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Cold winter soils enhance dissolved organic carbon concentrations in soil and stream water

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[1] Concentrations of dissolved organic carbon ([DOC]) have increased in lakes, streams and rivers across a large part of the northern hemisphere and raised an animated scientific debate about the underlying mechanisms. The lack of consensus about the role of climate in controlling the DOC trends highlights the need for understanding the regulation of surface water DOC. We found that longer and colder winters result in higher [DOC] in a boreal headwater stream during the subsequent snowmelt. In addition, prolonged soil frost increases the spring and summer [DOC] in the riparian soil water, which is a major contributor of stream water DOC in the studied area. We conclude that winter climatic conditions can play a substantial role in controlling stream [DOC] in ways not previously understood. These findings are especially important for northern latitude regions expected to be most affected by climate change. **Citation:** Haei, M., M. G. Öquist, I. Buffam, A. Ågren, P. Blomkvist, K. Bishop, M. Ottosson Löfvenius, and H. Laudon (2010), Cold winter soils enhance dissolved organic carbon concentrations in soil and stream water, *Geophys. Res. Lett.*, *37*, L08501, doi:10.1029/2010GL042821.

1. Introduction

[2] Dissolved organic carbon (DOC) is a defining feature of many lakes, streams and rivers in a large part of the world, since DOC controls metal export and speciation, acid-base behavior and food-web structures in many surface waters. The concentrations of [DOC] have recently increased in surface waters across a large part of the high latitude regions and caused a scientific debate about the relative importance of climate and variability in other external drivers as the mechanism for this increase [*Roulet and Moore*, 2006; *Monteith et al.*, 2007]. The lack of consensus about the role of climate in controlling the trends in DOC highlights the need for improved understanding of the mechanisms of DOC regulation in surface waters.

[3] The northern hemisphere boreal zone is characterized by a distinct winter season with persistent snow cover, and with a spring snowmelt which is the dominant hydrological event [*Barnett et al.*, 2005]. The snow cover not only accounts for a major fraction of the annual water budget, but also plays a fundamental role in regulating the biogeochemistry of the winter soil environment [*Williams et al.*, 1998; *Groffman et al.*, 2001]. The snow cover exerts control over the development of soil frost by reducing heat loss from the ground during winter [*Stieglitz et al.*, 2003], thereby influencing soil frost regimes. One important implication of the predicted climate change in many northern regions is that the timing, extent and duration of snow cover will be altered [*Intergovernmental Panel on Climate Change* (*IPCC*), 2001]. These changes are likely to affect the winter temperature and frost regime of soils, and increase the frequency of freeze-thaw events in the future [*Stieglitz et al.*, 2003].

[4] The riparian zone is, in many areas, a substantial store of organic soil carbon that has accumulated as a result of waterlogged conditions and slow mineralization rates, providing a local DOC source to streams. In northern Sweden, for instance, riparian peat is a major source of DOC to streams in forested catchments, particularly during high-flow episodes [*Seibert et al.*, 2009] in spite of its limited areal coverage. Changing the DOC pool in the riparian zone could, thus, have considerable impact on the [DOC] in stream waters.

[5] Based on the influence of winter climate on soil biogeochemistry and the known links between riparian soil biogeochemistry and stream chemistry, we hypothesized that winter climatic conditions play a key role in regulating [DOC] in boreal headwater streams. To test this, we statistically analyzed a long time series of stream [DOC] in relation to winter climate and environmental variables. As a complement we also carried out a long-term soil frost manipulation experiment to investigate the response of soil [DOC] in the riparian zone to changes in soil winter temperatures and soil frost regime.

2. Materials and Methods

2.1. Study Area

[6] The study stream drains the 50 ha Nyänget subcatchment in the Krycklan catchment (64°14′N, 19°46′E) in northern Sweden. The soil frost experiment is located in the riparian zone of the study stream. The catchment is mainly forested with 80 year old Norway Spruce (*Picea abies*) in wetter areas with a field layer primarily of blueberries (*Vaccinium myrtillus*), with *Sphagnum spp.* mosses on the small mire and riparian wetlands. On drier soils Scots pine (*Pinus sylvestris*) dominates with a field layer consisting mainly of heather (*Calluna vulgaris*) and lingonberries

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Table 1. PLS Analysis: $[DOC]_{max}$ in Response to Variables Representing Winter Climate, Preceding Conditions and Snowmelt Period[a]

Variable
Y-variable
Peak [DOC] during the snowmelt period ($[DOC]_{max}$) (mg L^{-1})
X-variables
Climatic variables in the preceding meteorological winter
Start date (Julian date)
End date (Julian date) [A]
Number of days with below-zero air temperature (days) [B]
Number of days with above-zero air temperature (days)
Accumulated daily below-zero air temperatures (positively transformed) (°C) [C]
Accumulated (sum of hourly recorded) soil temperature at a depth of 10 cm (positively and ln transformed) (°C) [D]
Maximum snow depth (cm)
Start date of permanent snow cover (Julian date)
End date of permanent snow cover (Julian date)
Number of days with snow cover (days)
Maximum frost depth (ln transformed) (cm)
Start date of soil frost thaw (Julian date)
Preceding condition variables
Specific discharge on Jan 1st (winter baseflow) (mm day^{-1}) [E]
Specific discharge one month prior to the commencement of snowmelt (mm day^{-1}) [F]
Total discharge during the preceding meteorological winter (mm) [G]
Total discharge during summer/fall (ln transformed) (mm) [H]
Total DOC export during summer/fall (ln transformed) (kg) [I]
Total DOC export during the preceding meteorological winter (kg) [J]
Mean [DOC] during the preceding winter baseflow (January–March)
[DOC] on January 1st (mg L^{-1})
Snowmelt variables
Start date of snowmelt (Julian date) [K]
Duration of the snowmelt rising limb (days) [L]
Number of days with specific discharge > 3 mm day^{-1} (days)
Number of days with specific discharge > 1 mm day^{-1} (days)
Maximum specific discharge during snowmelt (mm day^{-1})
Total discharge during snowmelt (mm)
Snowmelt intensity (Maximum daily discharge during snowmelt/Total discharge during snowmelt) (ln transformed)
Discharge from the onset of snowmelt until the peak-flow (mm)
Date of $[DOC]_{max}$ (Julian date)

[a] The significant X-variables are marked [A]–[L], and are included in Figure 1. Meteorological winter is the period in which the average daily air temperature is below 0°C. Summer/fall is defined as the period between the end of the previous snowmelt to the onset of the preceding meteorological winter.

(*Vaccinium vitis-idaea*). The annual mean air temperature (1980–2008) is 1.7°C, with average air temperatures in January and June of −9.6°C and 14.6°C, respectively. The mean annual precipitation (1981–2008) is 612 mm, with an average stream runoff of 323 mm. On average, the ground is covered by snow for 168 days per year (1980–2007) from mid November to early May. The average maximum snow depth is 76 cm (varying between 43 and 113 cm, 1980–2007). Maximum soil frost depth varies between 2.5 cm and 79 cm (1993–2007) as measured at a reference climate station at the Svartberget Experimental Forest, situated approximately 1 km from the study catchment.

2.2. Stream DOC, Discharge and Winter Climate Variables

[7] Discharge and stream [DOC] were monitored for a period of 15 years (1993–2007). Stream water was collected as grab samples in acid washed and stream rinsed high density polyethylene bottles on a weekly or more frequent basis. All water samples were immediately frozen after collection and, prior to 1995, analyzed using a Dohrmann Carbon Analyzer. After 1995, a TOC- 5000 Shimadzu analyzer was used. The analyses were conducted on unfiltered samples. Since numerous comparisons of the stream water over many years and under all flow conditions indicate that more than 95% of the organic carbon is in a dissolved form [*Köhler et al.*, 2008], we use the term DOC.

[8] The hourly stream flow was calculated from continuous height measurements collected using calibrated V-notch weirs located in a heated hut and recorded using a Campbell Scientific data logger equipped with a pressure transducer. Winter climate variables were measured at the Svartberget climate station. Hourly recorded soil temperature and soil moisture (measured with gypsum blocks) were used to determine the soil frost depth.

2.3. Field-Scale Soil Frost Manipulation Experiment

[9] To better understand the mechanisms that control the regulation of DOC sources reaching surface waters during snowmelt, we performed a long-term soil frost manipulation experiment (between 2003 and 2008) in the riparian zone; our aim was to induce changes in soil frost regimes [*Öquist and Laudon*, 2008]. We applied three soil frost treatments in triplicate 3*3 m^2 plots: Deep soil frost, Shallow soil frost and Control. These produced three significantly different winter soil temperature regimes. During winter, the Deep soil frost plots were covered with a roof to prevent snowpack formation, while the soil surface in the Shallow soil frost plots was insulated with water permeable geotextile bags filled with Styrofoam pellets. The Control plots were exposed to the ambient conditions. Each year in late winter, we transferred the accumulated snow on the roofs to the ground surface below to ensure comparable water balances between all treatments. The soil solution was sampled at five depths down the soil profiles (10, 25, 40, 60 and 80 cm) using suction lysimeters. The lysimeters were installed in the centre of each sampling plot with 2.9 ± 0.5 m (mean ± standard deviation) distance to the stream. The sampling was carried out 8–15 times per year, most intensively during the spring and summer. The soil solution DOC was analyzed using a TOC- 5000 Shimadzu analyzer. The soil temperature and water content were continuously monitored (using time-domain reflectometry, TDR) at all depths.

2.4. Data Analyses and Statistics

[10] We identified the peak [DOC] in the stream during the snowmelt period ($[DOC]_{max}$) and tested how this was correlated to twenty-nine variables representing the variation in winter climate, the preceding conditions and snowmelt (Table 1), with a partial least square analysis (PLS) using the SIMCA-P 11.0 statistical package (Umetrics, Sweden, 2005). Values were transformed to conform to normality according to a one-sample Kolmogorov Smirnov test, using SPSS 17.0 software (SPSS Inc., Chicago, IL, USA). The values were then scaled and centered prior to analysis. The PLS model was refined by limiting the predictor variables to those with statistical significance (90% confidence interval) and high PLS weight (Table 1).

[11] In the soil frost manipulation experiment, there was no data collected prior to the instrumentation of the sites and initiation of the manipulation in late 2002. However, the analyses of soil solution data were restricted to the years

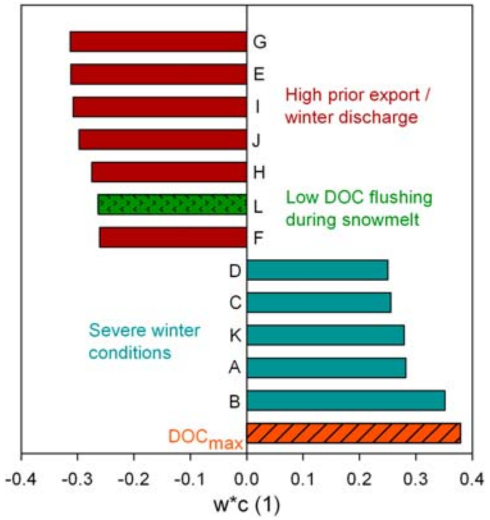

Figure 1. PLS weights (w*c) for the refined PLS model based on twelve significant X-variables describing the variations in $[DOC]_{max}$ in response to winter climate, preceding conditions and snowmelt period ($R^2X = 0.45$, $R^2Y = 0.74$, $Q^2 = 0.60$). Y-variable: $[DOC]_{max}$. X-variables: A. End date of the meteorological winter (transformed to positive numbers), B. Number of days with air temperature < 0°C in the preceding winter, C. Accumulated daily air temperatures < 0°C during the preceding winter, D. Accumulated soil temperature at a soil depth of 10 cm during the winter (transformed to positive numbers), E. Specific discharge on Jan 1st, F. Specific discharge one month prior to the commencement of snowmelt, G. Total discharge during the preceding winter, H. Total discharge during summer and fall, I. Total DOC export during summer and fall, J. Total DOC export during the preceding winter, K. Start date of snowmelt, L. Duration of the snowmelt rising limb.

2004–2008, to eliminate artifacts associated with establishment of the treatments. The mean (± standard deviation) maximum soil frost depths were calculated using the 5-year soil- temperature and TDR data, as described by Öquist *et al.*, 2008. Briefly, the maximum soil frost depth was estimated by interpolation between the frozen and unfrozen soil layers. "Frozen" was defined as temperature ≤ 0°C and TDR response indicating no liquid water, while "unfrozen" was temperature > 0°C and TDR response indicating liquid water. Because of a problem with temperature probes, the data for one of the control treatment plots as well as the data for winter 2008 at the other two control treatment plots were excluded (giving n = 15 for the manipulated plots and n = 8 for the control plots). The mean spring and summer [DOC] was calculated for the period March–October 2004–2008 at five depths in the soil profiles for each treatment (based on a total of 1214 soil solution samples collected when the soil was not frozen or dry). At each depth, the significance of soil frost treatment effect on soil solution [DOC] was tested with the non-parametric Mann-Whitney U-test using SPSS 17.0 software (SPSS Inc., Chicago, IL, USA) with analyses evaluated at the 5% significance level. The mean soil solution [DOC]s for the spring and summer (March–October 2004–2008) were calculated at a soil depth of 10 cm. A linear regression analysis was conducted to explain the variations in soil solution [DOC] as a function of the duration of soil frost during the preceding winter season (defined as the mean number of days with below-zero temperature at the 10 cm soil depth in the winters 2003–2007), using SPSS 17.0 software (SPSS Inc., Chicago, IL, USA).

3. Results

[12] Of the predictive variables, twelve were statistically significant with high PLS weights ($R^2X = 0.45$, $R^2Y = 0.74$, $Q^2 = 0.60$; one significant component; Figure 1). The PLS analysis revealed a strong positive correlation between stream water $[DOC]_{max}$ and the variables representing "severe winters" (variables A-D and K, Figure 1). Our analysis suggests, therefore, that longer and colder winter conditions result in higher stream water $[DOC]_{max}$ during spring snowmelt. In addition, $[DOC]_{max}$ exhibited a strong negative correlation with high export of DOC during the preceding summer/fall and winter (variables I and J, Figure 1) and high winter and summer/fall discharges (variables E-H, Figure 1) as well as low flushing of DOC during snowmelt (variable L, Figure 1).

[13] In the Deep soil frost treatment, the mean maximum depth of soil frost was 49 ± 6 cm (standard deviation), while the mean for the Control plots was 29 ± 3 cm. The corresponding mean depth in the Shallow soil frost treatment was 4 ± 5 cm. The average minimum soil temperatures at 10 cm depth were −5.2 ± 1.1°C (standard deviation), −2.2 ± 1.0°C and −0.2 ± 0.4°C for Deep soil frost, Control and Shallow soil frost plots, respectively.

[14] The mean [DOC] in spring and summer (March–October) for the Deep soil frost treatment was significantly higher (by a factor of two) than for the Shallow soil frost treatment at both the 10 and 25 cm depths. The [DOC] was significantly lower under the Shallow soil frost treatment than the Control at depths of 10 and 25 cm. Compared to the Control, the Deep soil frost treatment had a significantly increased level of DOC level at a depth of 10 cm (Figure 2). Testing the treatment effect for the snowmelt/spring (March–July) and summer/fall (August–October) periods

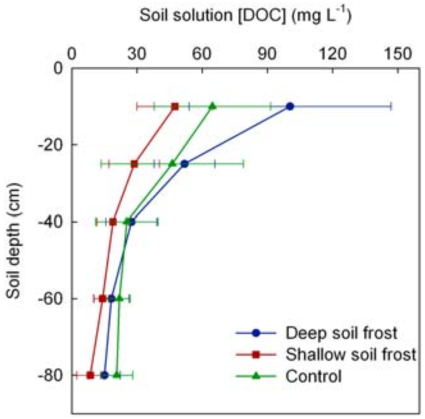

Figure 2. Mean [DOC] in the soil solution during spring and summer for the three soil frost treatments. The error bars indicate the standard deviations.

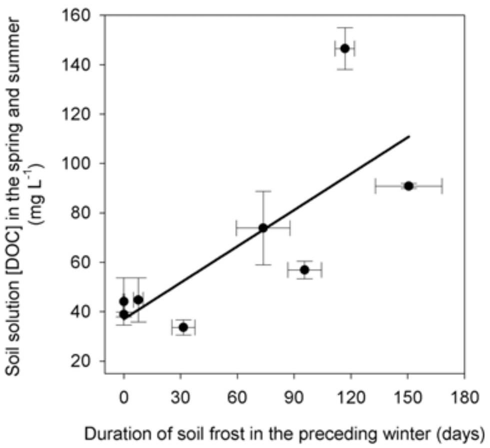

Figure 3. Soil solution [DOC] in spring and summer in relation to duration of soil frost in the preceding winter at the depth of 10 cm. ($Y = 0.5\ X + 37.0$, $R^2 = 0.57$, $n = 8$, $p = 0.03$). Each point represents a treatment plot. The error bars indicate standard errors.

showed that Deep soil frost treatment at 10 cm depth had significantly higher [DOC] than either Shallow soil frost or Control treatments in both periods.

[15] Expressing the soil solution [DOC] at 10 cm as a function of the duration of soil frost during the preceding winter season produced a significant regression, explaining *ca* 60% of the variation in soil solution [DOC] (Figure 3).

4. Discussion

[16] Based on our long-term analysis, we demonstrate, for the first time, that stream water [DOC] is strongly linked to the climatic conditions during the preceding winter. Our manipulation experiment provides evidence that a change in the winter climate that results in colder soil conditions would enhance soil frost development and increase [DOC] in the soil. This leads to an enhancement of [DOC] in the adjacent streams, since the riparian zone is a major source of DOC to the surface waters in the area. Physical disruption of the soil [*Kalbitz et al.*, 2000], mortality of fine roots [*Tierney et al.*, 2001] or lysis of freeze-damaged soil organisms [*Soulides and Allison*, 1961] are mechanisms that can increase [DOC] during periods of soil frost. Although the exact contribution of these potential mechanisms warrant further research, it is evident that winter conditions exert an integral control on soil [DOC] manifested throughout the following growing season. To date, a few short-term field-scale manipulation studies have been performed in order to examine the relationship between soil frost and [DOC] in soil solution [*Fitzhugh et al.*, 2001; *Austnes et al.*, 2008]. The studies which do exist report no, or inconclusive, effects on soil solution [DOC]. The strong influence of soil frost on [DOC] observed in our study is, however, similar to results obtained in laboratory-scale freezing experiments [*Austnes and Vestgarden*, 2008; *Vaz et al.*, 1994; *Wang and Bettany*, 1993]. The great effect of soil frost on DOC, in contrast to previous field experiments, could be related to our long-term experimental design, which closely mirrors the natural variability occurring in the region [*Öquist and Laudon*, 2008]. Another possible explanation is that previous studies have been conducted using upland soils with low organic carbon contents, whereas we investigated an organic rich riparian soil with longer soil frost duration. Furthermore, we maintained the water balance between the treatments.

[17] Our study shows that the [DOC] in riparian soils, and hence stream water, is strongly controlled by the preceding winter's climatic conditions. The extent of soil frost development ultimately depends on the integrated effect of air temperature and the extent and duration of the snow cover. Winter conditions in the northern boreal zone are expected to be especially affected by climate change [*IPCC*, 2001] but the net effect on soil frost conditions and hence on stream water [DOC] in the future is difficult to predict. Our results do, however, highlight that the role of winter climate for regulating DOC in areas with seasonally frozen soils should be considered when resolving the sensitivity of stream [DOC] to global environmental change. This role of winter climatic condition has not received sufficient attention in previous studies of factors regulating stream water [DOC].

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