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Research Article

Seasonal TOC export from seven boreal catchments in northern Sweden

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Abstract. Total organic carbon (TOC) concentrations from seven boreal catchments in northern Sweden were monitored between June 1996 and May 1998 to examine spatial and temporal variations in streamwater TOC export and its relationship with catchment characteristics. The annual average export of TOC ranged between 36 and 76 kg ha^{-1} yr^{-1} and correlated positively with the areal extent of wetlands ($r^2 = 0.72$; $p = 0.03$). The daily output of TOC was 5–11 times higher during the spring than during any other season. In total, the four week long spring period contributed between 50% and 68% of the annual TOC export from the seven catchments. The relative importance of the spring snow melt period for the annual TOC export, however, correlated negatively with the percentage of wetlands ($r^2 = 0.83$; $p < 0.01$). We suggest that the smaller relative importance of the spring runoff period for the annual TOC export from wetland dominated catchments is a result of the hydrological flow paths associated with the snow melt period. While a large fraction of the spring runoff from forested areas reaches the stream via subsurface flow paths across riparian soils rich in TOC, the flow paths through wetland dominated systems include a much larger component of low-TOC snow melt water via surface flow over ice and frozen peat.

Key words. Total organic carbon (TOC); dissolved organic carbon (DOC); stream export; snow melt; boreal zone.

Introduction

Total organic carbon (TOC) plays an important role in many biogeochemical processes in boreal surface waters. One of the more pronounced effects of TOC in many boreal streams and lakes is its strong influence on pH (e.g., Brakke et al., 1987; Köhler et al., 2002b), especially during times of high runoff (Laudon and Bishop, 2002; Laudon et al., 2001). TOC also strongly affects the transport of contaminants such as heavy metals from soils to surface waters because of its complexation capacity (Tipping, 1993). Another important role of TOC in boreal surface waters is as a source of microbial substrate (e.g., Jansson et al., 2000). Furthermore, it has been suggested that hydrological losses of TOC have the potential to affect the long-term dynamics of terrestrial organic carbon pools (Hope et al., 1997b). While the ecosystem export of carbon from boreal wetlands as CO_2 and CH_4 emissions has received increasing attention recently (Aurela et al., 2002; Granberg et al., 2001), there are few studies focusing on the influence of carbon export as stream TOC on the net carbon budget from boreal regions (Moore et al., 1998; Pastor et al., 2003).

While forested areas often dominate total watershed area in northern Sweden, they are historically thought to contribute a minority of the exported TOC through surface waters, due to retention of TOC by the underlying mineral soils (Thurman, 1985). Landscape topography has been identified as an important factor determining the fate of soil carbon (Clair et al., 1994; Mulholland,

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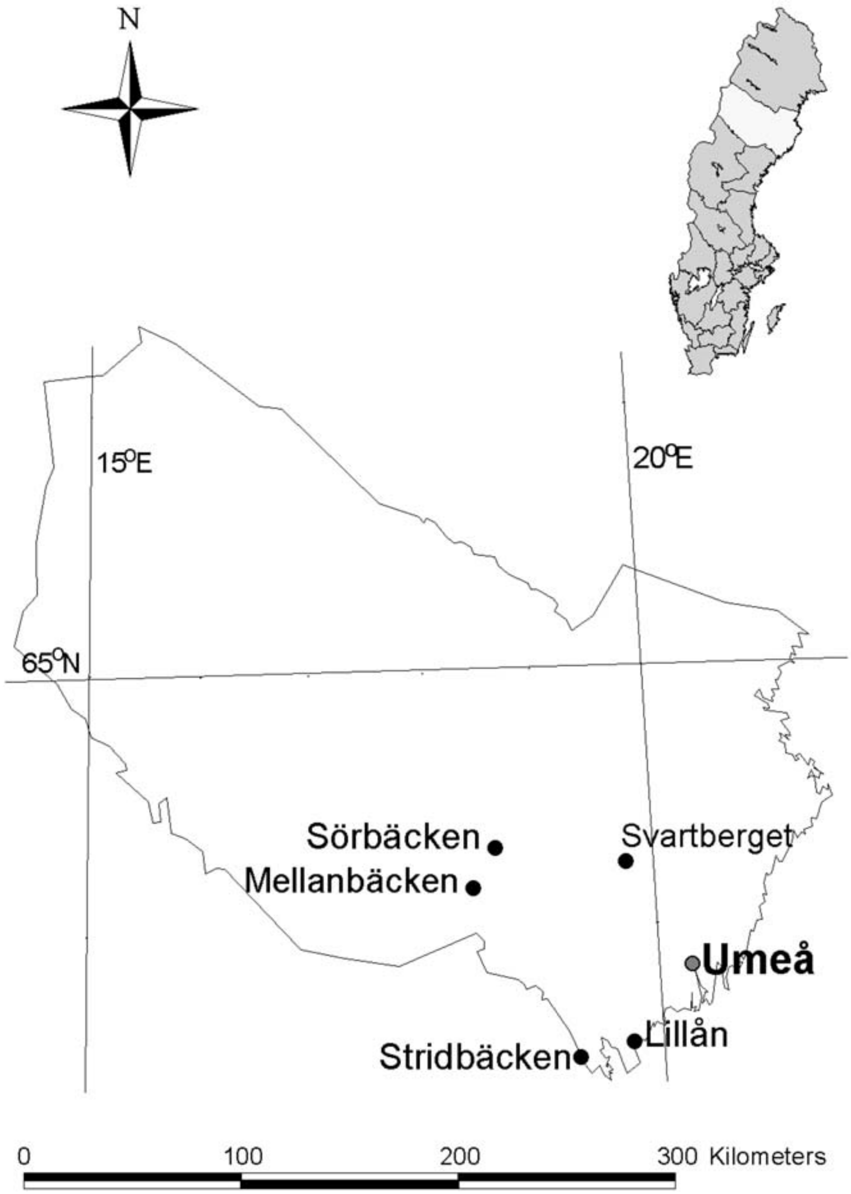


Figure 1. Site locations.

2003), and several studies have proposed that wetlands are the major contributor of TOC to streams and lakes (Hemond, 1990; Dillon and Molot, 1997; Hope et al., 1997a). Previous research on TOC has focused on the role of wetlands as a primary source of TOC for annual C export, but few studies have reported on the role of wetland versus forested areas in regulating the seasonal variation of stream TOC export. Here we study the export of TOC from seven catchments in northern Sweden between June 1996 and May 1998 to better understand the seasonal patterns in TOC export. This study focuses mostly on the snow melt period, which is the dominant hydrological period of the year and, hence, important for export of solutes in stream water from boreal catchments.

Study area

The study was conducted on seven streams in the County of Västerbotten, northern Sweden, from June 1996 to May 1998. The stream catchments range in size from 0.13 to 61 km^2. Two of the streams, Lillån and Stridbäcken, drain into the Gulf of Bothnia (Fig. 1). These streams are located below the highest post-glacial coastline. In this region, quaternary deposits have been reworked by marine wave action, resulting in a transport of fine fractions from exposed slopes to the valley floor. The Stridbäcken catchment consists of frequent bare rock outcrops, thin soils and large mire complexes in the upper reaches of the catchment. A major portion of the Lillån river basin is covered by thick marine-derived sulfide-rich post-glacial sediments. The other catchments, Västrabäcken, Kallkälsmyren, Kallkälsbäcken, Mellansjöbäcken and Sörbäcken, are located inland mainly above the highest post-glacial coastline. The quaternary deposits in the inland are often several meters thick. Kallkälsmyren and Västrabäcken are tributaries to Kallkälsbäcken and are located close to the Svartberget field station (Fig. 1). The mean annual precipitation at the Svartberget research station (1981–1999) is near 600 mm, of which approximately 35% falls as snow (Löfvenius et al., 2003). Detailed descriptions of the physiographical, hydrological and hydrochemical characteristics are provided by Bishop (1991) and Laudon and Bishop (2002).

Methods

Water sampling was carried out by collecting weekly to biweekly grab samples during low flow periods and daily sampling of rain fall and snow melt episodes. The sampling intensity was less frequent (~ monthly) during drought and ice covered periods. All samples were collected in acid-washed 250 mL HDPE bottles. Samples for absorbance measurements were stored at 4 °C until analysis, while samples for TOC measurement were frozen until analysis.

All samples were measured for absorbance at 254 nm in a flow cell using a 1 cm cuvette within a few days after sampling. TOC was measured for 270 of the 700 total samples with a Shimadzu TOC-5000 using catalytic combustion. The absorbance was calibrated against TOC analyses for each stream separately (Fig. 2). The standard deviations for the calibrations were between 0.35 and 0.80 mg L^{-1} for the different streams (Laudon et al., 2001). No significant seasonal variation was observed in the absorbance/TOC relationship in any of the streams.

A subset of samples during both baseflow and peakflow was analyzed for differences between filtered (0.45 µm pre-rinsed filters) and unfiltered samples. No statistically significant difference between the pairs was observed, suggesting that the particulate fraction contributes an insignificant portion of the organic carbon loss in these streams. Thus, TOC concentration is effectively equivalent to dissolved organic carbon (DOC) concentration for these streams.

Discharge was computed hourly from water level measurements (using pressure transducers connected to Campbell Scientific data loggers) in Västrabäcken, Kallkälsbäcken, Kallkälsmyren, Stridbäcken and during the second year in Lillån. In Sörbäcken, Mellansjöbäcken and during the first year in Lillån, stage heights were

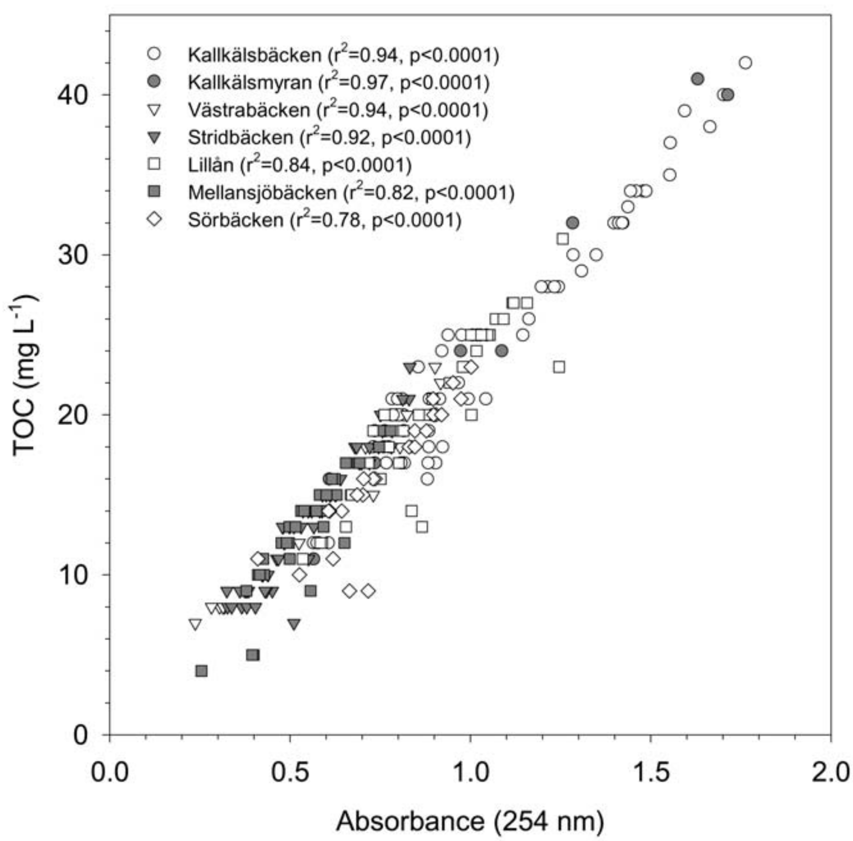


Figure 2. Absorbance/TOC relationship for the seven streams.

recorded manually concurrent with stream water sampling. Rating curves were derived using bucket-method measurements in Kallkälsmyren, Västrabäcken and Kallkälsbäcken and using hand-held current meters or a semi-automatic salt dilution technique in the remaining streams. Winter runoff was monitored continuously in Kallkälsbäcken, while in the other streams winter runoff was estimated from linear interpolation between measurement occasions.

TOC flux estimates were based on linear interpolation of TOC concentration and runoff. The seasonal TOC export was analyzed using four periods: Summer (June 1 – August 31), Fall (September 1-November 30), Winter (December 1 – April 30) and Spring (May 1 – May 31).

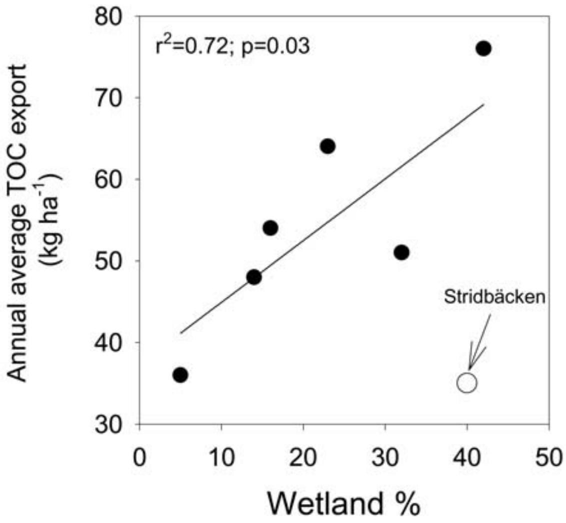
Results and discussion

The annual average export of TOC ranged between 36 and 76 kg ha^{-1} yr^{-1} for the seven catchments (Table 1) with export being positively correlated (Stridbäcken excluded from the analysis) with the areal extent of wetlands ($r^2 = 0.72$; $p = 0.03$) (Fig. 3a). The estimated catchment carbon loss as stream TOC is consistent with export rates reported from boreal streams in similarly-sized forest-dominated catchments in Finland, with long-term means ranging from 26 to 71 kg ha^{-1} yr^{-1} (Kortelainen et al., 1997). Boreal rivers in other regions of the world give a similar range, typically exporting between 10 and 100 kg ha^{-1} yr^{-1} (see Hope et al., 1994, and Mulholland, 2003 for reviews). Wetlands are suggested to be the most important source of TOC in boreal catchments, which is corroborated by the strong correlation between TOC export and areal extent of wetlands in our study (Fig. 3a). These results are in general agreement with several other studies showing strong correlations between the areal extent of wetlands and DOC export (Dillon and Molot, 1997; Hope et al., 1997a). The strong wetland contribution of TOC has important implications for northern Sweden where wetlands cover close to 25% of the land area in both coastal and inland regions. The low TOC export for Stridbäcken relative to its percentage wetland area could be explained by the location of wetlands within the catchment. While wetlands in the other catchments predominately are located as riparian wetlands or in the valley bottoms close to stream channels, the Stridbäcken wetlands are to a large extent located in the upper reaches of the catchment and not in direct contact with the stream.

The results presented by Dillon and Molot (1997) from catchments in south-central Canada showed a similar linear correlation between wetland area and DOC export. One important difference between these two studies is the relatively higher TOC export at low wetland percentage in the current study. Whereas the data from Dillon and Molot (1997) had an intercept at zero percentage wetland of 20 kg $ha^{-1}yr^{-1}$, our results suggest an export of close to twice that value (with an uncertainty at 95 % confidential interval of 12 kg ha^{-1} yr^{-1}) in non-wetland catch-

Table 1. Catchment characteristics and flux values of TOC and water.

	Kallkäls-bäcken	Västra-bäcken	Kallkäls-myren	Strid-bäcken	Lillån	Mellansjö-bäcken	Sör-bäcken
Catchment size (km^2)	0.50	0.13	0.19	9	21	26	62
Mire%	17	5	43	40	23	32	14
Annual discharge (mm yr^{-1})	230	204	228	192	219	223	248
Annual TOC export (kg ha^{-1} yr^{-1})	61	36	76	35	64	51	48
Relative seasonal TOC export							
Summer %	16	15	15	19	10	14	9
Fall %	12	9	11	10	17	13	10
Winter %	12	7	24	13	21	18	18
Spring %	61	68	50	57	53	55	64
Relative Seasonal runoff							
Summer	16	18	12	13	11	10	10
Fall	11	13	8	8	21	15	12
Winter	12	10	14	15	16	16	21
Spring	61	59	66	64	52	59	58
Daily export (kg ha^{-1} day^{-1})							
Summer	0.07	0.07	0.15	0.07	0.08	0.04	0.06
Fall	0.08	0.05	0.15	0.07	0.17	0.09	0.07
Winter	0.09	0.02	0.10	0.02	0.08	0.09	0.05
Spring	0.94	0.73	0.91	0.52	0.82	0.67	0.65
Number of samples	110	101	114	202	86	96	92



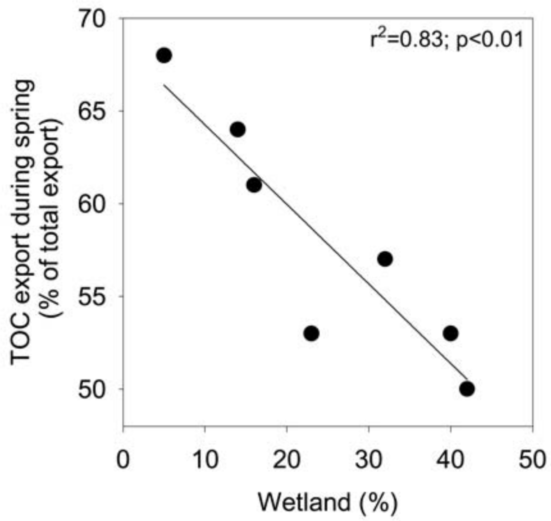


Figure 3. Correlation between annual TOC export and percent wetland area (upper panel). Correlation between relative spring flood TOC export and percent wetland area (lower panel).

ments (Fig. 3a). The relatively higher TOC export rates from entirely forested catchments in our study could be due to differences in climate or forest type, or to the fact that streams in northern Sweden generally have well-developed riparian wetlands lining most stream channels. Riparian wetlands in northern Sweden often cover <5% of the catchment areas, but are still a major source of TOC in forested catchments especially during high flow periods (Bishop and Pettersson, 1996).

Carbon dynamics of boreal regions play an important role in the global carbon balance. Boreal soil and wetland ecosystems constitute approximately 50% of the superficial carbon pool in the world (Schlesinger, 1997). Aurela et al. (2002) calculated an annual net carbon uptake of 70 ± 50 kg C ha^{-1} yr^{-1} in a wetland ecosystem in northern Finland using eddy covariance measurements of CO_2 together with CH_4 efflux estimates. In this context, the net catchment loss of 36 to 76 kg C ha^{-1} yr^{-1} that we observed as stream TOC is important in terms of boreal C budgets. If unaccounted for, this term could result in catchments which are in fact C sources being mistakenly identified as C sinks.

From a larger-scale perspective, the fate of this exported TOC will determine its potential impact on the environment and on the global C cycle. After entering the stream network, TOC may be transported, enter long-term storage as riverine/lacustrine/marine sediment, or be respired or otherwise oxidized to CO_2. The specific fate of stream TOC depends on both chemical properties of the TOC and physical, hydrological and biogeochemical characteristics of the drainage network. TOC is, at least in part, oxidized by microbes (Jansson et al., 2000; Stepanauskas et al., 2000) and photodegradation (Bertilsson and Tranvik, 2000; Köhler et al., 2002a), leading to increased partial pressure of CO_2 in organic rich headwaters (Sobek et al., 2003), and finally to evasion of CO_2 and a decreased downstream export of TOC. Dillon and Molot (1997) estimated the annual carbon loss as CO_2 evasion from seven small lakes in central Canada to range from –2 to 27 kg C ha^{-1} yr^{-1} or up to 30% of the annual TOC received by the lakes. Dillon and Molot (1997) also demonstrated that lake sedimentation is an important sink of carbon in these systems, especially in surface waters that have recently been acidified. Among the streams reported here, only Stridbäcken may be significantly acidified (Laudon et al., 2001) which potentially could explain some of the discrepancy in the correlation between TOC export and percentage wetland for that stream.

Of the exported TOC in this study, 50% to 68% occurred during the one month long spring flood period (Table 1). This translates to a daily TOC export rate of 5 to 11 times higher during the spring than during any other season of the year, largely due to differences in flow. Interestingly, the relative contribution of the snow melt period for the annual TOC export correlates negatively with the percentage of wetlands ($r^2 = 0.83$; $p < 0.01$) (Fig. 3b). This finding suggests that the relative importance of the spring flood for the TOC export is larger in more forested catchments, while TOC export from wetland dominated catchments is more evenly distributed over the year.

The variation in catchment TOC export during summer and fall is largely dependent on the amount and timing of precipitation events and snow melt (e.g., Ivarsson and Jansson, 1994; Hinton et al., 1997; Boyer et al., 1997; Buffam et al., 2001). Rain fall events led, in general, to TOC concentration increases for all catchments in this study. The two study years experienced close to the 20 year average precipitation for the Svartberget research station. In 1996–97 and 1997–98, the total precipitation was 625 mm and 586 mm, of which 34% and 39% was winter precipitation, respectively (M. Ottosson Löfvenius, unpublished data). TOC export values during wet years, especially in summer and fall, could be significantly higher than during this study period.

During snowmelt driven runoff episodes, significant variation in TOC-runoff patterns occurs depending on catchment characteristics. This variation is exemplified by the difference between the forested catchment, Västrabäcken and the wetland dominated catchment, Kallkälsmyren (Figs. 4 and 5). In Västrabäcken, the TOC concentration increases by two to three-fold during the snow melt period (Fig. 4). In contrast, during peak flow the TOC concentration in Kallkälsmyren declines to approximately one third of the baseflow level (Fig. 5). This variation may be explained by differences in flow paths during the snow melt period. Much of the snow melt runoff from forested areas reaches the stream via subsurface flow paths that activate new soil TOC sources in the riparian wetland lining most streams in the region (Bishop et al., 2004). In contrast, flow paths through wetland dominated systems include a larger component of snowmelt from overland flow over the frozen wetland surface as demonstrated by an oxygen-18 tracer study (Cory, 1999). As a result, the spring flood gives rise to a dilution in TOC concentration with increasing flow in wetland dominated catchments.

The reliability of flux estimates is to a large extent dependent on the sampling frequency, analytical precision of TOC measurement, and accuracy of flow measurements. Because the sampling frequency was greatest during periods of high flow and, therefore, during periods of large TOC flux, the gaps in sampling during low flow periods are not believed to cause large errors in the export values. Two interpolative methods of TOC load estimations were used to test this assumption. The first was a linear extrapolation of TOC concentrations between two subsequent sampling occasions, while the second used runoff related interpolation of TOC concentrations. Because the sampling was focused on high flow periods, the two methods produced comparable results (at most 10% discrepancy). The first method was used for the flux calculations presented in this study.

The uncertainties in both absorbance and TOC analyses and in the absorbance/TOC conversion are not believed to significantly bias the results. Because the analytical uncertainties are normally distributed, they will not cause systematic errors but merely generate a larger uncertainty in flux estimates. Furthermore, no seasonal variations in the absorbance/TOC relationship were observed that would alter the flux estimates (Fig. 2).

The TOC flux estimates are, however, sensitive to uncertainties in runoff measurements. A 10% systematic error in runoff during the spring flood would result in a 4% to 8% error in the TOC export value during the snow melt period. A biased annual runoff of 10% would generate a

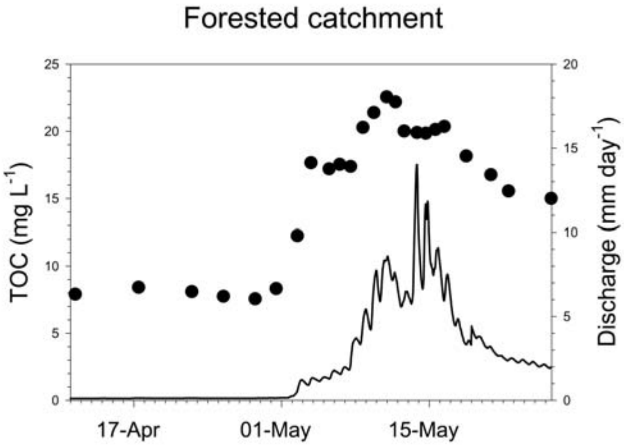


Figure 4. Spring flood 1997 in the forested Västrabäcken catchment.

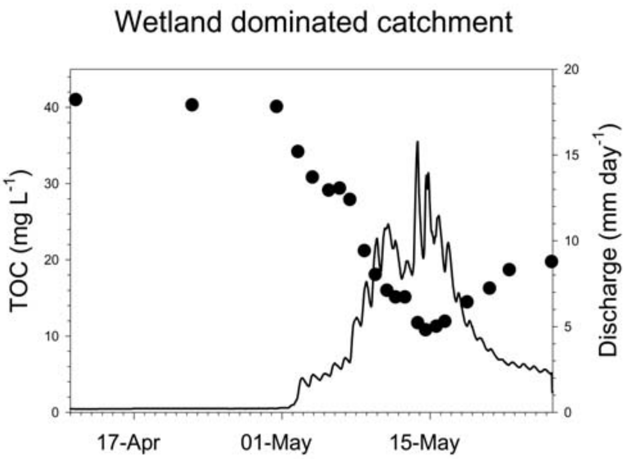


Figure 5. Spring flood 1997 in the wetland dominated Kallkälsmyren catchment.

TOC export error of 7% to 9%. For the smaller catchments (Västrabäcken, Kallkälsmyren and Kallkälsbäcken), the runoff measurement is estimated to be accurate to within 5% (K. Bishop, unpublished data). In the larger catchments, and especially in Mellansjöbäcken and Sörbäcken where no continuous runoff measurements were recorded, somewhat larger uncertainties in runoff measurements are to be expected. Another limitation with the flow measurements is that only Kallkälsbäcken had continuous runoff measurements throughout the entire winter. Although errors in the estimated winter flow measurements could result in large errors in winter TOC flux estimates, this will not substantially alter the annual TOC export rates, or the importance of the spring, due to low winter flow and TOC concentrations. A 25% systematic error in winter runoff would generate an error in the annual TOC export calculation between 3% and 10%, with the largest error being for Kallkälsmyren which has the highest winter TOC concentration. However, the specific runoff during the winter months in Kallkälsmyren and Kallkälsbäcken was similar (Table 1), suggesting that any systematic error in runoff in Kallkälsmyren is likely to be smaller than in the previous example.

Although the effect of future changes in climate on TOC export are difficult to predict, Clair et al. (1999) estimated that C export in Canada would increase on average by 14% with a doubling of atmospheric CO_2, using a neuronal network approach incorporating both effects of changes in flow and temperature. Other studies predict a decrease in export related to a decrease in runoff (Magnuson et al., 1997; Schiff et al., 1998; Pastor et al., 2003). Regional estimates for northern Sweden of the effect of climate change are predicting that the winter and, hence, spring snow melt are the periods that will be most affected (SWECLIM, 2001). Precipitation is predicted to increase by 10–20%, and the mean annual temperature is expected to rise by 4 degrees within 100 years as a result of global climate change. The temperature increase is predicted to be more prominent during the winter season, especially in the northern part of the country. One important consequence of a change in winter climate in boreal forests will be a change in the timing, extent and duration of snow cover (Venäläinen et al., 2001). Because one important role that snow has in the boreal landscape is to provide a major fraction of the annual runoff, a change in the extent and duration of the snow cover could lead to large changes in both total fluxes of TOC and in the timing of TOC export.

Conclusions

This study illustrates that wetlands are an important factor in explaining the annual export of TOC, ranging from 36 to 76 kg ha^{-1} yr^{-1} in seven boreal catchments in northern Sweden. The results also suggest that wetlands play an important role in regulating the timing of TOC export. Between 50% and 68% of the annual TOC export occurred during the four week long snow melt period, with a negative correlation between the percentage of wetlands and the relative importance of the spring flood. The smaller relative importance of the spring flood for annual TOC export from wetland dominated catchments is suggested to result from differences in hydrological flow paths associated with the snow melt period.

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