Journal of Hydrology 373 (2009) 44–56

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios

S.J. Köhler [a,*], I. Buffam [b,1], J. Seibert [c], K.H. Bishop [d], H. Laudon [b]

[a] *Institute of Applied Geosciences, Rechbauerstrasse 12, Technical University of Graz, Austria*
[b] *Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå, Sweden*
[c] *Department of Physical Geography and Quaternary Geology, Stockholm University, SE-106 91 Stockholm, Sweden*
[d] *Department of Environmental Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden*

ARTICLE INFO

Article history:
Received 7 November 2008
Received in revised form 10 March 2009
Accepted 9 April 2009

This manuscript was handled by L. Charlet, Editor-in-Chief, with the assistance of Eddy Y. Zeng, Associate Editor

Keywords:
Organic matter
TOC
DOC
Modelling
Riparian zone
Boreal region

SUMMARY

Two different but complementary modelling approaches for reproducing the observed dynamics of total organic carbon (TOC) in a boreal stream are presented. One is based on a regression analysis, while the other is based on riparian soil conditions using a convolution of flow and concentration. Both approaches are relatively simple to establish and help to identify gaps in the process understanding of the TOC transport from soils to catchments runoff.

The largest part of the temporal variation of stream TOC concentrations (4–46 mg L^{-1}) in a forested headwater stream in the boreal zone in northern Sweden may be described using a four-parameter regression equation that has runoff and transformed air temperature as sole input variables. Runoff is assumed to be a proxy for soil wetness conditions and changing flow pathways which in turn caused most of the stream TOC variation. Temperature explained a significant part of the observed inter-annual variability.

Long-term riparian hydrochemistry in soil solutions within 4 m of the stream also captures a surprisingly large part of the observed variation of stream TOC and highlights the importance of riparian soils. The riparian zone was used to reproduce stream TOC with the help of a convolution model based on flow and average riparian chemistry as input variables. There is a significant effect of wetting of the riparian soil that translates into a memory effect for subsequent episodes and thus contributes to controlling stream TOC concentrations. Situations with high flow introduce a large amount of variability into stream water TOC that may be related to memory effects, rapid groundwater fluctuations and other processes not identified so far.

Two different climate scenarios for the region based on the IPCC scenarios were applied to the regression equation to test what effect the expected increase in precipitation and temperature and resulting changes in runoff would have on stream TOC concentrations assuming that the soil conditions remain unchanged. Both scenarios resulted in a mean increase of stream TOC concentrations of between 1.5 and 2.5 mg L^{-1} during the snow free season, which amounts to approximately 15% more TOC export compared to present conditions. Wetter and warmer conditions in the late autumn led to a difference of monthly average TOC of up to 5 mg L^{-1}, suggesting that stream TOC may be particularly susceptible to climate variability during this season.

Introduction

The growing awareness of land use and climate change impacts on landscape biogeochemistry motivates the study of temporal and spatial variation of TOC in headwaters and higher order streams and lakes. There is evidence that trends over decadal time scales in both TOC concentrations and TOC fluxes have occurred in surface waters of some regions of the world (Worrall et al., 2004; Monteith et al., 2007). While the actual cause for this trend is disputed (Evans et al., 2006; Fenner et al., 2007; Erlandsson et al., 2008), there is clear evidence that changing quantity and character of organic carbon have a large impact on biota downstream (Jansson et al., 1996; Stepanauskas et al., 2000; Miller et al., 2006; Alexander et al., 2007). Increases in TOC and associated metals such as aluminium and iron may also negatively affect the processing of drinking water from artificial stream infiltrate (Lefebvre and Legube, 1993; Chow et al., 2003).

---

[*] Corresponding author. Tel.: +43 316 873 6363; fax: +43 316 873 6876.
E-mail address: koehler@tugraz.at (S.J. Köhler).

[1] Now at Ecosystem and Landscape Ecology Lab, Department of Zoology, University of Wisconsin, Madison, WI 53706, USA.

0022-1694/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhydrol.2009.04.012

Several studies have demonstrated that temporal variability of stream water TOC generally is controlled by runoff, soil wetness and temperature (Urban et al., 1989; Hope et al., 1994, 1997; Hinton et al., 1997; Ågren et al., 2008). A detailed analysis of the causes of the temporal variations of TOC revealed that the parameters stream flow, soil wetness and temperature exerted a very strong control on the temporal and inter-annual variation of stream TOC at a forested site in the boreal region of Sweden (Köhler et al., 2008).

The sources and ages of soluble organic matter are diverse (Thurman, 1985; Stevenson, 1994). Fresh organic matter enters the deeper soil layers from above during periods of intensive biological activity. These situations occur after the soil has been flushed during periods of intensive plant activity and concurrent exudation of fresh organic carbon through the roots, plant litter degradation and when optimum conditions for temperature, nutrients and humidity for the soil fungi and soil bacteria prevail. Then both fresh and old organic carbon are processed and transformed through oxidative processes and are thus available for the soil solution. In a series of experiments Winkler et al. (1996) and Christ and David (1996) demonstrated the significant and systematic effect of increased DOC production after the rewetting of the soil at various temperatures. The soil litter manipulations of Hongve (1999) indicate that the seasonal pattern of stream DOC is related to the seasonality of release of DOC from the soil. Clear seasonal patterns of TOC have also been observed in a range of catchment studies (Lydersen, 1995; Hessen et al., 1997; Tipping et al., 1999; Laudon et al., 2004a; Buffam et al., 2007). Thus there is strong evidence to believe that organic matter production is tightly related to soil temperature and soil wetness. Quite a large number of models have been presented that allow quantifying different Carbon pools in the soil and their subsequent transport to the stream (Tipping, 1996a; Kram et al., 1999; Michalzik et al., 2003; Lumsdon et al., 2005; Tipping et al., 2006; Futter et al., 2007; Yurova et al., 2008). From many of these modelling studies and others that analyze longer time series (Worrall et al., 2006; Mitchell et al., 2006; Eimers et al., 2008; Erlandsson et al., 2008) it is evident that the transfer of potentially available soluble soil organic matter into the soil solution also depends on a series of chemical factors such as pH, concentration of sulphate, aluminium and degree of hydrophobicity.

Ecologically relevant temporal TOC variability in headwaters occurs on time scales of hours to days (Miller et al., 2006; Jorgensen et al., 1998) while much of the literature on climate change effects has considered mean annual changes (Monteith et al., 2007). Intra-annual changes in quantity and quality of TOC and related parameters such as pH and dissolved organic nitrogen (DON) are in many cases much larger than those observed between years (Erlandsson et al., 2008; Köhler et al., 2008). The sensitivity of this short-term variability to climatic drivers remains to be explored. In boreal regions one important factor for the changing concentration and character of stream TOC over time is changing flowpaths and the extent of riparian zones (Hemond, 1990; Dosskey and Bertsch, 1994; Bishop et al., 2004; Hinton et al., 1997). Other factors that control the concentration of TOC in the soil solution include physical (i.e. protective layers acting as diffusive barriers, available surface area changes due to shrinkage or freezing), chemical (i.e. adsorption to hydro-ferrous oxides soil particles, ion-exchange with sulphate, change in solubility of hydrophobic components) (David and Vance, 1991; Kaiser and Zech, 1998; Mulholland, 2003; Kawahigashi et al., 2006; Eimers et al., 2008) and biological (i.e. nutrient availability, temperature influence on microbial activity) (Tipping et al., 1999; Kalbitz et al., 2000; Köhler et al., 2008).

A range of dynamic catchment models have been presented into which many of the above named processes/factors have been incorporated (Kram et al., 1999; Tipping, 1996b; Tipping et al., 2006, 2005; Lumsdon et al., 2005; Futter et al., 2007; Yurova et al., 2008). The use of these complex models is often limited to well characterized smaller catchments and applying these type of models elsewhere without prior knowledge may result in over-parameterization. Linear regression models of TOC as a predictor variable of flow or temperature have previously been used by a large number of authors on shorter time series (e.g. Lydersen, 1995; Kendall et al., 1999; Erlandsson et al., 2008 or Worrall and Burt, 2008). Convolution models on the other hand have been used quite frequently to decipher hydrological processes in catchments (e.g. Bishop et al., 2004; McGuire et al., 2005; Hantush, 2005 and references therein). The comparison of these simpler approaches may aid to decipher some of the underlying processes mobilizing TOC from headwater catchments.

The current study seeks to quantify the importance of flow, temperature and soil chemistry on the explained variance of modelled and measured instantaneous stream TOC values over the course of 15 years on a forested, 13 ha catchment. More specifically, we address the following questions: (1) Is TOC mobilisation limited by the water flux through the riparian soil? (2) To what degree is TOC mobilisation controlled by flow and temperature? (3) Do temporal changes in riparian soil chemistry affect TOC mobilisation? (4) How may TOC concentrations and loads change as a result of changed climatic conditions in the future?

Materials and methods

Site descriptions

In this study we focus on a 13-ha catchment which is part of the experimental 50 ha Nyänget catchment in the Vindeln Experimental Forests (64°14′N, 19°46′E), 60 km northwest of Umeå, Sweden (Fig. 1). The catchment is forested with 80 year old Norway Spruce (*Picea abies*) in wetter areas and Scots pine (*Pinus sylvestris*) on drier soils. The site was ditched to improve forest productivity in the early 1920s as was the case for many other sites in that region. Riparian wetland extension and morphology was mapped on both sides of the stream beginning at the stream and soil water sampling site and extending 1 km upstream. The thickness of the organic topsoil varies from around 50 cm within a few several meters of the stream channel to around 5 cm further upslope where typical podzols prevail. The runoff data used in this study was measured at the outlet of the Nyänget catchment using a V-notch weir sheltered by a small housing. The sampling site and methodology for acquisition of meteorological and hydrochemical data is described in great detail in Nyberg et al. (2001), Cory et al. (2007) and Köhler et al. (2008).

Sampling of soil and stream water

During autumn 1995 a riparian transect was installed in the flowline of the groundwater at 4 m (S4) from the stream, around 200 m upstreams of the *v*-notch of the western tributary (Laudon et al., 2004b; Petrone et al., 2007). At various depths (10, 25, 35, 45, 55 and 65 cm) acid washed and rinsed with ultrapure water (Milli-Q corporation) ceramic P80 suction lysimeters in triplicates as well as temperature probes and TDR (Time domain reflectometry for soil moisture measurement) were installed (Fig. 1). Sampling of soil water was not started until the following summer to let the system equilibrate during the rest of autumn, winter and spring. Soil water was sampled using acid washed and MQ rinsed 0.5 or 1 L Duran glass bottles using a starting suction of around −0.6 to 0.8 atm^{-1}. Around 200 individual soil water samples were taken in the riparian soil profile at different horizons during the period 1996 through 2004. Samples were analyzed for pH, major

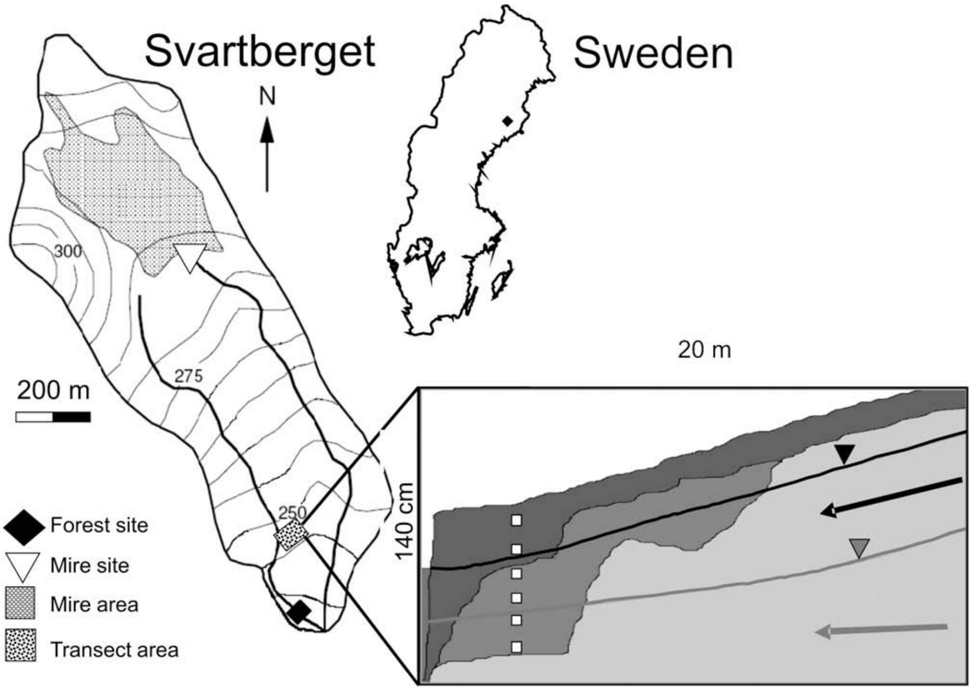

Fig. 1. Location of the catchment within Sweden and map with indication of the transect area and stream sampling site (♦). The inset displays the transect section, lowest groundwater level (grey line) and highest groundwater level (black line), sampling depths and location of the soil lysimeters (☐) at 4 m from the stream channel. The dark grey, grey and light grey areas display the extent of peat, organic soil and mineral soil, respectively.

cations and anions and TOC (Cory et al., 2007). During the years 1997 until 2002 the TDR and temperature probes were connected during specific periods covering more than 50% of the time to determine volumetric soil water content and temperature using Campbell loggers at the same depths as soil water was sampled. During the period (1993–2007) approximately 470 stream water samples were collected with the purpose of studying the temporal variations in TOC (Köhler et al., 2008) and other basic stream water chemical parameters.

Development of models

In a previous paper (Köhler et al., 2008) we identified the importance of seasons, annual precipitation, daily measured flow (Q) and daily soil temperature measured at 30 cm depth in the riparian soil profile S4 (T_{soil}) as the major driving variables for explaining patterns of average monthly and annual TOC variations in the studied stream. We divided the year into three consecutive (1–3) characteristic seasons: the "*snow covered season*" when the catchment is usually covered with snow (December to March – 1), the "*spring melt season*" when the snowmelt-driven spring flood occurs (April and May – 2) and the "*snow free season*" (June to November – 3) in which the hydrological processes and TOC export strongly differ (Laudon et al., 2004b; Ågren et al., 2007). As the highest TOC export and inter-annual variations in TOC are observed during the snow free period (Köhler et al., 2008), we focus primarily on this period.

Regression model

Temperature and runoff are known to be related to stream TOC concentrations. One key observation made in a recent study of this catchment (Köhler et al., 2008) was the appearance of significant inter-annual patterns in TOC concentration related to soil temperature, although this became clear only after distinguishing wet from dry years, when the autumn concentrations differed markedly. During the wet years, when sufficient rainwater has been stored in the soil, groundwater levels are constantly higher and rain or melt water flows through the organic rich topsoil that show the highest soil solution TOC. Measured groundwater levels in the riparian soil are proportional to the logarithm of Q (Bishop et al., 2004) and, thus this parameter was included as a proxy for groundwater levels. A thorough multivariate analysis of principal components (PCA) of the dataset has identified Q and T as the two major factors explaining more than 50% of the observed variation while other contributions to the explained variance from factors such as precipitation, air temperature, amount of antecedent dry days or flow and temperature interaction terms where either not significant or very small (<5%). To summarize the three parameters T_{soil}, Q and $\ln Q$ were chosen as potential variables for predicting instantaneous stream TOC [mg L^{-1}] using a multi-linear relationship (Eq. (1)). TOC_0 [mg L^{-1}] is the base TOC concentration, $T_{soil}(t)$ [°C] is the modelled soil temperature calculated from daily air temperature as described in (Köhler et al., 2008) and calibrated as described in that study to reproduce the measured temperatures at a depth of 30 cm in a soil profile 4 m from the stream. $Q_{(t)}$ [mm d^{-1}] is the specific runoff at time t and $Q*(t)_i$ [mm d^{-1}] is the average specific runoff during the preceding i days at time t. The specific runoff was calculated from the measured discharge at the outlet of the Nyänget catchment.

$$\mathrm{TOC}(t) = \mathrm{TOC}_{(0)} + aT_{soil}(t) + bQ(t) + c\ln(Q^{*}(t)_i) \tag{1}$$

While daily soil temperature fluctuations are always below 0.6 °C (Köhler et al., 2008), large changes in Q may occur within hours of a rainfall or snowmelt event. The wetting of soil and subsequent release of TOC might be lagged in time and carry some memory effect. This is why we systematically tested whether a lagged averaged signal in $\ln(Q)$ could improve the fit between modelled and measured stream water TOC. Also, in an effort to minimize the number of parameters, we tested whether the omission of different terms of equation 1 would significantly affect the model estimates. While the fitting factor c in Eq. (1) does show a systematic pattern throughout the year, no attempt was made to model the months separately. In this way the number of adjustable model parameters was limited to four. This approach will be referred to as regression model in the following.

Convolution model

As an alternative to the statistical approach of the regression analysis we tested a convolution model where stream TOC was computed as a flow-weighted mean of the average observed $TOC_{(j)}$ [$\mathrm{mg\,L^{-1}}$] at various soil depths (j) in the riparian soil based on the concept presented by Bishop et al. (2004). We used the flow-groundwater depth relationship established for the hillslope (e.g. Nyberg et al., 2001; Laudon et al., 2004b) to calculate the amount of water that flows laterally through each layer of the riparian zone, $q_{j\,(t)}$ [$\mathrm{mm\,d^{-1}}$], and then computed the flow-weighted means (Eq. (2)):

$$TOC_{(t)} = \frac{\sum_{i=0}^{100\,\mathrm{cm}} TOC_j * q_j(t)}{Q_{tot}(t)} \tag{2}$$

where $Q_{\mathrm{tot}}(t)$ is the sum of water [mm] travelling horizontally at each moment and $TOC_{(t)}$ [$\mathrm{mg\,L^{-1}}$] the flow weighted mean. The spatial resolution for the computations in Eq. (2) was set to 5 cm. This is half the spatial resolution that is available for the soil TOC data, which were sampled every 10 cm. Consequently average values for TOC between the sampled depths were calculated to attain a 5 cm resolution. Below the deepest lysimeter that was used for soil solution TOC sampling (65 cm) we assumed average TOC values of 6, 3 and 2 $\mathrm{mg\,L^{-1}}$ at −75, −85 and −95 cm depth, respectively following the observed decrease of TOC with depth from the layers above. In the following, this model is referred to as the convolution model.

Statistical analysis and uncertainty of models

The regression model was calibrated using stream water data from 1993 through 2003. After dividing the data into the three seasons the goodness of fit for this model were judged from the parameters adjusted R^2, p-value, error estimates in a, b and c assuming a 95% confidence interval and the parameter AIC (Akaike's information criterion). These latter parameter uses the residual of the sum of the squares of the error (SSE), the number of predictor variables ($n = 1$, 2 or 3) and number of observations ($n = 425$ for the period 1993–2003) to compare different model estimates. After the identification of the amount of parameters we systematically tested whether a time shift in $\ln Q$ would help to improve the model fits. For this purpose we used the SSE of the model and measured data during the snow free periods in the years 1993–2003. Given the long-term average errors for the determination of daily values for T_{soil} (±0.6 °C) and flow (±15%) we used the propagation of error method (Miller and Miller, 1993) to estimate the potential expected random variation and identify the largest source of error in this approach.

$$\sigma_{\mathrm{TOC}} = \sigma^2_{\mathrm{TOC}_{(o)}} + a^2\sigma^2_{T_{(\mathrm{soil})}} + b^2\sigma^2_Q + c\frac{\sigma_c}{Q^*} \tag{3}$$

To quantify systematic effects of flow pathways on in-stream TOC for the convolution model we chose varying the groundwater depth systematically 5 cm up and down. We selected five characteristic flow scenarios for daily Q with different return times, lower 5% (0.040 mm), lower 20% (0.109 mm), median (0.283 mm), upper 80% (0.972 mm) and upper 95% (2.371 mm). These characteristic flow values have been retrieved from the analysis of daily Q using the available data from 1990 until 2004. These are referred to as Q_5, Q_{25}, Q_{50}, Q_{75} and Q_{95} in the following. A final calculation that concerned a potential systematic variation of soil water TOC was made that used the fractional water flux with depth according to Eq. (2) using a solver function summing the SSE of difference between optimized and observed TOC ($TOC_{j(\mathrm{optimized})} = \beta_j * TOC_{j\ (\mathrm{measure})}$) to search for factors β_j by which the measured TOC in each of the six horizons would have to be multiplied to achieve a best fit.

$$TOC_{(t)} = \frac{\sum_{i=0}^{100\,\mathrm{cm}} TOC_j * \beta_j * Q_j(t)}{Q_{tot}(t)} \tag{4}$$

For a general evaluation of the two models we used the data from the period 2004 through 2007 for reporting SSE.

Potential effects of changing climate

The importance of changes in temperature and precipitation were evaluated using four different climate scenarios for the period 2091–2100. Following the procedure performed by (Mellander et al., 2007), these scenarios were based on simulations of a RCM (regional climate model) which was run using boundary conditions of a GCM (Hadley) run for different CO_2 emission scenarios from the IPCC's Special Report on Emission Scenarios (IPCC, 2000). The two scenarios were based on two differing sets of socioeconomic assumptions, the A-scenario describing changes leading to higher emissions than the B-scenario. Temperature and precipitation were on average assumed to increase by a ∼2.5 ºC and ∼150 mm which for precipitation is equivalent to a change in 25% compared to the current regime. Temperature and precipitation time series were generated using a delta approach, where the observed time series were modified using the monthly differences between the RCM simulation for the respective scenario and the control run. While this approach is rather straight-forward for temperature (Eq. (5)), for precipitation the question of how to distribute the increase over time is more difficult. Here we used two approaches. The first was to distribute the change evenly over all days with precipitation (moderate), the other approach was to put the entire change on the day with most precipitation in a month (extreme) (Eqs. (6) and (7))

$$T(t) = T_{\mathrm{actual}}(t) + \left(T_{\mathrm{future(Model)}} - T_{\mathrm{actual(Model)}}\right) \tag{5}$$

$$N^{\mathrm{daily}}(t) = N^{\mathrm{daily}}_{\mathrm{actual}}(t) + \frac{\left(N^{\mathrm{monthly}}_{\mathrm{future(Model)}} - N^{\mathrm{monthly}}_{\mathrm{actual(Model)}}\right)}{n_{\mathrm{days\ with\ rain}}} \tag{6}$$

$$N^{\mathrm{monthly}}(t) = N^{\mathrm{monthly}}_{\mathrm{actual}}(t) + \left(N^{\mathrm{monthly}}_{\mathrm{future(Model)}} - N^{\mathrm{monthly}}_{\mathrm{actual(Model)}}\right) \tag{7}$$

This leads to four scenarios A-moderate, A-extreme, B-moderate and B-extreme. For the month of September a 20 mm decrease in rainfall is predicted in the scenario B and in for two instances a negative numbers for rainfall were set to 0. These modified climate data series were then used to produce runoff using a conceptual runoff model, namely the Hydrologiska Byråns Vattenbalansavdelning model (HBV model) (Bergström, 1976; Lindström et al., 1997) similar to the approach presented by (Lindstrom et al., 2002). In the HBV model simple routines, such as the degree-day equation for snow melt, are used to simulate runoff on a daily time step. Descriptions of the model can be found, for instance, in (Bergström, 1992a; e.g. Bergström, 1992b; Lindström et al., 1997; Seibert, 1997). Before simulation of runoff for changed conditions the HBV model was calibrated for current conditions. A Monte Carlo approach was used where the 100 best parameter sets, according to the model efficiency (Nash and Sutcliffe, 1970), were selected from 1,000,000 model runs with randomly generated parameter values. More details of the procedure can be found in Seibert (2002). Based on the 100 simulated time series using the different parameter sets the median, lower 10% and upper 90% percentile of the expected runoff were simulated for the different climate scenarios. The climate scenario for 2071–2100 was applied to the whole series of current data between 1982 and 2007. The simulated median runoff and predicted air temperature were then used to calculate the stream TOC using the regression model. To assess the effects of a changed climate we computed the average change and the mean monthly changes during all months during the snow free season for the four different scenarios.

Results

Variations in stream TOC concentrations are driven by flow with temperature superimposing a seasonal variation. High TOC concentrations occur during days with high flow. TOC concentrations in the stream and the riparian soil solutions also vary as a function of the soil wetness and especially in relation to the water content in the upper TOC rich soil profile. We selected time series of the three consecutive years 1996–1998 that are representative for very dry (1996, annual *Q* 128 [mm]), dry to average conditions (1997, annual *Q* 212 [mm]) and very wet conditions (1998, annual *Q* 497 [mm]) as compared to the whole period of data acquisition between 1993 and 2007 (average annual *Q* 322 [mm] and range 130–570 [mm]. Excluding the signals observed during snow melt season where hydrological conditions differ from those occurring in the snow free season, increased soil wetness as an indicator of the average groundwater level in the transect is always associated with an increase in stream TOC. This is illustrated during the course of 1996 where stream TOC is higher than 20 mg L^{-1} during only two occasions and sharply declines shortly after the rain event in autumn (Fig. 2). Furthermore, in 1997 the drying out of the upper −35 cm horizon from July coincides with a decrease in stream TOC concentrations. In contrast concentration of 20 mg L^{-1} TOC is surpassed half of the time in 1998, with peak TOC reaching 46 mg L^{-1}. The soils below −50 cm are close to water saturated during that year (data not shown) and peak TOC coincides with slight changes in water content in the upper −35 cm horizon. When considering the whole time series we observed that sharp increases in flow during wet years lead to much higher TOC concentrations than during the dry years (data not shown).

The observed TOC concentrations in the riparian soil solutions decrease from around 65 to 15 mg L^{-1} with depth. A sharp decrease in TOC concentration is observed below around 40 cm depth. Both lower and higher soil horizons have a lower relative variation of TOC concentration, while the horizons that are only temporarily waterlogged indicate large variations in TOC concentrations and vary from 30 to 70 mg L^{-1} (Fig. 3). The observed changes in TOC concentrations in each soil horizon were evaluated statistically. In three of the horizons concentrations of soil water TOC concentration are positively related to the amount of water that has flown through respective horizon two weeks prior to the sampling occasion (Table 1). The groundwater variation in the riparian soil is large. At high flow conditions the groundwater level

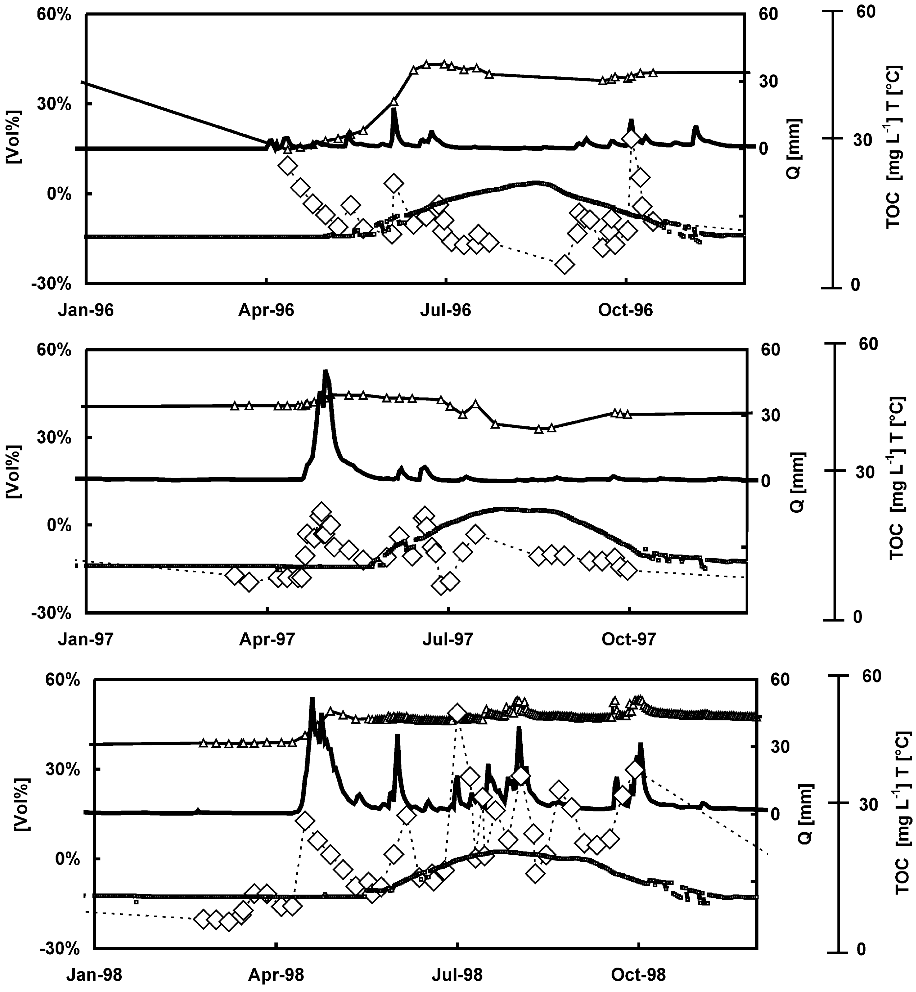

Fig. 2. Temporal variation of water content in the riparian soil profile at depths 35 cm (empty triangles and bold line), calculated soil temperature (T_{soil}) at 30 cm depth (lower bold line), stream flow (upper bold line) and measured stream TOC (diamonds and hyphenated line).

is 30 cm below the surface while the groundwater level at baseflow is approximately 40 cm deeper (Q_{20} in Fig. 3). The depth of the layer with the highest flow at the five characteristic flow values (Q_5, Q_{20}, Q_{50}, Q_{80} and Q_{95}) is marked with an arrow (Fig. 3).

Regression model

From the three different variables considered here it is the combination of all three that results in the highest R^2 (0.65) and lowest error in prediction for TOC (σ_{TOC}) (Table 2). While explaining around 50% of the observed variation (R^2 between 0.46 and 0.57), the degree of explained variance decreases when considering T and Q or T and ln Q as parameters only. There is a clear seasonal response of stream TOC. Model fits to the snow free season or the period excluding the snow melt season are as good as or better than when considering all the data. The increase in parameters has a strong effect on the value for $TOC_{(0)}$ which is considered as the baseline around which the values vary. The shifting of ln Q during the fitting procedure reveals that an averaging of Q over the last two preceding days ($Q_{(t)2}$) in the last term in Eq. (1) improves the predictive power of the model. The final equation for the regression model is:

$$\mathrm{TOC}(t) = 13.2 + 0.89T_{\mathrm{soil}}(\mathrm{t}) + 1.50Q(t) + 3.33\ln\left(\mathrm{Q}^{*}(t)_2\right)$$

Except during the snow melt season the regression model rarely overestimates stream TOC concentrations. A comparison of the modelled and measured TOC values is displayed (Fig. 4). In the lower range small deviations may be observed that increase when the observed flow increases. The performance of this model varies during different seasons (Table 3). A good performance is observed during the snow cover and snow free season. During the snow melt season which has almost the same range of observed TOC concentrations as the snow free season (20 mg L^{-1}) large deviations are evident. This model fails to capture some of the peak TOC values during the wet year 1998 and the dry year 1996 (Fig. 5). The temperature dependence of the regression model allows for some variation of TOC at given flow (Fig. 6) There is no systematic difference between the observed deviations in the calibration and the validation period (Table 3).

Table 1
Effect of flow on TOC in the riparian soils during 1996–2004.

Depth	Intercept	Slope	n	ρ
25	63.1 (6.8)	0.28 (0.22)	28	0.18
35	23.6 (2.2)	0.34 (0.07)	25	0.67[*]
45	14.7 (1.8)	0.22 (0.05)	30	0.69[*]
55	13.7 (1.4)	0.12(0.04)	30	0.45[*]
65	12.6 (1.9)	0.11 (0.06)	30	0.41[*]

[*] Significant at the level of 95% for the two-tailed test.

Convolution model

The temporal patterns of episode specific TOC values may also be reproduced using the convolution model, which routes water flow through the riparian TOC profile. Significantly higher scatter is observed at higher flow while the comparison between measured and modelled TOC for values below 20 mg L^{-1} is acceptable (Fig. 4). Time series of two representative dry (1996 and 2002) and two representative wet years (1993 and 1998) highlight when

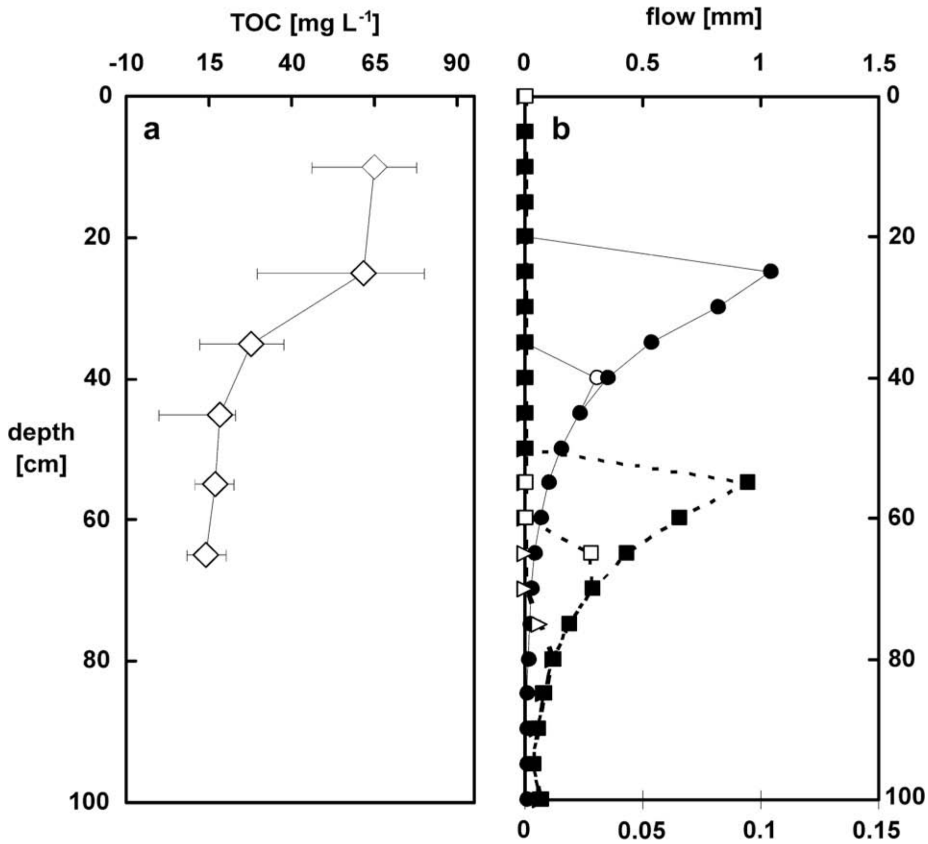

Fig. 3. (a) Measured average TOC concentration and variation in the soil solutions during 1996–2004 as a function of depth in the riparian soil (upper and lower 90% and 10% percentile). (b) Distribution of water flux at various soil levels in the riparian soil at five different flow scenarios Q_5 (white triangles, lower scale), Q_{20} (white squares, lower scale) Q_{50} (black squares, lower scale) Q_{80} (white circles, upper scale) and Q_{95} (black circles, upper scale) that refer to the text. The groundwater depth of the highest flux at each situation is highlighted with an arrow.

Table 2
Comparison of linear regression models.

	Comparison of linear regression models							
	$TOC_{(base)}$ (mg L^{-1})	a (mg L^{-1} mm^{-1})	b (mg L^{-1} °C^{-1})	c	R^2	σ_y	n	AIC
No snow melt	7.98 ± 0.49	1.00 ± 0.11	3.58 ± 0.24		0.57	4.69	314	973
Snow free	9.09 ± 9.09	0.85 ± 0.85	3.42 ± 3.42		0.48	5.29	212	709
All year	8.65 ± 0.42	1.08 ± 0.1	2.27 ± 0.14		0.47	4.87	425	1349
No snow melt	13.3 ± 0.75	0.89 ± 0.1	1.19 ± 0.35	3.28 ± 0.38	0.65	4.22	314	908
Snow free	13.0 ± 1.06	1.05 ± 1.05	0.86 ± 0.86	3.80 ± 0.55	0.57	4.78	212	667
All year	13.8 ± 0.57	0.98 ± 0.08	0.14 ± 0.22	3.50 ± 0.30	0.59	4.25	425	1234
No snow melt	16.9 ± 0.71	1.39 ± 0.39		3.68 ± 0.42	0.56	4.72	314	980
Snow free	17.4 ± 17.4	1.40 ± 1.40		3.19 ± 0.59	0.49	5.22	212	704
All year	17.4 ± 0.55	−0.16 ± 0.25		3.87 ± 0.35	0.46	4.89	425	1352

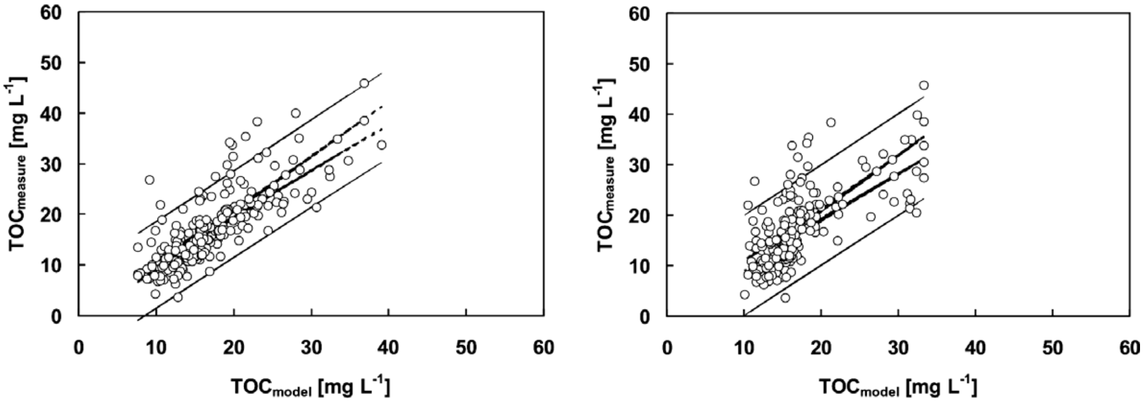

Fig. 4. Comparison between instantaneous measured and instantaneous modelled TOC using the regression model (white circles) and the convolution model (black circles) during the snow free season. The four lines present the upper prediction, upper 95% confidence, lower 95% confidence and lower prediction interval of both models, respectively.

Table 3
Comparison of performances of the regression and the convolution model given as calculated differences with respect to measured TOC (mg L^{-1}).

		Regression model				Convolution model			
		All	Season 1	Season 2	Season 3	All	Season 1	Season 2	Season 3
Calib	Median	−0.62	0.47	−2.47	−0.95	−1.92	−1.96	−6.28	−0.38
	Stdev	4.79	2.58	5.85	4.73	8.89	2.92	11.09	7.39
	Average	−0.74	0.34	−2.63	−0.26	−3.68	−1.57	−10.79	−0.96
Valid	Median	0.33	1.29	3.81	1.55	−0.43	2.17	11.38	3.20
	Stdev	3.41	2.49	3.45	3.39	9.12	2.38	9.71	3.80
	Average	3.44	2.17	4.16	2.49	9.20	2.92	13.18	3.67

the convolution model fails to reproduce TOC (Fig. 5). During the snow covered season this model, apart from some few instances of overestimation, captures the observed temporal variation through the last 10 years. During the snow melt season the measured TOC concentrations are systematically overestimated with an average deviation of 11 mg L^{-1} and a standard deviation of 11 mg L^{-1} (Table 3). During the snow free season a much larger variation of TOC versus flow is apparent but the general pattern in TOC is well captured (Table 3 and Fig. 6). During wet years the convolution model reproduces the observed TOC during the whole year while some systematic underestimation is observed during dry years during the snow free season. A comparison of the flow dependence of TOC stream water concentrations and the respective response to flow also reveals a seasonal pattern (Fig. 6). There is no systematic difference between the observed deviations in the calibration and the validation period (Table 3) and given that no calibration was done this model still captures the observed dynamics in the stream during either situation. During some years the convolution model actually performs better than the regression model (data not shown).

The analysis of the best-fit β_j values reveal that comparably slight changes in soil TOC concentration or flow would be sufficient to successfully model the mean stream TOC data over the range of flows Q_5 through Q_{95}. The respective best fit multiplicators β_j for the depths of 35, 45, 55, 65 and 80 are 0.95, 1.23, 1.36, 0.70 and 0.91, respectively. The predicted TOC of the convolution model systematically deviates from the observed TOC values when routing the water through the soil according to Fig. 3 at two characteristic flow situations Q_{20} and Q_{80}. The deviations are much smaller at Q_5, Q_{50} and Q_{95}, respectively. The effect of systematically varying the groundwater depth level with 5 cm up and down reveals that the systematic offset of the convolution model is significantly affected at the Q_{80} value and somewhat at Q_{20} while only minor changes occur at Q_5, Q_{50} and Q_{95} (Fig. 7). Decreasing the GW level generally

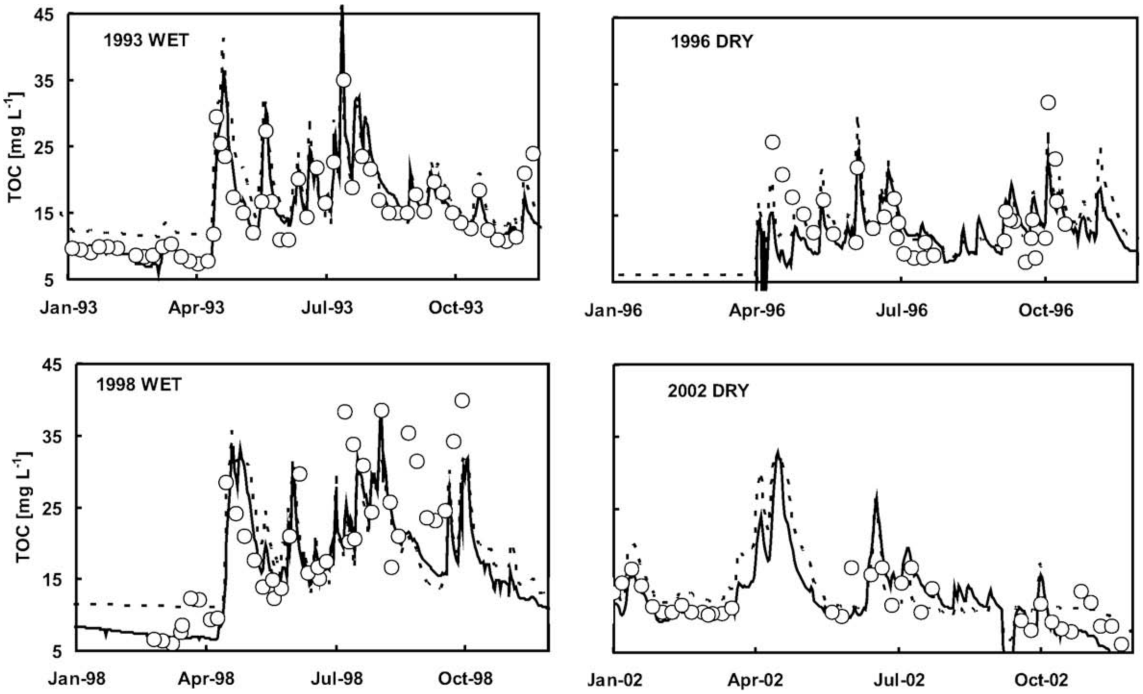

Fig. 5. Temporal variation in TOC using the regression model (bold line), convolution model (hyphenated line) and instantaneous measured TOC (white circles) for four characteristic years during the period 1993 through 2003.

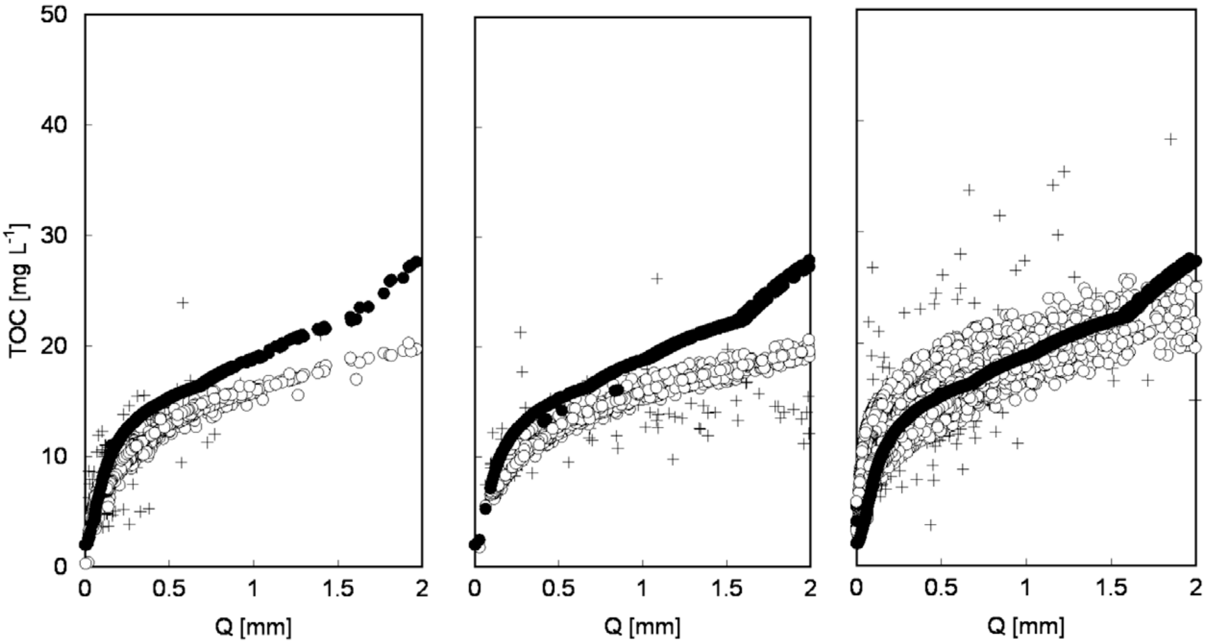

Fig. 6. Relationship between measured (black cross), and predicted TOC using the regression model (white circles) and the convolution model (black circles) as a function of flow Q during the snow covered, snow melt and snow free season from left to right.

improves the fit at low flow conditions (Q_5 and Q_{20}) while increasing the GW helps to approach the measured situation at moderately high flows (Q_{80}). The observed differences at Q_{20} and Q_{80} are around 3 mg L^{-1} which translates into relative errors of TOC of 36% and 15%, respectively.

The error propagation method reveals that the largest error resides in the uncertainty of the calibration parameter c that concerns the additive term of ln Q, while the other sources such as flow are of minor importance. Using σ_c (0.38) from Table 2 for the best model ("season 1 and 3" in row four) reveals that the estimated error in TOC (σ_{TOC}) is a function of flow. The values in the parenthesis indicate the calculated σ_{TOC} at the chosen characteristic Q with different return times. At the respective flow (Q in [mm]) an estimated error in TOC (σ_{TOC} in [mg L^{-1}]) at situations with Q representative of the lower 5% of flow (Q_5) of 0.04 mm results in σ_{TOC} of are 32.0. For the other flow situations the following scenarios arises: Q_{25} 0.109 mm and σ_{TOC} = 12.3 mg L^{-1}, Q_{50} 0.283 mm and σ_{TOC} = 5.3 mg L^{-1}, Q_{75} 0.972 mm and σ_{TOC} = 2.2 mg L^{-1} and finally

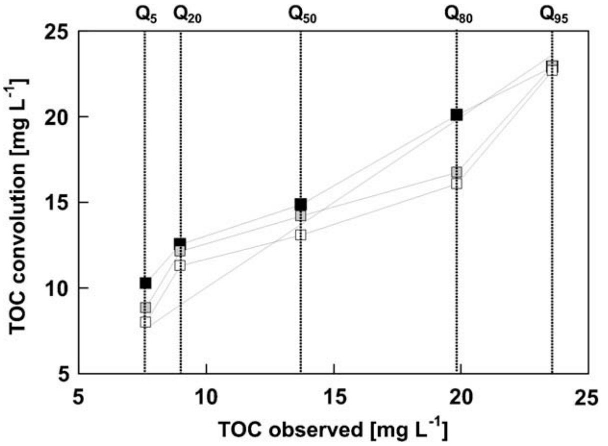

Fig. 7. Comparison of the sensitivity analysis of changing flow pathways on modelled TOC versus measured stream water TOC using the convolution model at five characteristic flow scenarios (Q_5, Q_{20}, Q_{50}, Q_{80} and Q_{95}) with the unchanged convolution model in grey squares, the one where the flow level was increased by 5 cm in black squares and that where a 5 cm decrease in flow level was modelled in white squares. The black line represents a 1:1 relationship to guide the eye of the reader.

Q_{95} 2.37 mm and $\sigma_{TOC} = 1.5$ mg L^{-1}. When σ_c is set to 0.04 then flow dominates the error with an error of TOC larger than 3 mg L^{-1} as flow drops below 0.5 mm d^{-1} or when its is higher than 7 mm d^{-1}.

Climate change scenarios using the regression model

The HBV model was in general capable to reproduce the observed runoff for current conditions with model efficiency values around 0.8. The error in prediction of flow during the three different seasons was 0.2, 1.1 and 0.4 mm with an adjusted coefficient of correlation R^2 of 0.48, 0.77 and 0.83, respectively. The median deviation between measured and modelled flow was 79%, 36% and 43% when considering days with flows higher than Q_5. Significantly higher deviations occur at flow situations below that value as situations are included where Q of the model or the measurement is close to zero.

The long term climate data from 1982 through 2007 were transformed into predicted temperature and estimated flow using the calibrated HBV model. From each individual day we modelled TOC during separate months June through November during the snow free season for each of the four scenarios and then calculated the monthly average TOC. This average predicted TOC during these 25 years is then plotted against the measured or predicted mean flow to evaluate seasonal patterns of the flow TOC relationship (Fig. 8). In addition we evaluated the effect on median predicted TOC using predicted median flow (Table 4). These values are in accordance with shifts in the two calibration curves plotted in Fig. 8 as the average expected changes in TOC are increases of around 2–3 mg L^{-1} depending on the scenario chosen.

The error in predicted TOC during the future climate scenarios during season 3 (*snow free season*) is larger. After accounting for a median error in flow of 43% the error in TOC is larger than 3 mg L^{-1} when flow is either below 0.6 mm d^{-1} or higher than 2.5 mm d^{-1}.

Discussion

One undisputed key parameter for the transfer of TOC from the soil to the stream is the temporal variation of flow pathways and the mixing of waters from different sources such as diluted snow melt or groundwater. Potential feedbacks here are the antecedent conditions of wetness and its effect on the stream hydrochemistry during subsequent storms (Mitchell et al., 2006). Volumetric water content (Θ) in the soil will control which pores are available for water flow. One hypothesis is that during heavy rainfall after a period of prolonged drought, initially only larger pores contribute TOC as the hydraulic connection with the smaller pores that dominate the overall specific surface area, and therefore constitute an important TOC pool has been interrupted. After prolonged rainfall and consecutive wetting up of the soil the soil water in the smaller pores may begin to contribute TOC to the soil solution by convective and diffusive processes. In the following more TOC may be leached from the soil after the flush event leading to a hysteresis effect of TOC. More data are needed to confirm this and at this stage we cannot fully disentangle whether the TOC increase in the soil solution is due to increased biological activity or due a simple physical process of activating micropores.

The use of both ln Q and Q in our regression model may thus be caused by two distinct processes one related to flow and the other to soil wetness. The offset parameter $TOC_{(0)}$ has at least in our case some physical meaning as it is close to the TOC concentration determined in the riparian soil in the soil layers at −65 cm that is almost permanently is saturated and constantly contribute to stream flow. The observed temporal variation is then mainly controlled by the observed variance in flow during the different seasons. As the annual fluctuation of T_{soil} is around 10° (0–9 °C) we may compare the numerical value 0.89 of the factor a in Eq. (1) to the average TQ_{10} reported by (Christ and David, 1996) of around 1.7 that describes the temperature sensitivity of biologically mediated reactions in soil.

The second approach of using the riparian soil TOC data is also defensible based on earlier studies. Hemond (1990) concluded that "near-stream wetlands account of the bulk of humic DOC seen in freshwater streams in *glaciated catchments*." Dosskey and Bertsch (1994) quantified the amount of carbon originating from upland soils that cover 94% of the area to below 10% while the riparian zone which covers only 6% of the area contributed the rest. Schindler and Krabbenhoft (1998) highlight the importance of "the last few centimetres beneath the sediment/water interface" in their study of the sources of DOC in a temperate forested watershed. Transformations of solid organic matter or the production of fresh organic matter in the riparian zone are thus of major importance for the temporal variations of stream water TOC.

The four parameters used in the regression model are easy to implement. Both air temperature and flow are fundamental meteorological data that are widely available. The inclusion of soil temperature helps to mimic the biological activity in the riparian zone. Both models capture the range of stream TOC observed in the stream during the three seasons. The slightly better performance of the regression model has several possible reasons. First of all it has been calibrated and then a possible biological control through seasonally changing temperature is also incorporated. The flow based convolution model captures both relative and sometimes even the absolute dynamics of the system. Especially the absolute variation of TOC versus flow (Q) under conditions of Q below 2 mm confirm the assumptions of the importance of the riparian soil chemistry on stream TOC concentrations at our site (Fig. 6). The systematic difference between modelled and measured TOC during the snow melt season of both models is likely due to a combination of lower temperatures and soil frost. Simple routing of water through the riparian soil overestimates TOC by 50% and the regression model still overestimates TOC by around 30% (Fig. 6). As Laudon et al. (2004b) quantified the percentage of pre-event water at this site during snow melt to below 20% we may conclude that dilution alone does not explain this phenomena. At high flow both models produce a large scatter around the measured values

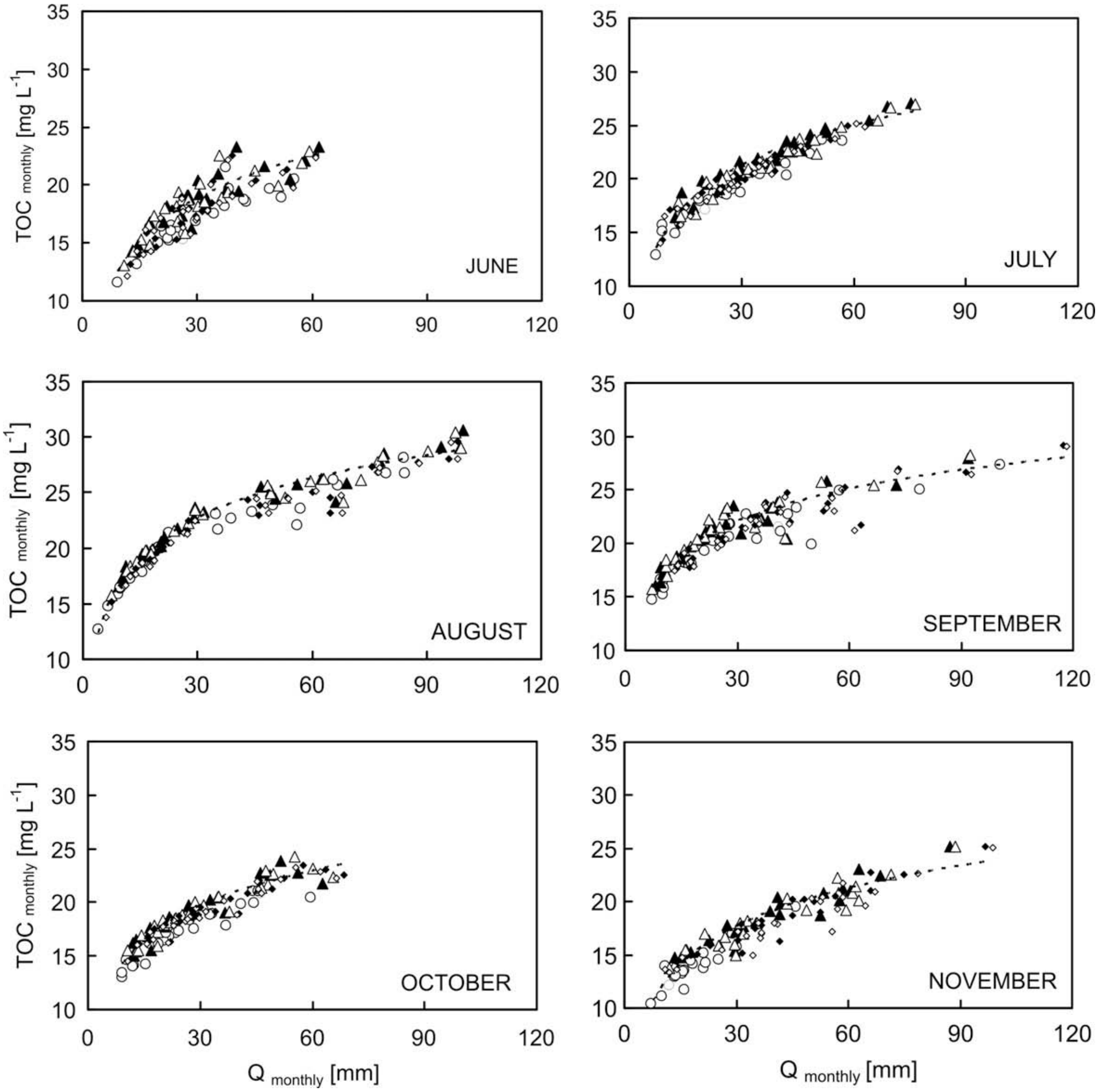

Fig. 8. Mean modelled and mean measured TOC during the 25 year time series for current (white circles), HA-mod (black triangles), HA-ext (white triangles), HB-mod (white diamonds) and HB-ext (black diamonds) during the snow free season. The curves in this figure depict the fitted logarithmic relationship between flow and TOC for the current climate (bold line) and the scenario HA-mod (hyphenated line).

Table 4
Effect of climate scenarios on predicted stream TOC during the snow free season for the period 1982–2006.

		Q_{median}	ΔTOC	Q_{10}	Q_{90}
Current	Median	17.6 ± 3.1		17 ± 3.1	18.1 ± 3
	Upper 95%	25.8		25.1	26.4
HAD_A_mod	Median	17.6 ± 0	2.5	17.1 ± 0	18.1 ± 0
	Upper 95%	28.4	2.6	27.5	29.2
HAD_A_ext	Median	20.1 ± 2.8	2.2	19.5 ± 2.8	20.6 ± 2.8
	Upper 95%	29.2	3.4	28.3	30.2
HAD_B_mod	Median	17.2 ± 0	1.9	16.6 ± 0	17.7 ± 0
	Upper 95%	27.9	2.1	27.0	28.7
HAD_B_ext	Median	19.7 ± 3.1	1.5	19.2 ± 3.1	20.3 ± 3.1
	Upper 95%	28.6	2.8	27.7	29.6

(Fig. 4). The convolution model overestimates TOC at most of those situations and saturates at around 50 mg L^{-1}, which is close to the highest TOC value recorded ever at this site, namely 54 mg L^{-1}. Potential causes for the overestimation might be intermittently changing flow pathways or kinetic effects limiting the solubilisation of TOC and thus its transfer from the soil to the solution. A large part of the observed variation when using the convolution model resides in the fact that we use the average observed long-term TOC concentration in the riparian soil without taking into account seasonality or the effect of wetness on soil TOC (Table 1). The relatively large fluctuations of TOC observed in the riparian soil in the soil layers that are activated at high flow (−25 and −35 cm) are within what has been measured in the soil solutions of seven other riparian soils within the catchment during 2007. From the analysis of the sensitivity of flow pathways and from the best fit β_i values that were all around 30%, we conclude that these seemingly small temporal or spatial changes are of importance. This temporal and spatial variation of TOC is thus a very valuable and significant response to environmental signals such as changes in biological activity, soil water content and temperature and is promising for a future more systematic approach and refined model.

Both the Dy-DOC model presented by Michalzik et al. (2003) and the CHUM model Tipping (1996a) rely on diffusion processes controlling freshly produced DOC to diffuse from micro- to macropores and thus limiting their release through a kinetic approach. Both models require a large number of calibration parameters. The Dy-DOC approach has the possibility of tracking the Carbon isotope signal through the soil solutions into the stream and thus allows for a validation of the age structure of modelled C dynamics. The INCA-C model (Futter et al., 2007) contains a much lower amount of model parameters and may be easily expanded to larger areas and coupled catchments. Also in this model solubilisation is controlled by a kinetic process. As a big difference to the two aforementioned models the convolution model reproduces stream water TOC without the need of incorporating a kinetic step based on a soil chemical or soil physical process. Recently Lumsdon et al. (2005) based on the work of Tipping and Woof (1990) has identified hydrophobicity as a key parameter for solubilisation of DOC. Varying only hydrophobicity allows reproducing the temporal variations of DOC in a O-horizon over the time span of ten years. This temporal variation of a major driving variable that is solely controlled by temperature is similar to the changing effect of temperature in the regression model presented here. Often good model fits can be obtained while the validation of the parameters used such as solubilisation and adsorption kinetics, degradation and production, diffusion and chemical interaction with soil or soil solution components etc. have rarely been validated independently.

Response of TOC export to different climate scenarios

The analysis of modelled stream TOC concentrations using four different climate scenarios reveals only minor changes in predicted mean monthly TOC concentrations. This finding is in accordance with the analysis of Erlandsson et al. (2008) who predict a change in 1.5% in TOC per year based on a 10–25% increase in annual rainfall that was predicted to result in a increase of runoff by 5%. This modelled change in TOC is much smaller than the observed interannual variation they observed. Larger variations arise when considering individual periods within the year such as those expected to occur during increased rainfall and increased temperature in November where TOC might rise by more than 5 mg L^{-1}. The highest potential changes for TOC occur in the warmer months of August and September (Fig. 8) where the slope of TOC versus Q is generally steeper. The error propagation analysis reveals that the inherent uncertainties of this approach are comparably large. During most of the flow occasions however the error remains below 3 mg L^{-1} which would translate into a relative error of below 25% but is still larger than the mean TOC change predicted. The observed natural variation in the last 10 years in average TOC concentration (5–50 mg L^{-1}) and flux is also larger than what we predict for the future scenarios (Köhler et al., 2008). We conclude that the largest impacts will most probably be related to very wet summers and autumns. The average TOC concentration in the snow free season in the stream is 12 mg L^{-1} when annual precipitation is below 400 mm but doubles when runoff is as high as 600 mm (Köhler et al., 2008). Additional effects arise when TOC concentrations sharply rise after very intensive periods of rainfall.

Model improvements, potential implications and outlook

A logic next step would consist in a systematic analysis of the long time series to identify situations when both models fail. Then additional chemical or biological parameters would need to be incorporated to increase the described variance. From our data we may conclude that the inclusions of realistic variations in climate during the calibration and validation period are of uttermost importance as the forested ecosystem studied here behaves completely different between dry and wet years.

Disadvantages to the two approaches explored here exist however. In both models we have to assume steady-state processes and have no possibility of capturing variations of different Carbon pools in different compartments or deciphering long-term trends. Potential long-term trends not considered here are systematic changes in soil chemistry or flow pathways that may be caused by long-term variations in the riparian water balance such as increased evaporation. The increase of TOC in our riparian soil after periods of prolonged wetting may be due to an increase of biological productivity. The frequency of soil solution sampling is not high enough to test whether there is a significant additional effect of soil temperature. In more sophisticated models both processes, long-term trends and the effect of wetness, are worth to be implemented. A fully developed model should include both aluminum and sulphate as additional drivers when modelling the solubilisation of organic matter in soils. As the aerial export of organic carbon and concentration in soil solution is tightly related to the Carbon/Nitrogen ratio in the soil (Aitkenhead and McDowell, 2000) a quantitative description of nitrogen dynamics in the soil must ultimately be incorporated in models for future scenarios of TOC export.

The two approaches presented here for the temporal stream water TOC dynamics may be used to quantify the concentration of trace compounds such as mercury (Åkerblom et al., 2008), persistent organic pollutants (Schriever et al., 2007) and aluminium or other metals (Björkvald et al., 2008) that are all known to be very tightly related to the flux of organic carbon.

The simple approach chosen here has the advantage of allowing easy tests of different hypotheses about current TOC export mechanisms. Similar flow-temperature–TOC relationships seem to hold true for larger landscapes even when there are several orders of magnitude of difference in size (Köhler et al., 2008). The established relationships are a tool to differentiate whole scale landscape patterns without a need for very detailed datasets. Should large differences be obtained in different landscapes then relevant processes can be implemented in the form of mathematical relationships that model mobile soil TOC as a function of water level, moisture content and soil temperature, character of organic matter or even available nutrient concentrations.

Conclusions

The temporal variation of stream water TOC during almost two decades in a forested headwater catchment may be captured with two simple approaches: (a) a single equation with three parameters using air temperature and flow as input variables and (b) a flux based model that uses observed riparian soil chemistry to reproduce stream water TOC as function of water moving through different sections of a riparian soil profile. Both approaches have their value and the convolution model documents the large importance of riparian soil chemistry for temporal changes in stream water chemistry. The regression model highlights the significant effect of temperature on stream water TOC. This study has also highlighted the importance of the riparian soil hydrochemistry on the temporal variation of stream TOC concentrations in a boreal forested catchment. Systematic deviations between measured and modelled TOC help to identify periods under which TOC mobilisation or fixation processes are active that are not yet incorporated into the model. These may include systematic temporal changes in soil water TOC or flow pathways. Simplified approaches such as the one presented here may help to reproduce the temporal variations, without requiring a large amount of calibration data, in areas where large amounts of organic C are stored in the soil. Processes that would change this C stock in the catchment require a mechanistic and dynamic approach.

Four potential climate scenarios were used to quantify the potential effect of stream water TOC in the future. The predicted changes are around 15% which is much smaller than the present inter-annual and intra-annual variation observed during 1993–2007.

References

Ågren, A., Buffam, I., Jansson, M., Laudon, H., 2007. Importance of seasonality and small streams for the landscape regulation of DOC export. Journal of Geophysical Research-Biogeosciences 112, G03003. doi:10.1029/2006JG000381.

Ågren, A., Berggren, M., Laudon, H., Jansson, M., 2008. Terrestrial export of highly bioavailable carbon from small boreal catchments in spring floods. Freshwater Biology 53 (5), 964–972.

Aitkenhead, J.A., McDowell, W.H., 2000. Soil C:N ratio as a predictor of annual rivereine DOC flux at local and global scales. Global Biogeochemical cycles 14 (1), 127–138.

Åkerblom, S., Meili, M., Bringmark, L., Johansson, K., Kleja, D.B., Bergkvist, B., 2008. Partitioning of Hg between solid and dissolved organic matter in the humus layer of boreal forests. Water Air and Soil Pollution 189 (1–4), 239–252.

Alexander, R.B., Boyer, E.W., Smith, R.A., Schwarz, G.E., Moore, R.B., 2007. The role of headwater streams in downstream water quality. Journal of the American Water Resources Association 43 (1), 41–59.

Bergström, S., 1976. Development and Application of a Conceptual Runoff Model for Scandinavian Catchments. Swedish Meteorological and Hydrological Institute, Norrköping.

Bergström, S., 1992a. The HBV model – its structure and applications. 4, SMHI Reports RH, Norrköping, Sweden.

Bergström, S., 1992b. The HBV model – its structure and applications. SMHI Reports RH, No. 4, Norrköping, Sweden.

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

Björkvald, L., Buffam, I., Laudon, H., Morth, C.M., 2008. Hydrogeochemistry of Fe and Mn in small boreal streams: the role of seasonality, landscape type and scale. Geochimica Et Cosmochimica Acta 72 (12), 2789–2804.

Buffam, I., Laudon, H., Temnerud, J., Morth, C.M., Bishop, K., 2007. Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. Journal of Geophysical Research – Biogeosciences (G1), 112.

Cory, N., Laudon, H., Köhler, S., Seibert, J., Bishop, K., 2007. Evolution of soil solution aluminum during transport along a forested boreal hillslope. Journal of Geophysical Research – Biogeosciences (G3), 112.

Chow, A.T., Tanji, K.K., Gao, S.D., 2003. Production of dissolved organic carbon (DOC) and trihalomethane (THM) precursor from peat soils. Water Research 37 (18), 4475–4485.

Christ, M.J., David, M.B., 1996. Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol. Soil Biology and Biochemistry 28 (9), 1191–1199.

David, M.B., Vance, G.F., 1991. Chemical character and origin of organic acids in streams and seepage lakes of central Maine. Biogeochemistry 12, 17–41.

Dosskey, M.G., Bertsch, P.M., 1994. Forest sources and pathways of organic matter transport to a blackwater stream – a hydrological approach. Biogeochemistry 24 (1), 1–19.

Eimers, M.C., Watmough, S.A., Buttle, J.M., Dillon, P.J., 2008. Examination of the potential relationship between droughts, sulphate and dissolved organic carbon at a wetland-draining stream. Global Change Biology 14 (4), 938–948.

Erlandsson, M., Buffam, I., Folster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G.A., Bishop, K., 2008. Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. Global Change Biology 14 (5), 1191–1198.

Evans, C.D., Chapman, P.J., Clark, J.M., Monteith, D.T., Cresser, M.S., 2006. Alternative explanations for rising dissolved organic carbon export from organic soils. Global Change Biology 12 (11), 2044–2053.

Fenner, N., Freeman, C., Lock, M.A., Harmens, H., Reynolds, B., Sparks, T., 2007. Interactions between elevated CO_2 and warming could amplify DOC exports from peatland catchments. Environmental Science and Technology 41 (9), 3146–3152.

Futter, M.N., Butterfield, D., Cosby, B.J., Dillon, P.J., Wade, A.J., Whitehead, P.G., 2007. Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. Water Resources Research 43 (2), W0242. doi:10.1029/2006WR004960.

Hantush, M.M., 2005. Modeling stream-aquifer interactions with linear response functions. Journal of Hydrology 311 (1–4), 59–79.

Hemond, H.F., 1990. Wetlands as the source of dissolved organic carbon to surface waters. In: Bernhard, S. (Ed.), Organic Acids in Aquatic Ecosystems. J. Wiley & Sons, Chichester, pp. 301–313.

Hessen, D.O., Gjessing, E.T., Knulst, J., Fjeld, E., 1997. TOC fluctuations in a humic lake as related to catchment acidification, season and climate. Biogeochemistry 36, 139–151.

Hinton, M.J., Schiff, S.L., English, M.C., 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochemistry 36 (1), 67–88.

Hongve, D., 1999. Production of dissolved organic carbon in forested catchments. Journal of Hydrology 224 (3–4), 91–99.

Hope, D., Billet, M.F., Cresser, M.S., 1994. A review of the export of carbon in river water: fluxes and processes. Environmental Pollution 84, 301–324.

Hope, D., Billett, M.F., Cresser, M.S., 1997. Exports of organic carbon in two river systems in NE Scotland. Journal of Hydrology 193 (1–4), 61–82.

IPCC, 2000. In: Nebojsa Nakicenovic, Rob Swart (Eds.), Cambridge University Press, UK. 570 pp.

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

Jorgensen, N.O.G., Tranvik, L., Edling, H., Graneli, W., Lindell, M., 1998. Effects of sunlight on occurrence and bacterial turnover of specific carbon and nitrogen compounds in lake water. FEMS Microbial Ecology 25, 217–227.

Kaiser, K., Zech, W., 1998. Rates of dissolved organic matter release and sorption in forest soils. Soil Science 163 (9), 714–725.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Science 165, 277–304.

Kawahigashi, M., Kaiser, K., Rodionov, A., Guggenberger, G., 2006. Sorption of dissolved organic matter by mineral soils of the Siberian forest tundra. Global Change Biology 12 (10), 1868–1877.

Kendall, K.A., Shanley, J.B., McDonnell, J.J., 1999. A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. Journal of Hydrology 219, 188–205.

Köhler, S.J., Buffam, I., Laudon, H., Bishop, K., 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. Journal of Geophysics Research 113, G03012.

Kram, P., Santore, R.C., Driscoll, C.T., Aber, J.D., Hruska, J., 1999. Application of the forest–soil–water model (PnET-BGC/CHESS) to the Lysina catchment, Czech Republic. Ecological Modelling 120 (1), 9–30.

Laudon, H., Köhler, S., Buffam, I., 2004a. Seasonal TOC export from seven boreal catchments in northern Sweden. Aquatic Sciences 66 (2), 223–230.

Laudon, H., Seibert, J., Köhler, S., Bishop, K., 2004b. Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff. Water Resources Research 40 (3), 3102 (art. no. W03102).

Lefebvre, E., Legube, B., 1993. Coagulation–floculation par le chlorure ferrique de quelques acides organiques et phenols en solution aqueuse coagulation–flocculation by ferric chloride of some organic compounds in aqueous solution. Water Research 27 (3), 433–447.

Lindstrom, G., Bishop, K., Lofvenius, M.O., 2002. Soil frost and runoff at Svartberget, northern Sweden – measurements and model analysis. Hydrological Processes 16 (17), 3379–3392.

Lindström, G., Johansson, B., Persson, M., Gardelin, M., Bergström, S., 1997. Development and test of the distributed HBV-96 hydrological model. Journal of Hydrology 201 (1–4), 272–288.

Lumsdon, D.G., Stutter, M.I., Cooper, R.J., Manson, J.R., 2005. Model assessment of biogeochemical controls on dissolved organic carbon partitioning in an acid organic soil. Environmental Science and Technology 39 (20), 8057–8063.

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

McGuire, K.J., McDonnell, J.J., Weiler, M., Kendall, C., McGlynn, B.L., Welker, J.M., Seibert, J., 2005. The role of topography on catchment-scale water residence time. Water Resources Research 41 (5).

Mellander, P.E., Lofvenius, M.O., Laudon, H., 2007. Climate change impact on snow and soil temperature in boreal Scots pine stands. Climatic Change 85 (1–2), 179–193.

Michalzik, B., Tipping, E., Mulder, J., Lancho, J.F.G., Matzner, E., Bryant, C.L., Clarke, N., Lofts, S., Esteban, M.A.V., 2003. Modelling the production and transport of dissolved organic carbon in forest soils. Biogeochemistry 66 (3), 241–264.

Miller, M.P., McKnight, D.M., Cory, R.M., Williams, M.W., Runkel, R.L., 2006. Hyporheic Exchange and Fulvic Acid Redox Reactions in an Alpine Stream/Wetland Ecosystem, Colorado Front Range, pp. 5943–5949.

Miller, J.C., Miller, J.N., 1993. Statistics for analytical chemistry. Analytical Chemistry Series. Ellis Horwood, New York. 233 pp.

Mitchell, M.J., Piatek, K.B., Christopher, S., Mayer, B., Kendall, C., McHale, P., 2006. Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. Biogeochemistry 78 (2), 217–246.

Monteith, D.T., Stoddard, J.L., Evans, C.D., de Wit, H.A., Forsius, M., Hogasen, T., Wilander, A., Skjelkvale, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopacek, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450, 537–540.

Mulholland, P., 2003. Large-Scale Patterns in Dissolved Organic Carbon Concentration, Flux, and Sources. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Elsevier, New York. pp. 139–159.

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I – a discussion of principles. Journal of Hydrology 10, 282–290.

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

Petrone, K.C., Buffam, I., Laudon, H., 2007. Hydrologic and biotic control of nitrogen export during snowmelt: a combined conservative and reactive tracer approach. Water Resources Research 43, WO6420. doi:10.1029/2006WR005286.

Schindler, J.E., Krabbenhoft, D.P., 1998. The hyporheic zone as a source of dissolved organic carbon and carbon gases to a temperate forested stream. Biogeochemistry 43 (2), 57–174.

Schriever, C.A., von der Ohe, P.C., Liess, M., 2007. Estimating pesticide runoff in small streams. Chemosphere 68, 2161–2171.

Seibert, J., 1997. Estimation of parameter uncertainty in the HBV model. Nordic Hydrology 28 (4–5), 247–262.

Seibert, J., 2002. HBV light version 2 User's manual, Environmental Assessment, SLU, Uppsala.

Stepanauskas, R., Laudon, H., Jorgensen, N.O.G., 2000. High DON bioavailability in boreal streams during a spring flood. Limnology and Oceanography 45, 1298–1307.

Stevenson, F.J., 1994. Humus Chemistry Genesis, Composition, Reactions. John Wiley & Sons, New York, 512 pp.

Thurman, E.M., 1985. Organic geochemistry of natural waters. Developments in Biogeochemistry. Kluwer Academic Publisher, Dordrecht.

Tipping, E., 1996a. CHUM: a hydrochemical model for upland catchments. Journal of Hydrology 174 (3–4), 305–330.

Tipping, E., 1996b. Hydrochemical modelling of the retention and transport of metallic radionuclides in the soils of an upland catchment. Environmental Pollution 94, 105–116.

Tipping, E., Froberg, M., Berggren, D., Mulder, J., Bergkvist, B., 2005. DOC leaching from a coniferous forest floor: modeling a manipulation experiment. Journal of Plant Nutrition and Soil Science-Zeitschrift Fur Pflanzenernahrung Und Bodenkunde 168 (3), 316–324.

Tipping, E., Lawlor, A.J., Lofts, S., 2006. Simulating the long-term chemistry of an upland UK catchment: major solutes and acidification. Environmental Pollution 141 (1), 151–166.

Tipping, E., Woof, C., 1990. Humic substances in acid organic soils – modeling their release to the soil solution in terms of humic charge. Journal of Soil Science 41 (4), 573–586.

Tipping, E., Woof, C., Rigg, E., Harrison, A.F., Ineson, P., Taylor, K., Benham, D., Poskitt, J., Rowland, A.P., Bol, R., Harkness, D.D., 1999. Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. Environment International 25 (1), 83–95.

Urban, N.R., Bayley, S.E., Eisenreich, S.J., 1989. Export of dissolved organic carbon and acidity from peatlands. Water Resources Research 25, 1619–1628.

Winkler, J.P., Cherry, R.S., Schlesinger, W.H., 1996. The Q(10) relationship of microbial respiration in a temperate forest soil. Soil Biology and Biochemistry 28 (8), 1067–1072.

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

Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P., 2004. Trends in dissolved organic carbon in UK rivers and lakes. Biogeochemistry 70 (3), 369–402.

Worrall, F., Burt, T.P., 2008. The effect of severe drought on the dissolved organic carbon (DOC) concentration and flux from British rivers. Journal of Hydrology 361 (3–4), 262–274.

Yurova, A., Sirin, A., Buffam, I., Bishop, K., Laudon, H., 2008. Modeling the dissolved organic carbon output from a boreal mire using the convection–dispersion equation: Importance of representing sorption. Water Resources Research, 44. W07411.