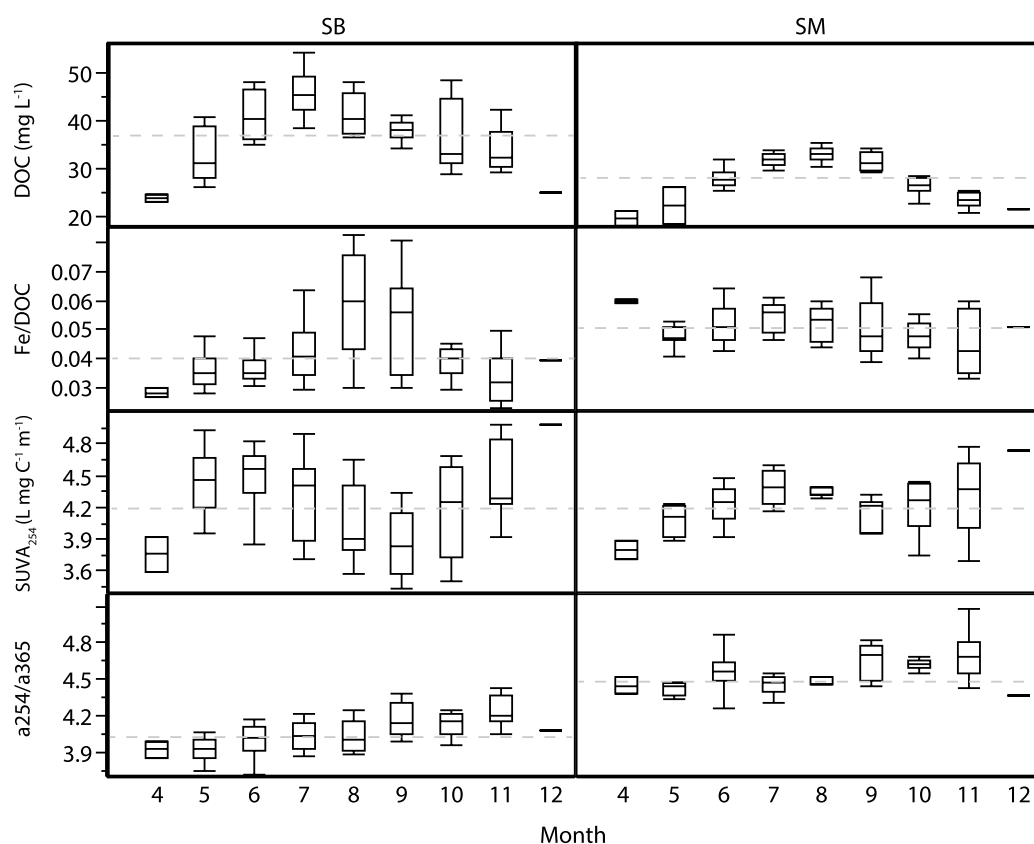
Figure 3. Monthly distribution of DOC concentration, Fe/DOC concentration ratio, SUVA$_{254}$, and a254/365 for SB and SM. Median value of all data is given by the grey dashed line. Data are based on the 2 years of the study (2012–2013).

October in SB was 52% higher in 2013 than in 2012 (47.8 mg L^{-1} and 31.5 mg L^{-1}). The corresponding interannual difference for October in SM was 22% higher DOC in 2013 than in 2012 (31.6 mg L^{-1} and 26.0 mg L^{-1}) (data not shown). The maximum October DOC concentrations in 2013 were for both streams almost equal to the overall maximum observed during the summer.

According to the PLS analyses, temperature was generally the best predicting variable determining temporal variability in stream DOC concentrations for both streams (Table 1). The temperature control was stronger for SM than for SB (i.e., VIP was higher in the PLS analysis; Table 1). A set of variables describing the average temperature for different time periods prior to sampling were most influential for the explanatory power of the model. T_{avg30} was the most influential variable explaining temporal variability in DOC concentration for both SM and SB. In SM, T_{avg60}, T_{avg30}, T_{avg90}, and T_{avg14} were all influential having with VIP values ranging from 1.48 to 1.20. The two principal components that were extracted in the model explained 87% of the temporal variability in DOC concentration for SM. Although temperature variables were in majority among the influential variables explaining DOC for SB, the model also contained discharge measures. T followed by q_{-14}, T_{avg30} and T_{avg14} were the most influential variables ranging in VIP values from 1.27 to 1.19. The three principal components that were extracted in the model explained 53% of the temporal variability in DOC concentration for SB. T_{avg30} was also related to DOC for both streams when considered as a single explanatory variable in linear regression models (Figure 4). The T_{avg30}-DOC relationship was stronger for SM ($R^2 = 0.70$, $p < 0.0001$) than for SB ($R^2 = 0.35$, $p < 0.0001$). The slope of the regression models was 1.06 for SB, to be compared with 0.91 for the SM and with an intercept difference of 8.9 mg L^{-1}. The residuals for both regression models where normally distributed and uncorrelated with q. The explanatory power increased, especially for SB (SM, $R^2 = 0.80$ and SB, $R^2 = 0.62$), if the sampling occasions in middle to late October 2013, just after the drought period, were excluded (Figures 2 and 4).

Table 1. Ranked Driver Variables (According to VIP Values), R^2 and Q^2 for the Temporal Variability Models of DOC, SUVA and a254/a365 According to the PLS Analysis for Stream Mineral (SM) and Stream Bog (SB)[a]

SM								
DOC			**SUVA$_{254}$**			**a254/a365**		
Variable	*VIP*	+/−	Variable	*VIP*	+/−	Variable	*VIP*	+/−
T_{avg60}	1.48	+	q_{-14}	1.87	+	Month	1.81	+
T_{avg30}	1.36	+	T_{avg60}	1.24	+	q	1.68	+
T_{avg90}	1.30	+	T_{avg30}	1.16	+	T_{-60}	1.29	+
T_{avg14}	1.25	+	q_{-7}	1.09	+	T	1.24	−
T_{-30}	1.22	+	T_{avg90}	1.09	+	T_{avg90}	1.24	+
T_{-14}	1.20	+	T_{avg14}	1.04	+	q_{-14}	1.14	−
			T_{-30}	1.02	+	T_{avg14}	1.01	−
$R^2 = 0.87, Q^2 = 0.83$			$R^2 = 0.26, Q^2 = 0.17$			$R^2 = 0.31, Q^2 = 0.24$		

SB[b]								
DOC			**SUVA$_{254}$**			**a254/a365**		
Variable	*VIP*	+/−	Variable	*VIP*	+/−	Variable	*VIP*	+/−
T	1.27	+	q_{avg14}	1.40	+	Month	2.04	+
q_{-14}	1.26	−	q_{avg7}	1.38	+	T_{-60}	1.47	+
T_{avg30}	1.21	+	q	1.30	+	T_{avg90}	1.29	+
T_{avg14}	1.19	+	q_{-7}	1.30	+	T	1.29	+
T_{-14}	1.09	−	q_{-3}	1.29	+	q	1.06	+
T_{avg60}	1.06	+	q_{-14}	1.25	+			
q_{-7}	1.04	−						
$R^2 = 0.53, Q^2 = 0.45$			$R^2 = 0.65, Q^2 = 0.60$			$R^2 = 0.51, Q^2 = 0.49$		

[a]In addition to q and T for the day of sampling, q and T measured x days prior to the sampling day (denoted q_{-x} and T_{-x}) and average values of q and T for a certain time period y days prior to the sampling day (denoted $q_{avg(y)}$ and $T_{avg(y)}$) were used in the PLS-analysis.

[b]VIP = Variable Importance of the Projection. Only important driver variables for the model performance (VIP > 1) are shown.
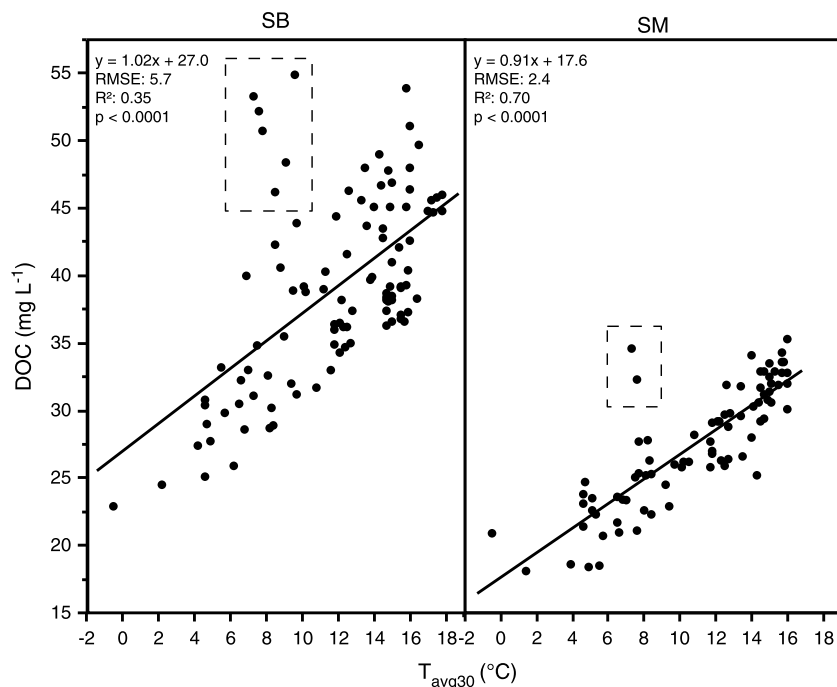
Figure 4. DOC concentration as a function of average air temperature 30 days prior to sampling (T_{avg30}) separated for the two streams SB and SM. Highlighted data within boxes represent October 2013 samples taken after the period of drought.
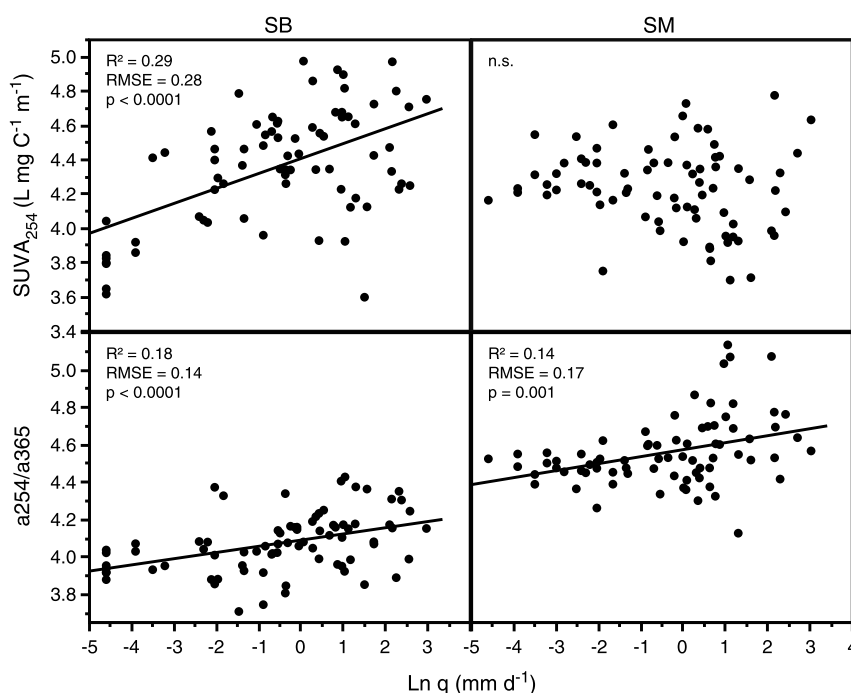
Figure 5. (top) $SUVA_{254}$ and (bottom) a254/365 as functions of ln-transformed specific discharge (q) for the two streams SB and SM.

3.3. DOC Character

In contrast to the DOC concentration, the median $SUVA_{254}$ (as a measure of aromaticity) was not statistically different between the two streams (4.2 L mg C^{-1} m^{-1} and 4.3 L mg C^{-1} m^{-1} for the SM and SB, respectively) ($p = 0.97$, Wilcoxon's test) (Figure 3). Also, the seasonal variability in $SUVA_{254}$ showed a similar pattern in the two streams with a relatively low initial $SUVA_{254}$ (<3.9 L mg C^{-1} m^{-1}) in April, reaching a first maximum during early summer (June/July), deceasing until early autumn and then increasing again to reach an almost annual maximum (close to 5.0 L mg C^{-1} m^{-1}) in December (Figures 5). The seasonal pattern in $SUVA_{254}$ was similar also when treating the data separately for the 2 years (data not shown). Despite the similar seasonal pattern for the two different years, annual median $SUVA_{254}$ was significantly higher during 2012 than 2013 for both streams (SM, 2012 = 4.3 L mg C^{-1} m^{-1}, 2013 = 4.1 L mg C^{-1} m^{-1}; SB, 2012 = 4.5 L mg C^{-1} m^{-1}, 2013 = 3.9 L mg C^{-1} m^{-1}, both $p < 0.0001$, Wilcoxon's test).

While temporal variability in $SUVA_{254}$ was mostly explained by different discharge measures for SB, a combination of discharge and temperature measures yielded the best model for SM (Table 1). The six different discharge variables explaining temporal variability in $SUVA_{254}$ for SB had very similar VIP values (1.40–1.25). For SM, q_{-14} (VIP = 1.87) was much more important than the remaining variables (VIP = 1.24–1.02) explaining temporal variability in $SUVA_{254}$. The two principal components that were extracted for both SM and SB explained 26% and 65% of the temporal variability in $SUVA_{254}$ for, respectively, stream. For SB, $SUVA_{254}$ was also related to q when considered as a single explanatory variable in a linear regression model (Figure 5).

The absorbance ratio, a254/a365 (as a measure of mean molecular weight) was in contrast to $SUVA_{254}$ significantly different between the two streams with a higher median ratio observed for SM (4.5) than for SB (4.1) ($p < 0.0001$, Wilcoxon's test) (Figure 3). $SUVA_{254}$ and a254/a365 were negatively correlated in SM ($\rho = -0.28$, $p = 0.01$ Spearman rho) but showed no correlation for SB ($\rho = 0.97$, Spearman rho). The median monthly a254/a365 ratio was relatively stable in both streams but tended to increase toward the autumn. As observed for the $SUVA_{254}$, SB showed a higher intermonthly variability in a254/a365 than SM. In contrast to $SUVA_{254}$, only SB showed a significant difference in annual median a254/a365 ratio between the 2 years (SM, 2012 = 4.5, 2013 = 4.5; $p = 0.48$; SB, 2012 = 4.1, 2013 = 3.9, $p = 0.0005$, Wilcoxon's test). The
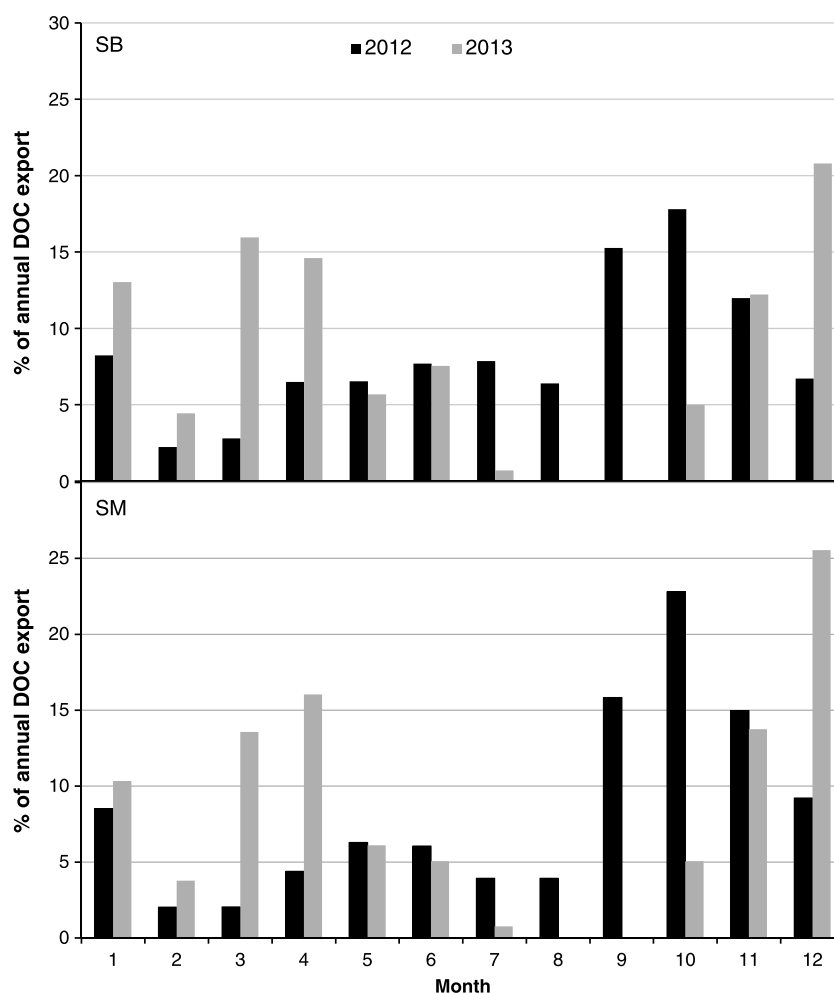
Figure 6. Monthly distribution of the annual DOC export (in percent) for the two streams SB and SM separated by the two different years of the study (2012 and 2013).

most influential variable for explaining temporal variability in a254/a365 was month for both SB and SM according to the PLS analysis (Table 1). Whereas q was the second most important for SM, T_{-60} was the second most important variable for SB. The two components that were extracted for SM and SB explained 31% and 51% of the temporal variability in a254/a365, respectively. SB and SM had similar slopes (0.041 and 0.039, respectively) of the linear regression models of a254/a365 as a function of ln-transformed q (Figure 5). The explanatory power of the regression models was low but slightly higher for SB (18%) than for SM (14%).

3.4. DOC Export

The mean annual DOC exports (based on the 2 years) were 10.7 ($\pm$1.3) t C or 18.8 ($\pm$2.3) g C m^{-2} yr^{-1} for SB and 5.7 ($\pm$0.7) t C or 11.9 ($\pm$1.4) g C m^{-2} yr^{-1} for SM. The interannual variability was high with monthly export rates ranging from 0 to 4.5 ($\pm$0.5) g C m^{-2} for SB and from 0 to 3.2 ($\pm$0.4) g C m^{-2} for SM (Table 2). There were, however, large differences in exports between the 2 years, with significantly higher rates determined for both streams in 2012. Year 2012 had a much higher annual precipitation (58%) and runoff (on average 44% based on the two streams) than 2013. As a consequence of both streams drying out completely during late summer 2013 (August and September), no DOC export occurred during those months (Figure 6 and Table 2). The highest export rates were determined during October 2012 coinciding with a high-precipitation period. SM had a higher intraannual variability in the DOC export (CV = 57%) than SB (CV = 39%). The relative export contribution of single months like October 2012 and December 2013

Table 2. Stream Export of DOC (g C m^{-2}) for Stream Bog (SB) and Stream Mineral (SM) Separated by Month and With the Total Annual Export

	SB		SM	
	2012	2013	2012	2013
Jan	2,1	1,6	1,2	1
Feb	0,6	0,5	0,3	0,4
March	0,7	2,0	0,3	1,3
April	1,6	1,8	0,6	1,5
May	1,6	0,7	0,9	0,6
June	1,9	0,9	0,9	0,5
July	2,0	0,1	0,6	0,1
Aug	1,6	0,0	0,6	0
Sep	3,9	0,0	2,2	0
Oct	4,5	0,6	3,2	0,5
Nov	3,0	1,5	2,1	1,3
Dec	1,7	2,6	1,3	2,5
Annual	**25,2**	**12,4**	**14,1**	**9,6**

were higher for SM, showing that more than 25% of the annual export can occur during single months in these types of catchments (Figure 6).

4. Discussion

4.1. Control on Stream DOC Concentrations

The strong air temperature control on the DOC concentration was, in contrast to our hypothesis, surprisingly similar between the two catchments despite their distinctly different soil and land use properties. A positive discharge-DOC concentration relationship has commonly been observed for various catchments across boreal and temperate regions [*Hinton et al.*, 1998; *Raymond and Saiers*, 2010; *Laudon et al.*, 2011]. But a strong temperature control on stream DOC concentration has previously only been suggested for catchments with a homogenous soil DOC profile typically found in peatland dominated areas [*Winterdahl et al.*, 2014]. This study showed, however, that a strong temperature control could also be found for a hemiboreal catchment draining mineral soils. Forest soils, in general, and boreal and hemiboreal mineral soils, in particular, often show a clear organic content profile decreasing with depth [*Jobbágy and Jackson*, 2000]. But since the SM catchment consists of reforested agricultural land, which historically has been managed for more than 100 years, the soil profile has, expect from the top moor layer, relatively small differences in the vertical organic matter distribution (O. Karlsson, University of Gothenburg, unpublished data, 2012). This results in that stream DOC concentration in SM was relatively unaffected to changes in the groundwater table position something that is manifested by the absence of any discharge-DOC concentration relationships (Table 1).

Although stream DOC concentrations followed air temperature patterns, the time lag in the temperature response on DOC was slightly different between the streams, with a more rapid response observed in SB than in SM. In SB, T and T_{avg30} were the most influential temperature variables controlling the temporal variability in stream DOC concentration, while for SM, T_{avg60} and T_{avg30} were the most influential temperature variables. A time lag of 60 days in SM is identical to findings from a small forested catchment in Norway [*Futter and de Wit*, 2006] and similar to the findings of DOC leaching from the O-horizon in forest podzol soils across Sweden where a time lag of two months was observed [*Fröberg et al.*, 2006]. The authors of that study attributed the delay in temperature response to sorption-desorption mechanisms rather than to an effect coupled to DOC production. It has further been found that before a significant increase of DOC in the soil solution could be observed, a buildup of "sorbed" DOC is needed [*Michalzik et al.*, 2003]. We cannot separate the temperature control on sorption processes from the control on processes related to production/degradation of stream DOC in this study. However, because the temperature response on stream DOC concentration was very similar (the slopes of the regressions in Figure 4) between the two distinct different systems in terms of soil type, we believe that the temperature control on the production rather than the mobilization of DOC was the major explanation to the observed pattern. This is further supported by findings of soil organic matter (OM) content, being a fundamental regulator for DOC adsorption rates in soils, with less adsorption potential at higher OM content [*Moore et al.*, 1992]. Furthermore, the temperature control on the stream DOC concentration in SM fits into the conceptualization of terrestrial production/mineralization, being the regulator for DOC available for stream runoff in forested catchments with a MAT $> 3°C$ [e.g., *Laudon et al.*, 2012]. However, the observed DOC concentrations found for SM are more than 300% higher than projected by the DOC concentration-MAT trajectory suggested by *Laudon et al.* [2012]. Our finding highlights the need for expanding the hydrometeorologial/geographical coverage of stream DOC studies in boreal and hemiboreal Scandinavia.

On a spatial scale, stream DOC concentrations are known to be tightly coupled to the amount of organic-rich soils in the catchment [*Eckhardt and Moore*, 1990; *Mattsson et al.*, 2005; *Wallin et al.*, 2010]; hence, the

significantly higher DOC concentrations observed in SB than in SM were expected. The flow-weighted annual mean DOC concentration for SB ($30.5\,mg\,L^{-1}$) was similar to annual mean or flow-weighted mean concentrations found for mire-dominated catchments in northern Sweden ($28.0–32.3\,mg\,L^{-1}$) [*Nilsson et al.*, 2008; *Wallin et al.*, 2013]. The flow-weighted annual mean DOC for SM ($22.0\,mg\,L^{-1}$) was slightly higher than the range in flow-weighted mean found for a 4 year study of a forested headwater catchment in northern Sweden ($16.1–23.2\,mg\,L^{-1}$) [*Wallin et al.*, 2013]. For comparison on a spatial scale, measured base flow concentrations of total organic carbon (TOC) for 99 randomly selected forested headwater catchments along the west coast of Sweden (with a similar MAT and precipitation as observed for this study) were ranging from 16.6 to $42.3\,mg\,L^{-1}$ [*Wallin et al.*, 2014]. To summarize, we believe that the SM and SB catchments are representative in their DOC concentrations for a large part of the boreal and hemiboreal regions of Scandinavia.

After the period of drought during summer/early autumn 2013, in congruence with the first increase in stream discharge, both streams showed an increase in DOC concentrations. These October DOC concentrations were falling outside the strong DOC-T_{avg30} relationship, which was observed for the rest of the sampled year (Figure 3). *Fenner and Freeman* [2011] have described similar drought-induced C losses (including DOC) after rewetting peatland systems. They suggested that increased anaerobic conditions due to rewetting after a period of drought and high oxygen availability decreased the enzymatic activity and hence slowed down the mineralization process. As indicated by the difference in mean October concentration between the two years, the largest drought-induced effect on the DOC concentration was observed for SB, but still, the effect was significant for SM as well with on average 22% higher October DOC during 2013 than 2012. However, based on this study, we cannot determine if the enzymatic activity is the main control or whether DOC could for example be simply accumulated in the soil profile upon production and then being mobilized during the rewetting period as suggested by *Raymond and Saiers* [2010].

4.2. Control on DOC Character

Despite draining two such distinctly different catchments in terms of land cover, the median, total range, and seasonal pattern in SUVA$_{254}$ ($3.4–5.0\,L\,mg\,C^{-1}\,m^{-1}$) as a proxy for aromaticity were all very similar between the two streams (Figure 3). However, SB showed a much higher intermonthly variability in SUVA$_{254}$ than SM, which we suggest is a result of the higher overall hydrological influence on SUVA$_{254}$ for the mire-dominated area of SB (Table 1). The similarity in SUVA$_{254}$ between the two systems was unexpected and in contrast to findings from other studies. *Ågren et al.* [2008] found, for example, in a study of boreal streams a very similar overall range in SUVA$_{254}$ ($3.8–5.6\,L\,mg\,C^{-1}\,m^{-1}$), but with clear differences in mean SUVA$_{254}$ between streams draining wetland and forested dominated catchments. They generally found higher SUVA$_{254}$ (or higher aromaticity) in wetland-dominated streams. Similar findings concerning differences in SUVA$_{254}$ with more aromatic C observed for peatland than forest-derived DOC have been found in laboratory studies [*Kalbitz et al.*, 2003]. Our study indicates that such differences are not always clear and that upland forested mineral soils can export DOC with similar SUVA$_{254}$ as peatland systems.

Even though the two streams in our study showed similarities in SUVA$_{254}$, there was a significant difference in the a254/a365 ratio (Figure 3). Despite that the difference in a254/a365 between the two streams was relatively small (difference in median a254/a365 = 0.3), it still indicates that the two streams on average export DOC of different quality. The median a254/a365 ratio in SB was lower than in SM, suggesting that the mire provides DOC of higher mean molecular weight compared to the forested mineral catchment. This is in congruence with findings from boreal streams in northern Sweden, where a clear negative a254/a365 versus wetland percentage relationship was observed [*Ågren et al.*, 2008]. The a254/a365 tended to increase toward the autumn for both streams, suggesting an increased contribution of low molecular weight compounds to the bulk DOC pool. Although we found high DOC concentrations at rewetting after a period of drought, no statistical difference in either SUVA$_{254}$ or a254/a365 was observed compared to prior or after the rewetting period, suggesting no difference in character of this high DOC pulse.

The temporal control on the optical properties of DOC (SUVA$_{254}$ and a254/a365) was rather complex, with generally weak influence of any of the included *q* or *T* measures. However, it is indicated that a higher groundwater table at higher stream discharge mobilize soil C sources with a different character (higher

$SUVA_{254}$) compared to at base flow. Also, the slight increase in a254/a365 toward the autumn was predominately related to absorbance changes at the 365 nm wavelength since $SUVA_{254}$ showed no such seasonal influence. The a254/a365 ratio has previously been linked to the metabolism in boreal streams, where a positive correlation between bacterial growth efficiency and a254/a365 has been shown [*Berggren et al.*, 2007]. However, *Berggren et al.* [2007] did not find any correlation between bacterial respiration rates and the a254/a365 ratio, so whether the DOC being exported from SM will be more easily respired than DOC from SB remains unclear.

4.3. DOC Export Rates

The ranges in DOC export (based on 2 years of data) for the two distinct different headwater catchments of this study (13.5–26.2 g C m^{-2} yr^{-1} for SB and 10.7–14.8 g C m^{-2} yr^{-1} for SM) were among the highest determined in boreal and hemiboreal Scandinavia. For comparison, TOC export rates typically found for small boreal catchments with various forest/mire land cover mixtures in northern Sweden (3.6–9.3 g C m^{-2} yr^{-1}) [*Laudon et al.*, 2004; *Wallin et al.*, 2013] and in Finland (2.3–14.8 g C m^{-2} yr^{-1}) [*Rantakari et al.*, 2010; *Huotari et al.*, 2013] were generally lower. Also, the range for SB was typically higher than TOC exports reported for a small stream draining a peatland systems in northern Sweden (11.9–14.0 g C m^{-2} yr^{-1}) [*Nilsson et al.*, 2008], but within the same DOC export range observed for streams draining peatland systems in Canada (13.2–21.0 g C m^{-2} yr^{-1}) [*Roulet et al.*, 2007] and in Scotland (18.6–32.2 g C m^{-2} yr^{-1}) [*Dinsmore et al.*, 2010]. In addition, the DOC export rates were significant in comparison to net ecosystem exchange (NEE) estimates of Swedish forest stands, which usually range from -300 to 100 g C m^{-2} yr^{-1} [*Lindroth et al.*, 2008], indicating a substantial lateral loss of C from the studied types of catchments.

The calculated annual DOC export rates are dependent on DOC concentrations and stream discharge. Since the DOC concentrations found in our study were similar to concentrations found for other streams in boreal Scandinavia, the higher export rates are a result of higher stream discharge, i.e., higher precipitation. Furthermore, variability in precipitation has been shown to have a first-order control on the C balance of boreal forests for duplicate reasons; higher precipitation increases the lateral export of C but also reduces the terrestrial net ecosystem exchange (NEE), leading to an overall reduced net ecosystem carbon balance [*Öquist et al.*, 2014]. Although stream discharge is the major control for the DOC export in our catchments, the timing of the precipitation and generated stream discharge during the year influence the amount of DOC being exported. This is especially true for our (and similar) catchments due to the pronounced seasonal DOC concentration pattern driven by temperature and with little influence of variability in discharge. Furthermore, the distribution of annual precipitation is important for the intraannual as well as interannual variability in DOC export. Whether the DOC export occurs during spring/summer or during autumn/winter will likely have implications for the processing potential in downstream aquatic systems. Since sunlight and temperature are major controls for the photochemical and biological mineralization of the organic C, it is reasonable to assume that DOC, being exported during autumn/winter, will to a higher degree be exported to downstream aquatic systems upon mineralization than DOC, being exported during spring/summer.

5. Conclusions

We conclude that the temporal variability in DOC concentrations for these two hemiboreal streams is to a large extent driven by air temperature in spite of different soil characteristics, probably via regulation of the production/degradation of DOC available for stream runoff. Although no substantial hydrological influence on the DOC concentration was observed, the increasing a254/a365 ratio with increasing stream discharge indicates a mobilization of soil C with different character (and possibly bioavailability) at different discharge conditions. We suggest that these findings of a different control on DOC concentration and character need to be considered in the future design of sampling programs of similar headwater systems. The very high DOC export rates largely driven by precipitation, together with the combined hydrometeorological control on stream DOC quantity and character, are central information, which needs to be considered in improved landscape C models including a temporal dimension. Also, since northern latitudes are projected to undergo climatic changes including changes in temperature and/or precipitation [*IPCC*, 2013], our findings need to be considered to make future projections of C fluxes and sequestration more reliable.

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