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Discussions

Long cold winters give higher stream water dissolved organic carbon (DOC) concentrations during snowmelt

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Abstract

We show that long cold winters enhanced the stream water dissolved organic carbon (DOC) concentrations during the following spring flood. Using a 15 year stream record from a boreal catchment, we demonstrate that the interannual variation in DOC concentrations during spring flood was related to the discharge, and winter climate. That discharge is important for DOC concentration agrees with previous studies. By controlling for discharge we could detect that the winter climatic conditions during the preceding winter affected the soil water DOC concentrations, which in turn affected the concentrations in the stream. The results from the stream time-series were also supported by a riparian soil frost experiment, which showed that a long period of soil frost promoted high DOC concentrations in the soil water.

1 Introduction

Dissolved organic carbon (DOC) is a fundamental descriptor of biogeochemical processes in small catchments and affects biogeochemical processes (Kalbitz et al., 2000; Hope et al., 1994), food web structure (Jansson et al., 2007) and the carbon balance (Cole et al., 2007; Nilsson et al., 2008). It is well established that hydro-climatic conditions control much of the episodic (Boyer et al., 1997), seasonal (Dawson et al., 2008) and interannual variability of DOC (Köhler et al., 2008), but also long term trends (Erlandsson et al., 2008). A warmer and wetter climate has been predicted to result in an increase in stream DOC concentrations in many regions (Köhler et al., 2009; Sebestyen et al., 2009; De Wit and Wright, 2008). Much less is known about the spring flood, which is the most important hydrological period of the year in many seasonally snow covered regions. Given the large amount of water leaving the catchment during this period, it is important to better understand what controls the spring flood DOC concentrations. Discharge has a strong control on the concentrations during spring flood (Seibert et al., 2009; Ågren et al., 2007; Laudon et al., 2004a; Bishop and Pettersson, 1996). However, it was only recently demonstrated that stream DOC concentrations during snowmelt can also be strongly controlled by winter climatic conditions (Haei et al., 2010). Climate change scenarios predict a change in the duration and timing of the snow-cover (IPCC, 2001). At the same time, regional climate models suggests that the temperature and precipitation will increase most in northern latitudes and during the winter months (Bergström et al., 2001). How this will affect the DOC concentrations and exports during snowmelt in the future is however not well understood.

In many forested catchments, the riparian zone has been found to be the most important source of DOC for stream water (Hinton et al., 1998; Vidon et al., 2010; McGlynn and McDonnell, 2003; Bishop et al., 2004). A shallow water table adjacent to the stream results in anaerobic conditions with a low decomposition rate; hence resulting in a build-up of organic material which leads to a peat formation along the stream channel (Vidon et al., 2010). As the water moves through the riparian peat the concentrations of organic carbon increase markedly before it enters into the stream (Fiebig et al., 1990; Bishop et al., 1990). In till dominated watersheds the soil water DOC concentrations increase toward the top of the soil profile. There is also a temporal variation in the soil water concentrations which increase during the snow free period and are at their minimum during spring flood (Seibert et al., 2009).

Hydrology is a first order control on the stream water DOC concentrations (Dawson et al., 2008; Boyer et al., 1997; Ågren et al., 2007). When new water (precipitation or snowmelt) enters into the catchment during a rain or snowmelt event, it recharges the soils and pushes out old previously stored water from the soil and into the stream. Between 70–90% of the water that enters the stream during snowmelt will be old water previously stored in the soil (Rodhe, 1989; Laudon et al., 2007). Given the fact that soil water DOC concentrations increase upward in the soil profile the lateral transport of DOC from soil to stream will increase if the water entering the streams is draining shallower more organic rich soil horizons (Sebestyen et al., 2008; Inamdar et al., 2004).

Although discharge has a fundamental control on stream water DOC concentrations, it is not the only controlling factor. The conditions in the soil before a rain or snowmelt event affect the concentrations during the event. During the vegetation period the soil moisture is important for the DOC leaching, but drying and rewetting have produced conflicting results. Inamdar et al. (2008) found higher DOC concentrations after a drought period, while Köhler et al. (2009) found (in the study catchment) that increases in flow during wet years lead to much higher DOC concentrations than during the dry years. In the autumn input of fresh leaf litter to the soils has been suggested to lead to higher DOC concentrations (Hongve, 1999). Flushing of the soils can deplete the amount of carbon in the soil and lead to decreasing concentrations (Boyer et al., 1997). In a climate change perspective it is important to better understand how soil temperature affects the DOC concentrations in the streams. Christ and David (1996) found that the production of DOC increased exponentially with temperature, with $Q(10)$ value of 1.7. Increasing temperature has also been suggested as one of the explanations for the increasing long-term trends in DOC (Sarkkola et al., 2009). Many processes interact to determine the stream water DOC concentrations and the importance of the processes vary between catchments and throughout the year.

Because of the limited understanding of what controls stream water DOC concentrations during the spring flood in northern latitude catchments, we combined a long-term stream record and an eight year soil frost experiment in the riparian soils of the same stream. We hypothesized that the winter climatic conditions have an important influence on stream water DOC concentrations during the spring flood. To test this hypothesis we separated the hydrological and climatic control on DOC concentrations during spring flood using a stream DOC concentrations model that could separate the effect of discharge from other causes (Seibert et al., 2009). The residual DOC concentration was then coupled to climatic- and hydrological data to test what controls the inter-annual variations in DOC during snowmelt using a fifteen year record of stream DOC concentrations combined with a winter manipulation experiment in the riparian zone of the study stream.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◂ ▸
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

2 Material and method

2.1 Study catchment and sampling

The study catchment was selected because of the availability of a long time-series of stream chemistry, discharge records, and meteorological data both from the air and the soil. The data were collected during 15 years, between 1993 and 2007. The study catchment, Västrabäcken (C2) (Fig. 1), is a small catchment (12 ha) that is entirely covered by forest, dominated by Norway spruce (*Picea abies*). The catchment is included in the interdisciplinary Krycklan Catchment Study (KCS) at Vindeln Experimental Forests (64°14′ N, 10°46′ E) in northern Sweden (Buffam et al., 2007). The major soil type is a typical podzolic soil with a 10 to 15 cm organic layer overlying the mineral soil which is a glacial till. Along the stream there is a riparian zone with organic riparian peat formation.

Winter climate data were recorded at the nearby Svartberget Research Station, following the standards of the Swedish Meteorological and Hydrological Institute (SMHI). The metrological station is situated 1.2 km southwest of Västrabäcken, C2. We give average as well as minimum and maximum values for the years 1993 to 2007 in our short description of the climate conditions in the watershed. The climate was characterized by long winters (winter starts when mean air temperature falls below 0 °C for three consecutive days and ends when mean air temperature rises above 0 °C for three consecutive days), on average 165 (133–195) days. The mean annual temperature was +2.2 (1.2–3.1) °C and the January temperature was −8.5 (−5.8 to −13.5) °C, with the lowest recorded daily temperature at −30.6 °C. The mean annual precipitation was 620 (446–827) mm with an average runoff of 309 (128–576) mm. The snow-cover generally forms sometime in November (14 Oct–13 Dec) and usually ends in the beginning of May (13 Apr–16 May). The maximum snow depth is on average 77 (55–98) cm and maximum soil frost is on average 18 (2.5–79) cm. The soil frost duration at 5 cm soil depth and at 10 cm depth is 121 (12–188) days and 81 (0–167) days, respectively.

Discharge has been calculated using established rating curves and water level measurements, which has been recorded hourly and then aggregated to daily values. The measurements were conducted just downstream from the study catchment, where a 90° V-notch weir is located inside a heated housing that prevents ice formation and enables measurements throughout the whole year. Assuming that the specific flow is the same throughout the whole catchment (47 ha) the discharge was calculated for the stream water sampling site C2 – Västrabäcken (12 ha) (Fig. 1).

The stream water was collected as grab samples. Before 2002 samples were collected weekly with more intensive sampling during the snow melt periods. After 2002 samples were collected monthly during base-flow prior to the onset of the snow melt, and then every second to third day during the spring until the flow receded to levels close to base-flow. The stream water samples were frozen immediately after collection. TOC analyses were carried out using a Dohrmann Carbon Analyzer before 1995, after that samples were analyzed using a Shimadzu TOC-5000. Linear interpolation was applied to obtain daily values.

Climate data was measured in an open field according to the Swedish standard. The numbers may therefore show an offset to that of the catchment because of the effect of the forest cover. Given the fact that the offset should be systematic for all years, the climate data are still valid in the context of inter-annual variations. The discharge data may also differ at our forested site C2, compared to what we measure just below the stream junction due to the effect of the wetland (wetland coverage of the whole 47 ha catchment is 16%). However, the interannual variations are greater than the variation between the wetland and the forest (Laudon et al., 2004b) and the use of specific flow to calculate discharge is adequate for this study.

2.2 Effect of discharge on stream DOC concentrations

The relationship between discharge and concentrations was explored using Log-Log relationships (Godsey et al., 2009; Clow and Mast, 2010). We plotted the regression between DOC concentrations in the study stream versus the instantaneous discharge

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

on logarithmic scales (Fig. 3; n=71) and compared the slope of the regression to the reference slopes. On a log-log-scale a slope of −1 means simple dilution and a slope of 0 means that the catchment shows a chemostatic behavior (Godsey et al., 2009; Clow and Mast, 2010). The analysis was conducted on both annual and monthly basis. To test if the slope of the regression differed significantly from zero the t-ratio was calculated. According to Helsel and Hirsch (2002) a t-ratio above 2 indicate a significant difference from a slope of zero (if $\alpha = 0.05$ and $n > 30$). The t-ratio was calculated as:

$$\text{t-ratio} = \frac{b_1}{\frac{\text{RMSE}}{\text{SS}_x}} \tag{1}$$

where b_1 = slope of the regression, RMSE = Root Mean Square Error and SS_x = Sums of Squares x.

From previous work in the study catchment we know that the discharge is a key component for controlling the DOC concentrations (Köhler et al., 2009; Seibert et al., 2009). Because of the important effect of discharge on the DOC concentration, the signal from other contributing processes could not be observed clearly. We therefore removed the hydrological effect on DOC concentration by applying a conceptual mathematical model of how the riparian zone and the hydrology control the stream water chemistry. The **R**iparian Profile Flow-Concentration **I**ntegration **M**odel (RIM) has been developed in the study stream starting with Bishop (1991) and formalized by Seibert et al. (2009). The riparian zone has been identified as the most important source of carbon in the study stream (Bishop et al., 1994; Köhler et al., 2009; Seibert et al., 2009) and in short, DOC concentration in the stream can be modeled based on the groundwater level (Fig. 2, left panel) and a schematic soil DOC gradient in the riparian soil (Fig. 2, right panel). The concentrations in the stream are modeled by multiplying the lateral water flux at a certain depth with the concentration of the soil water at that depth and then integrating over the horizons with lateral flow i.e. the ones below the ground water table. The DOC concentrations in the soil vary between years and within seasons, these variations are exemplified by grey dashed lines (Fig. 2, right panel).

The DOC concentrations in the soil solution for each depth in the riparian soil can be described by an exponential relationship:

$$C = c_0 e^{f\,\text{depth}} \tag{2}$$

where C in the concentration at a certain depth, c_0 is the concentration at depth 0, and f is a shape factor describing the change in DOC concentrations with depth in the soil water profile. The grey lines (Fig. 2, right panel) show the variation in f (1.7–2.8) that was observed in May according to Seibert et al. (2009). By applying the model using an average f during May (Seibert et al., 2009) (black line, Fig. 6b, c_0=45, f=2.2) we model the expected DOC at a certain discharge. The residual DOC, observed minus the modeled, was used as a proxy for the variability in the soil water DOC concentrations that is not controlled by hydrology. A high (positive) residual DOC indicates that higher concentrations are measured in the stream compared to predicted, i.e. that soil water DOC concentrations (inferred from stream DOC) were higher than the average, and vice versa. Partial least square (PLS) analysis (see below) was used to study the residuals.

2.3 Effect of winter climate on soil water DOC concentrations

For the stream DOC time-series we selected two ecologically interesting response (Y) variables: 1) DOC concentration during maximum discharge, "flood DOC" (DOC_F) (a variable that coincides with the minimum pH in these boreal headwaters due to the dilution of base cations by snow melt water). 2) The maximum concentration during spring flood, "max DOC" (DOC_M). DOC_M occurred on average eight days before the peak in discharge. We also calculated RIM-modeled DOC concentrations for the same dates and calculated the residual DOC_M and DOC_F (i.e. the difference between measured and modeled values) (Fig. 4). We use the residual DOC_M and DOC_F as a proxy for the soil water concentration profiles in the riparian zone.

In total 31 variables were collected as predictors (X) for the interannual variation in spring flood DOC. They were divided into 3 major groups; Snowmelt variables –

different measures to categorize the spring flood, Winter climate variables – Climate data that describe the winter condition in the air and soil, and Antecedent conditions variables – Variables describing the summer and autumn prior to the spring flood. For a complete list of included variables and how they were defined see Table 1. Partial least square analysis (PLS) is an appropriate method for datasets with less observations than variables (15 observations versus 31 variables in our case), many of which may covary. SIMCA-P 11.0 statistical package (Umetrics, Sweden, 2005) was used for the PLS analysis. Prior to analysis all variables were checked for normality using one-sample Kolmogorov Smirnov test in SPSS 17.0 (SPSS Inc., Chicago, IL, USA). Some variables were transformed to fit normality and all were scaled and centred using z-scores.

All PLS models were refined until only the variables that had significant coefficients in the model (using 90% confidence interval) were included. The initial PLS model was an exploratory model with $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ as Y against all X variables. After removal of the hydrological effect on the DOC concentrations (using RIM) during spring flood, we wanted to test if hydrology still explained part of the residual DOC concentrations or if we had removed the effect of hydrology. This was tested by constructing a PLS model with the residual DOC concentrations as Y and the snowmelt variables (Table 1) as X.

The individual PLS models for residual $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ produced similar results and presenting them separately did not give any additional information. We therefore present them in the same model. The final PLS model presented is a model with the residual $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ as Y and all variables (Table 1) (except the snowmelt variables, since the effect of discharge was removed) as X. The model was refined until only the significant X variables (90% confidence interval) remained.

2.4 Soil frost experiment

In combination with the stream water time-series of DOC we used a field-scale soil frost manipulation experiment that was initiated in 2003 in the riparian zone of the study stream. A full description of the experiment is provided by Öquist and Laudon (2008), but in short three soil frost treatments was conducted, with three replicates each. First, the experiment consists of a "no soil frost" treatment, by insulating the soil with water permeable geotextile bags filled with Styrofoam pellets. Second, in the "normal soil frost" plots, no frost treatment was applied, and third, an "extended soil frost" was induced by removing the snow by means of a roof, thereby decreasing the soil temperatures and increasing the duration of the soil frost. In late winter, the accumulated snow was transferred from the roofs to the ground, to maintain the water balance between the plots. Here we show DOC concentrations in the soil solution measured at 10 cm depth. The soil water was collected using suction lysimeters (pore size 1 μm) and the DOC (without any additional filtration) was analyzed using a TOC-5000 Shimadzu analyzer. The sampling was carried out 8–15 times per year and more intensively during the spring and summer. Because of practical difficulties in soil water sampling at 10 cm depth (due to soil frost in early spring and drought in summer) we here present all the DOC data for the period March–August, over a 4 year period, providing in total 76 DOC samples. For "normal soil frost" the average soil frost duration at 10 cm was 72 days, while it was 144 days for the "extended soil frost". For the "no frost" treatment, the soil frost never reached 10 cm depth. To test for a significant difference between treatments we used independent sample t-test (in SPSS), and tested all pairs.

3 Results

The discharge in May varied more (with a factor of 49) compared to the DOC concentrations which varied with a factor of 2.5 (Fig. 3). The Log-Log relationship between DOC and Q indicate how discharge and concentrations interact (Fig. 3, left panel) ($y = 0.13x + 1.14$, $R^2 = 0.39$, $p < 0.001$, $n = 71$). For the month of May the slope was 0.13 (standard error = 0.023) which was significantly different from zero as indicated by the t-ratio (Eq. 1). This means that the stream DOC concentrations during spring flood increased more with flow than expected given a chemostatic behavior of the catchment. The annual slope was even higher: 0.22 (standard error = 0.012) for the annual relationship ($y = 0.22x + 1.19$, $R^2 = 0.41$, $p < 0.001$, $n = 469$). The lowest slopes were found during spring and the highest in late autumn and mid winter (Fig. 3, right panel).

There were also large interannual variations in DOC during spring flood. $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ ranged between 17.7–30.1 and 15.6–29.3 mg $\mathrm{L^{-1}}$, respectively, over the 15 years, hence varying with a factor of 1.7 and 1.8, respectively (Fig. 4). During some years the discharge explained almost all the variation in the snowmelt DOC concentrations (RMSE = 4.34 mg $\mathrm{L^{-1}}$ for the RIM-modeled values for May), but other years, other factors were clearly also important as indicated by a large residual DOC after applying RIM (Fig. 4).

After refining the initial PLS model (90% significance level) only two variables remained that could explain the $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ concentrations. It was the length of the spring flood (days >1 mm) and the amount of discharge (mm) during the rising limb ($R^2X = 0.798$, $R^2Y = 0.17$, Q^2=0.101), again showing that discharge has a first order control on the DOC concentrations.

After applying RIM, no significant PLS model could be constructed between residual DOC and the snowmelt variables, which supports the notion that we effectively removed the effect of discharge. The refined PLS model with the residual $\mathrm{DOC_M}$ and $\mathrm{DOC_F}$ as Y and all X variables (Table 1) (except snowmelt variables) is displayed in Fig. 5 ($R^2X = 0.567$, $R^2Y = 0.432$, $Q^2 = 0.268$). The model was not suited for predictions given the low Q^2 value, but suggests that the winter climate variables explain 43% of the variation in the residual concentrations in the stream. All four explaining variables correlated positively to the Y-variables. The two most important variables were the number of days below zero °C during the metrological winter and the length of the metrological winter. A long winter could also result a delayed soil frost thaw, which was the third most important variable. The temperature sum in the air was also a significant variable, but had the least weight (closest to the plot origin). The soil water carbon concentrations during spring flood thus seem to be foremost dependent on the length of the winter and not so much on previous export of DOC during the antecedent summer/fall and winter (which correlated negatively to the residual DOC concentrations in the PLS model, but not significantly).

The soil frost manipulation experiment in the riparian soil confirmed that long winter enhanced the DOC concentrations in the soil solution (Fig. 6). Because we included samples from March to August, the boxplots includes both temporal variability and variability between replicates. However, despite the large variability a treatment effect could still be detected. The independent sample t-test between the treatments indicated a significant difference between all three groups. During normal winters the DOC concentrations at 10 cm depth were on average about 10 mg L^{-1} higher compared to the no soil frost scenario. When the length of the winter was extended, by removing the insulation from the snow, the DOC concentrations increased markedly with another 50 mg L^{-1} compared to the no soil frost scenario. These findings support the PLS analysis based on the stream water time-series where long winters, with many days below-zero temperature, increased the DOC concentrations in the stream. The effect on average DOC concentrations due to the soil frost manipulations (no soil frost to extended soil frost) ranged 60 mg L^{-1} compared to the calculated residual DOC_F and DOC_M which ranged 39 and 30 mg L^{-1}, respectively. We expect a higher effect of the manipulation experiment because the soil frost manipulation is stronger than the natural variability in the winter climate.

4 Discussion

By using data from the intensively monitored Västrabäcken catchment, coupled with experiments in the riparian zone, we may elucidate the processes that control the interannual variations in DOC concentration during snowmelt. The riparian soils are the most important source of carbon for the study catchment (Bishop et al., 1994; Köhler et al., 2009; Seibert et al., 2009). According to Hinton et al. (1998) the riparian zone can contribute as much as 84% of DOC during a storm and according to Dosskey and

Bertsch (1994), the riparian organic peat provided 93% of the organic carbon entering the stream despite only covering 6% of the catchment area. Because the riparian soil is the most important source of carbon for the stream, we placed the soil frost experiment in that zone to study the effect of winter climate on riparian soil water DOC concentrations. That runoff is an important controlling factor of the DOC concentrations in forested catchments has been found in many previous studies (Köhler et al., 2009; Hinton et al., 1997; Ågren et al., 2007; Hornberger et al., 1994; Bishop, 1991). RIM is an attempt to describe this regulation mathematically and is a result of many years of monitoring and process based research on the study catchment. This has resulted in several articles over the years and a development of a mechanistic understanding of the importance of the riparian zone as a source for the stream organic carbon and other chemical parameters, as well as how these elements are transported across the soil/stream interface (Bishop et al., 1995; Cory et al., 2007; Laudon et al., 2004b; Köhler et al., 2009; Seibert et al., 2009; Öquist et al., 2009b; Klaminder et al., 2006).

The Västrabäcken catchment does not show a true chemostatic behavior (Godsey et al., 2009; Clow and Mast, 2010). If that would have been the case, the concentration would be independent of flow. The positive annual slope of the Log-Log relationship indicates that the concentrations increase with discharge. This is in line with the exponential increase in DOC concentrations upward in the soil profile that gives higher concentrations during high flows, as described in RIM (Seibert et al., 2009). The monthly analysis showed that the slope of the regression increased from spring flood to January, indicating that the soil water DOC concentrations (inferred from stream DOC) continue to increase during growing season and into winter, and then decreased at the onset of snowmelt. An increase in soil solution DOC concentrations over the growing season has been found in other studies (Cronan and Aiken, 1985; Kalbitz et al., 2000; McDowell and Likens, 1988). Here we show that this increase might continue during winter.

The DOC concentrations in the soil water are controlled by several mechanisms. In short, it is a combination of the production of DOC in the soil by soil organic matter breakdown (Moore et al., 2008) and the subsequent transport from the soil into streams, adsorption to minerals (Guggenberger and Kaiser, 2003) and mineralization in the soil into CO_2 (Bengtson and Bengtsson, 2007). The production of DOC has been found to be controlled by high microbial activity, high fungal abundance and seasonality of plant growth. Concentration of anions and cations in the soil are also important (Kalbitz et al., 2000). High moisture and temperature promotes the production of DOC (Christ and David, 1996). Köhler et al. (2009) showed in the study stream, that DOC in the snow free period could successfully be predicted from temperature and soil wetness (runoff was used as a proxy for soil wetness) during the growing season. In that study DOC is predicted to increase by 15%, due to a future warmer and wetter climate. This might be true for the growing season. However, our study indicates that other controlling climatic factors are important for DOC export during spring flood in this boreal system.

This study identifies another important controlling mechanism; winter climate. The PLS analysis on the residual DOC concentration showed that a long winter with many days with sub-zero temperatures promoted the DOC concentrations in the stream (Fig. 5), which was further corroborated by the soil frost experiment (Fig. 6). The increase in DOC concentrations following a long winter can be a result of an increased production rate of DOC or that more DOC is conserved in the soil. By “conservation” we mean that the carbon that was produced during the vegetation period is mineralized into CO_2 at lower rates in subzero temperatures during winter (Panikova et al., 2006; Öquist et al., 2009a). An increased winter production of DOC might be explained by both physical and biological processes. Physically, the freezing temperature itself may cause freeze damage to the cells (Soulides and Allison, 1961). Disruption of the soil caused by frost heaving, formation of ice lenses and/or capillary water movement may damage fine roots (Tierney et al., 2001) or ectomycorrhizal fungi and free living microorganisms (Giesler et al., 2007), or make previously sorbed organic matter more available for leaching (Kalbitz et al., 2000; Yurova et al., 2008). A biological process that might be important for the DOC production during winter is the adaption of organisms to cold temperatures. Elevated levels of carbohydrates have been suggested to function as osmoregulators for freeze protection in trees (Wong et al., 2009). According to a study by Scott-Denton and co-workers (2006) in a lodgepole pine stand, soil sucrose concentrations were eight times higher during winter than during other times, possibly derived from the mechanical damage of shallow roots with high levels of sucrose for protection against low-temperature extremes. The microbial community decomposes soil organic matter into DOC, foremost by secreting exoenzymes (Sinsabaugh, 1994). The microbial community during winter can be dominated either by fungi (Schadt et al., 2003) or bacteria (Lipson et al., 2009). The microbial community can also adapt to sub-zero temperatures (Rilfors and Lindblom, 2002) or shift in species composition towards fast growing, cold-adapted microbes that can grow in low temperatures (down to −5 °C) (Lipson and Schmidt, 2004). The cold-adapted microbial biomass reaches its maximum levels in late winter (Schmidt and Lipson, 2004) and this might lead to an increased DOC production during a long winter. From this study we cannot identify the exact processes behind the increasing DOC concentrations following a long winter, but a combination of the above processes seems plausible.

One of the explanations to the long term increase in DOC in surface waters in parts of North America and Europe is the increase in temperature. Future predictions on the long-term changes of DOC concentrations suggest that DOC will continue to increase as a result of increasing temperature and precipitation (Futter et al., 2009; Köhler et al., 2009; Hongve et al., 2004). Studies by Futter and de Wit (2008), as well as Erlandsson et al. (2008) showed that both climate and deposition explained the observed variations in surface water DOC concentration, and seasonal and inter-annual patterns were primarily driven by climate while long-term trends were driven mainly by deposition. Some studies suggests that climate change scenarios leading to warmer temperature will increase the amount of DOC in streams, especially during summer and autumn (Futter and de Wit, 2008; Köhler et al., 2009). These studies are either considering the growing season only or represent more southerly areas where snowmelt is not of such fundamental importance for the annual water and carbon flux.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

In this study we show that winter climate can be of fundamental importance for controlling snowmelt DOC concentrations in northern latitudes. How future climate will affect stream water DOC concentrations in this catchment depends on the interacting effects of winter temperatures as well as the timing, duration and depth of snow accumulation. The impact of climate change on snow and soil temperature has been modeled for the study region (Mellander et al., 2007). The authors predict that in 100 years, the duration of the snowpack will decrease with about 80 days and soil temperatures at 10 cm will increase with about 1 °C, while the frequency of freeze-thaw cycles are expected to increase by about 35%. Mellander et al. (2007) predicted a warming of the soils during winter, but, a decrease in the snow-cover might also lead to colder soils (Groffman et al., 2001), especially during a transition period, as a result of reduced depth of the insulating snow-cover (Isard et al., 2007; Hardy et al., 2001). Precipitation is predicted to increase in the future. As wet soils require longer time to freeze because of more latent heat, future winter soils may become warmer instead of colder, however the moisture will also delay warming in spring. The increased soil frost due to the removal of snow in the soil frost manipulation experiment could possibly suggest an increasing DOC in a future climate. At the same time our PLS analysis of the stream record suggests that a shorter winter with more days above zero degrees would decrease the DOC concentrations. While these results are difficult to directly translate to a future climate change prediction, they highlight the importance of winter climate conditions for controlling spring flood DOC concentrations in northern boreal systems.

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Table 1. List of predictor variables (X) used in the PLS analysis.

Winter climate variables	Short name
Start date of the meteorological winter (Julian date) (when mean air temperature falls below 0 °C for three consecutive days)	Start winter
End date of the meteorological winter (Julian date) (when mean air temperature falls above 0 °C for three consecutive days)	End winter
Length of the metrological winter (Days)	Length winter
Number of days with below-zero air temperature in the preceding meteorological winter (days)	Days<0 °C winter
Number of days with above-zero air temperature in the preceding meteorological winter (days)	Days>0 °C winter
Accumulated daily air temperatures during the meteorological winter (positively transformed) (°C)	Temp sum air
Temp. sum (sum of hourly recorded) soil temperature at a depth of 10 cm during the meteorological winter (positively and ln transformed) (°C)	Temp sum soil
Maximum snow depth (cm)	Snow depth
Start date of permanent snow-cover (Julian date)	Start snow
End date of permanent snow-cover (Julian date)	End snow
Number of days with snow-cover (days)	Days snow
Maximum soil frost depth (ln transformed) (cm)	Frost depth
Start date of soil frost thaw (Julian date)	Soil frost thaw
Antecedent condition variables	
Mean [DOC] during the antecedent winter baseflow (January–March)	DOC baseflow
Total DOC export during the antecedent meteorological winter (kg)	DOC exp winter
Specific discharge on 1 January (winter baseflow) (mm day^{-1})	Q Jan
Specific discharge one month prior to the commencement of snowmelt (mm day^{-1})	Q month prior
Total discharge during the antecedent meteorological winter (mm)	Q winter
Total discharge from the end of the previous snowmelt to the onset of the antecedent meteorological winter (ln transformed) (mm)	Q summer/fall
Total DOC export from the end of the previous snowmelt to the onset of the antecedent meteorological winter (ln transformed) (kg)	DOC exp summer/fall
[DOC] on 1 January (mg L^{-1})	DOC Jan
Snowmelt variables	
Start date of snowmelt (Julian date)	Start snowmelt
Duration of the snowmelt rising limb (days)	Duration rising limb
Number of days with specific discharge >3 mm day^{-1} (days)	Days $Q>3$ mm
Number of days with specific discharge >1 mm day^{-1} (days)	Days $Q>1$ mm
Maximum specific discharge during snowmelt (mm day^{-1})	Q max
Total discharge during snowmelt, Q (mm)	Q tot
Discharge on the day of maximum [DOC]	QE
Discharge from the onset of snowmelt until the peak-flow (mm)	mm rising limb
Date of [$\mathrm{DOC_M}$] (Julian date)	Date $\mathrm{DOC_M}$
Date of [$\mathrm{DOC_F}$] (Julian date)	Date $\mathrm{DOC_F}$

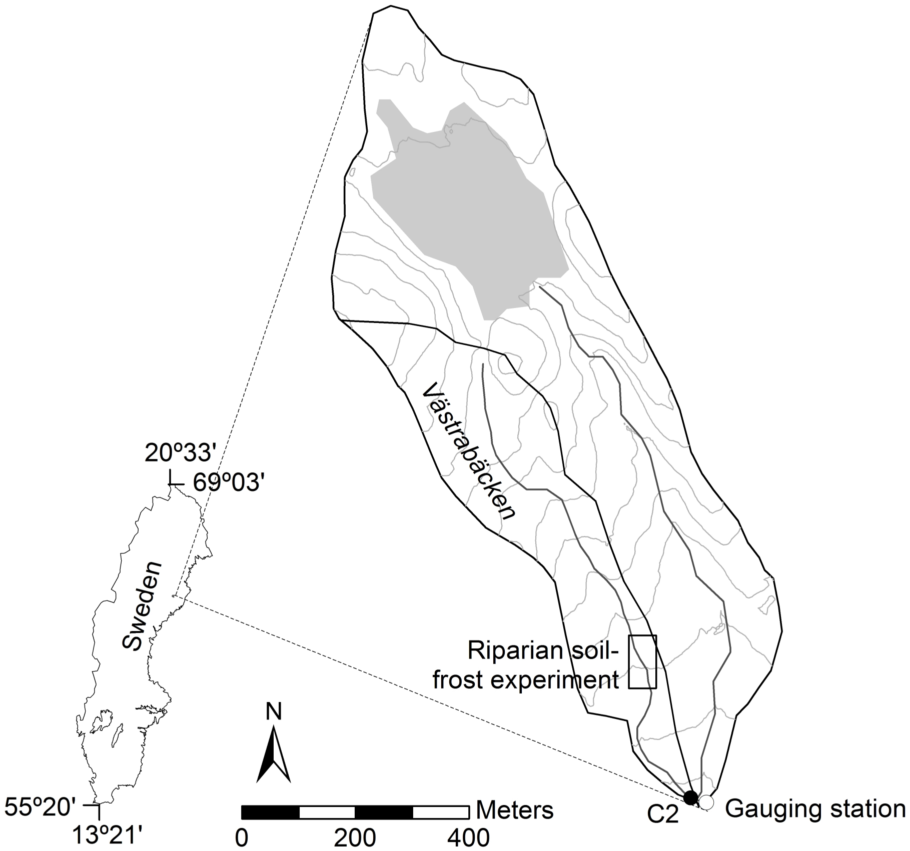

Fig. 1. Map of the study catchment. Sampling site for water chemistry is indicated by a filled circle and discharge measurements by an open circle. Dark grey lines indicate streams, white areas are covered by forests and the gray area indicates mire. Light grey lines indicate the topography using a 5 m contour interval.

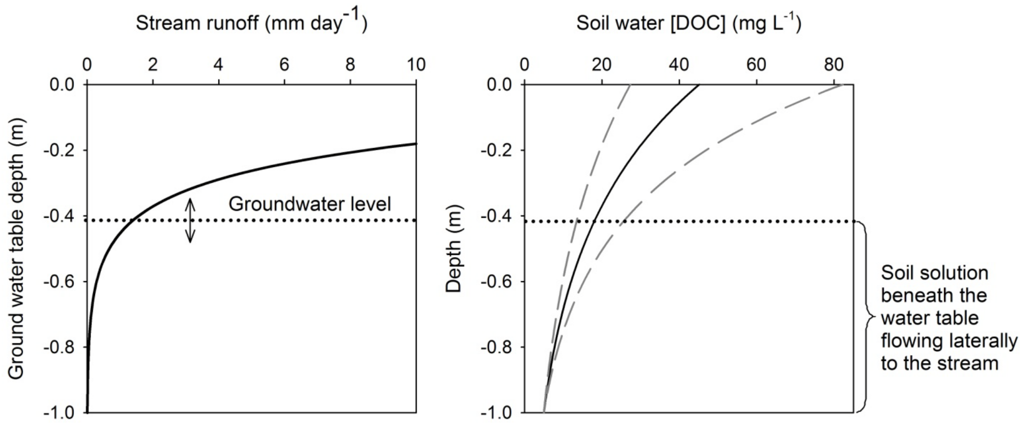

Fig. 2. Schematic view of RIM, modified from Seibert et al. (2009). The left panel shows the relationship between stream runoff and groundwater level. The left panel shows the shape of the soil water DOC concentration profile, grey dashed lines indicate the variation in f-factor (the shape of the profile) in May.

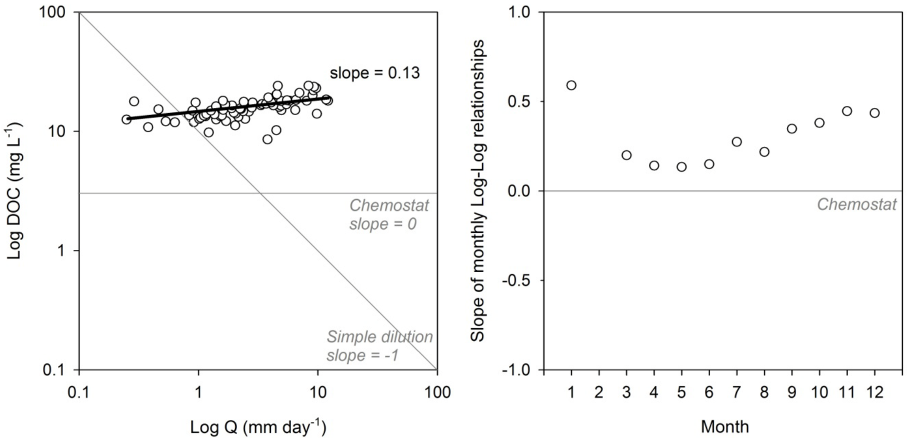

Fig. 3. Scatterplot of concentration – discharge relationship in May during 15 years in Västrabäcken, plotted on a Log-Log scale (Left panel). Reference lines indicate the slopes 0 and −1, which correspond to chemostatic behavior and simple dilution, respectively. The right panel displays the monthly slopes of the Log-Log concentration – discharge relationships. All (but February) were significant on the 0.05 level.

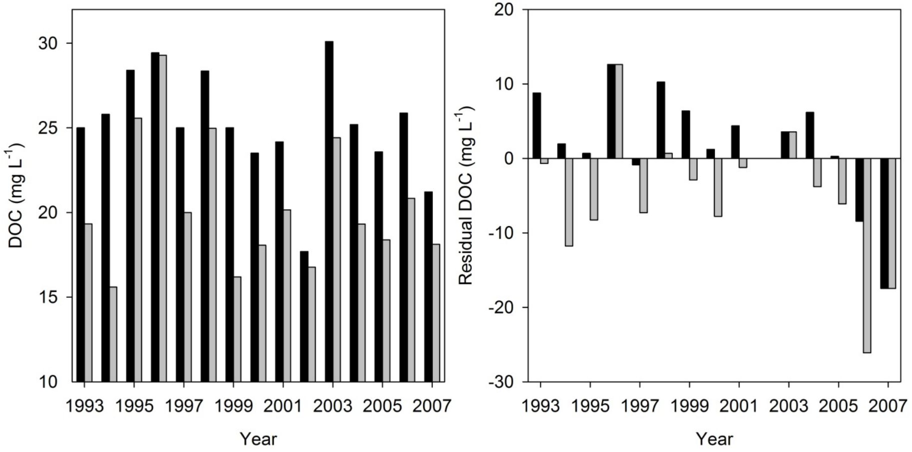

Fig. 4. The left panel is the inter-annual variation in DOC_M (Black bars) and DOC_F (Grey bars) and the right panel is the residual DOC_M (Black bars) and DOC_F (Grey bars) after subtraction with the RIM modelled values. A positive residual DOC indicates high soil water DOC during spring inferred from stream DOC concentrations, and vice versa.

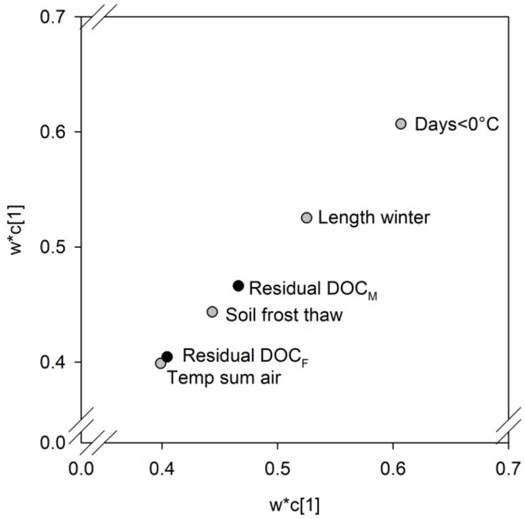

Fig. 5. PLS weight plot, showing that high soil water DOC concentrations, inferred from stream DOC (indicated by Residual DOC$_M$ and DOC$_F$) correlates positively to long cold winters. This means higher DOC$_M$ and DOC$_F$ after long winters. The *Y* variables are marked in black and the four significant *X* variables in grey.

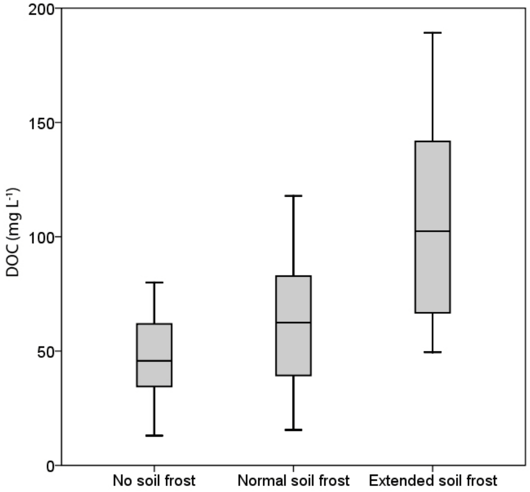

Fig. 6. The treatment effect of soil frost duration on DOC concentrations in the soil solution at 10 cm depth. The normal soil frost lasted on average 72 days and the extended soil frost 144 days. Modified from Haei et al. (2010).