Riparian zone hydrology and soil water total organic carbon (TOC): Implications for spatial variability and upscaling of lateral riparian TOC exports

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Abstract

Groundwater flowing from hillslopes through riparian (near stream) soils often undergoes chemical transformations that can substantially influence stream water chemistry. We used landscape analysis to predict total organic carbon (TOC) concentrations profiles and groundwater levels measured in the riparian zone (RZ) of a 67 km^2 catchment in Sweden. TOC exported laterally from 13 riparian soil profiles was then estimated based on the riparian flow-concentration integration model (RIM). Much of the observed spatial variability of riparian TOC concentrations in this system could be predicted from groundwater levels and the topographic wetness index (TWI). Organic riparian peat soils in forested areas emerged as hotspots exporting large amounts of TOC. These TOC fluxes were subject to considerable temporal variations caused by a combination of variable flow conditions and changing soil water TOC concentrations. From more mineral riparian gley soils, on the other hand, only small amounts with relatively time-invariant concentrations were exported. Organic and mineral soils in RZs constitute a heterogeneous landscape mosaic that potentially controls much of the spatial variability of stream water TOC. We developed an empirical regression-model based on the TWI to move beyond the plot scale to predict spatially variable riparian TOC concentration profiles for RZs underlain by glacial till.

Keywords: Krycklan, Valley Bottom Wetland, Buffer, Stream Water Quality, Topographic Wetness Index TWI, Terrain Analysis, Hydrological Connectivity, Flow Pathways, Riparian, Near-stream

1. Introduction

Being located directly adjacent to streams, the riparian zone (RZ) is the last strip of land in contact with groundwater before it discharges into the stream network or into the hyporheic zone. Due to its location at the land-stream interface, the RZ can hydrologically and biogeochemically ‘buffer’ lateral subsurface fluxes (McGlynn and Seibert, 2003; Jencso et al., 2009; Rodhe and Seibert, 2011). The RZ thus controls ecologically-significant short-term variations of surface water quality (Cirmo and McDonnell, 1997; Hooper et al., 1998; McClain et al., 2003; Serrano et al., 2008; Berggren et al., 2009) and quantity (Dunne and Black, 1970; Ocampo et al., 2006; McGlynn and McDonnell, 2003). The RZ often distinguishes itself from the surrounding landscape by characteristic hydromorphic features including different soils (Hill, 1990) and vegetation (Jansson et al., 2007). These hydromorphic features have normally evolved over long periods of time ranging from several years to millennia. Understanding RZ functioning is important for understanding long-term and short-term effects of upslope hydrological controls (Vidon and Smith, 2007) on riparian vegetation and soils, which in turn can chemically modulate hydrological fluxes from upslope areas.

A specific example of RZ functioning was put forward by Bishop et al. (2004) to explain part of the hydrological ‘paradox’ of rapid mobilization of ‘old’ water with a variable streamflow chemistry presented by Kirchner (2003). In essence, old (pre-event) water can be quickly mobilized during a hydrological event by rapidly rising groundwater tables in soils with a marked decrease of conductivity with depth. This has also been described as a transmissivity feedback mechanism (e.g., Rodhe, 1989; Bishop et al., 2011). As the groundwater table rises into more shallow riparian soil horizons, these horizons become hydrologically connected to the stream. If the soil water in the newly connected soil horizons is chemically different from lower horizons, then this can result in the substantial shifts of stream water chemistry observed during flow episodes.

This perceptual view has been further developed into a mathematical framework called the riparian flow-concentration integration model (RIM) (Seibert et al., 2009). In RIM incremental solute mass effluxes are computed by multiplying solute concentrations with lateral groundwater flow at each layer of a riparian soil profile. Total solute fluxes are then calculated by integrating the incremental solute mass fluxes across the soil profile. The RIM concept has provided a physically plausible linkage between observed streamflow, groundwater tables and stream water and soil water chemistry when tested for a small catchment based on a single riparian soil transect with respect to the flux of dissolved organic carbon (Bishop, 1991), mercury (Bishop et al., 1995), aluminum (Cory et al., 2007), lead (Klaminder et al., 2006) and water as quantified by stable isotopes (Laudon et al., 2004b). A limitation of the original RIM concept, however, is the underlying assumption of spatially homogenous concentration-depth profiles and groundwater table positions, since data from only one RZ location was available in these earlier studies.

To asses the hydrological and chemical variability of the riparian zone across a landscape, we recently established a Riparian Observatory in Krycklan (ROK). The ROK is a unique study design for monitoring the interaction between soil and stream water chemistry based on 13 riparian plots located in the 67 km^2 Krycklan catchment. We analyzed hydrometric and total organic carbon (TOC) concentrations observed during 9 sampling occasions in 2008 and 2009 along with continuous groundwater and streamflow measurements. TOC was chosen over other solutes because several studies have recognized the RZ as the dominant TOC source (Hinton et al., 1998; Fiebig et al., 1990; Bishop et al., 1990; Dosskey and Bertsch, 1994) and because TOC is a key controlling factor for stream water quality (Hruška et al., 2003; Shafer et al., 1997; Erlandsson et al., 2008) that is sensitive to climatic change (Köhler et al., 2009). Moreover, the assessment of riparian TOC exports can provide much needed insights into the mechanisms that control contributions of inland waters to the global carbon cycle (Öquist et al., 2009; Battin et al., 2009; Cole et al., 2007).

In this study we investigated the spatiotemporal variability of groundwater levels, soil water TOC concentrations, and TOC export rates from the RZ of a boreal catchment in Sweden. This also tests the suitability of a lumped RZ representation in catchment-scale water quality models, such as the RZ representation in the RIM model (Seibert et al., 2009). We further combined soil water TOC measurements and hydrometric observations with landscape analysis to explore the idea that terrain indices can be used to predict groundwater levels and soil water TOC concentrations in riparian soils. This implies that combining terrain analysis with a spatially distributed RIM concept would make it possible to predict the spatial variability of riparian TOC concentrations, lateral flows and, thus, TOC exports from RZs in boreal forested catchments.

2. Study design

2.1 Location

Riparian groundwater tables and soil water chemistry were monitored in the 67 km^2 boreal Krycklan catchment, which lies within the Vindeln Experimental Forests (64° 14’N, 19° 46’E) about 50 km northwest of Umeå, Sweden (Figure 1). The catchment is underlain by poorly weathered gneissic bedrock covered with sediment deposits at lower elevations and moraine (glacial till) deposits at higher elevations. The till deposits are hydrologically characterized by a sharp decrease of hydraulic conductivity with depth (Bishop, 1991). Most streams have their headwaters in the till parts of the catchment where the combination of gentle topography and less permeable substrate has led to the formation of some small lakes, wetlands and hydromorphic riparian peat soils. In the sedimentary parts of the catchment, several higher order streams become more defined in the landscape as channels within deeply eroded ravines bordered by mineral riparian soils (mostly gley). With increasing terrain slope or increasing distance from the stream, hydromorphic (mineral or organic) soils give way to well-drained podzols (spodosols), which represent the dominant soil type in Krycklan.

The transition from wet, riparian hydromorphic soils to well-drained, upland podzols farther away from streams is accompanied by vegetation changes from mosses (*Sphagnum spp.*), deciduous trees (*Betula spp*, *Alnus spp.*) and Norway spruce (*Picea abis*) at humid locations to vaccinium shrubs (*Vaccinium spp.*) and Scots Pine (*Pinus sylvestris*) at drier locations.

Based on records from 1980 to 2008 the mean annual air temperature in the catchment is 1.7 °C and the mean annual precipitation is 612 mm, of which approximately half falls as snow (Laudon et al., 2011). About half of the precipitation leaves the catchment as evapotranspiration and the other half flows out as surface water through the stream network (Köhler et al., 2008). Each year a large spring flood (freshet) occurs and marks the end of the average 168 days of snow coverage. This spring flood is the dominant hydrological event in the year with peak flow values between 8 and 12 mm day^{-1} (Laudon et al., 2011). Streamflow has been monitored continuously since 1980 at a thin 90° V-notch weir in a heated dam house located at the outlet of the 50 ha Svartberget catchment (Figure 1c).

Over the course of millennia, considerable amounts of organic matter were built up in boreal ecosystems (particularly in areas underlain by glacial till) through the formation of valley bottom peat soils and wetlands (paludification). More recently, i.e., over the past several hundred years (Zackrisson, 1977), human activities began to influence large parts of northern Sweden, including the Krycklan catchment. To favor forest production under moist conditions, most stream channels in the region were deepened and additional ditches excavated since the end of the 19th century or earlier (Esseen et al., 1997).

In 1923 the Svartberget research forest was created. It covers about 25% of the Krycklan catchment. Since then, forestry has continued to be practiced at low intensity. Forests still cover most of the catchment area (88 %) followed by wetlands (8 %), agricultural land (3 %) and lakes (1%). Its history and land cover hence make the Krycklan area fairly representative for much of the interior of northern Sweden and probably similar to other boreal ecosystems influenced by paludification and low intensity forestry.

2.2 Riparian observatory in Krycklan (ROK)

The ROK consists of 13 soil profiles located in the riparian zone (Figure 1) that have been instrumented at five depths (15 cm, 30 cm, 45 cm, 60 cm, 75 cm). The sites were located based on an initial terrain analysis of 1 m resolution airborne light detection and ranging (LiDAR) data and subsequent field visits to distribute sites across a range of potentially different wetness conditions. Ten sites were placed in the till part, two in the sedimentary part and one site was placed at the transition between the till and the sedimentary part of the catchment. Placing the majority of the sites in the till part was motivated by a detailed riparian soil survey (Blomberg, 2009). Data from the survey showed that sedimentary riparian soils were mineral soils with no or only very shallow organic horizons while most till riparian soils had thick peat horizons (≥ 30 cm). All sites were installed in October 2007 and have been operational since then. Each site was constructed by excavating an approximately 1 m deep and 1 m wide pit 1-2 m from the stream. Pairs of ceramic cup suction lysimeters (K100 suction cups, UMS©, pore size 1± 0.1 µm) were inserted at each of the 5 depth intervals in the upslope face of the pit 30 cm horizontally into the pit face. During back-filling of the pit, shallow groundwater wells made from perforated PVC pipes (sealed at the bottom) were installed at the center of the pit (Figure 2). These wells were equipped with Trutrack© capacitance rods to record hourly groundwater table positions. Thus, at each site in the ROK, it was possible to monitor water table position continuously and to extract groundwater or soil water for chemical analysis. Each installation was documented by noting site characteristics including signs of variable groundwater tables as well as the thickness of the organic horizon. Based on the organic horizon thickness the soils at each ROK site were further classified as organic, mineral-organic or mineral soils. Organic soils were peat (O-horizon thickness ≥ 30 cm), mineral soils were gley without organic matter (O-horizon thickness ≤ 0.5 cm) while all other soils were classified as organic-mineral (gley with shallow O-horizons).

2.3 Soil water TOC measurements

Soil water samples were extracted manually from all suction lysimeters at the 13 ROK sites at 9 individual sampling occasions; in 2008 once per month from May to October and on three occasions (June, August and September) in 2009. Prior to sampling, the suction lysimeters were flushed by extracting up to 50 ml of water which were discarded. After flushing, soil water samples were extracted during a period of 24-48 hours and collected in acid-washed and pre-evacuated (pressure -1 bar) Milli-Q® rinsed Duran glass bottles. The samples were kept dark and cool until they were sub-sampled and frozen for later analysis. The time from sampling to freezing was typically less than 24 hours. Soil water TOC was measured by a Shimadzu TOC-5000 using catalytic combustion. The TOC values of the water samples extracted from lysimeter pairs were individually analyzed and then averaged to obtain a single TOC concentration for each of the 5 levels monitored at each site on every sampling occasion.

It should be noted that suction lysimeters filter out particles of diameters larger than 1 µm. It has also been shown that boreal surface waters usually carry negligible amounts of particulate organic carbon (POC) making dissolved organic carbon (DOC) the dominant fraction (~95 %) of TOC (Laudon et al., 2011). Consequently, the riparian soil water TOC concentrations presented in this study are directly comparable to dissolved organic carbon (DOC) concentrations in the adjacent streams.

3. Combined analysis of hydrometric observations and TOC concentrations

3.1 Lateral flow profiles

Hourly groundwater levels measured at the individual ROK sites for the period May 2008 to September 2009 were related to the corresponding values of specific discharge q [mm day^{-1}] measured at the outlet of the Svartberget catchment (50 ha). In this study, lateral flow profiles represent the total specific groundwater discharge passing laterally through a soil profile expressed as a function of groundwater table position. Lateral flow profiles were subsequently used to calculate specific TOC export rates. To construct a lateral flow profile, observed groundwater table positions, $z_{Gw,}$ [m] were first offset by the maximum observed groundwater table position z_0 [m]. The offset groundwater positions were then fit to specific discharges using an exponential function with a flux variable k_0 [mm d^{-1}] and shape variable b [m^{-1}] (Equation 1). These parameters were determined by linear regression with log-transformed specific discharge.

$$q(z_{Gw}) = k_0 \cdot e^{b(z_{Gw}-z_0)} \qquad (1)$$

The mathematical derivation of such a lateral flow profile can also be illustrated using Darcy's law. The derivation (Equation 2) is valid under the assumptions that (1) the transmissivity feedback concept (Bishop et al., 2011) coupled with Darcian flow is applicable, (2) hydraulic gradients dh/dl [-] are time-invariant and (3) specific discharge rates are spatially homogenous. These assumptions are similar to those adopted by Seibert et al. (2009), who derived an analytical expression for their suggested riparian profile flow-concentration integration model (RIM). The specific discharge from a hillslope with an area A_c [m^2] flowing into the stream along a stream segment of length L [m] can be estimated based on Darcy's law. A_c and L can be combined into specific lateral contributing area $a_c = A_c/L$ [m] (Beven and Kirkby, 1979) and groundwater fluxes from below 1 m depth ($\mathrm{z_{base}} = \text{-}1\,\mathrm{m}$) are assumed to be negligible, i.e. $q(z \le z_{base}) \approx 0$.

$$q(z_{Gw}) = \frac{K \cdot dh/dl}{a_c} \cdot \int_{z_{base}}^{z_{Gw}} e^{b(z-z_0)} dz = \frac{K \cdot dh/dl}{b \cdot a_c} \cdot e^{b(z_{Gw}-z_0)} = k_0 \cdot e^{b(z_{Gw}-z_0)} \quad (2)$$

To reduce scatter in the groundwater-streamflow relationships, hourly discharge records were binned at 1 cm groundwater levels intervals across the total depth profile (1 m). In addition periods with surface flow (defined as periods when measured groundwater tables were above the soil surface, see Table 1) were removed from the time series of groundwater levels. These periods were removed because surface flow violates the assumption of matrix flow when fitting flow profiles. Surface flow occurred intermittently and mainly at sites adjacent to wetlands.

Suitable exponentially shaped lateral flow profiles were established for all ROK sites except for site R14. At this site the groundwater table varied little with streamflow and remained within 5 cm below the soil surface during most of the period of observation. Consequently an exponential curve (Equation 1) could not be fit to the observed data and a linear flow profile was chosen instead (Equation 3).

$$q(z) = k_0 \cdot \left| \frac{z - z_{base}}{z_{base}} \right| \quad (3)$$

As before the value of the profile base z_{base} was set to -1 m. The linear flow profile was manually adjusted to observed data by assuming no flow below z_{base} and a specific discharge rate of 5.8 mm d^{-1} (corresponding to the average specific discharge at high groundwater tables) when the groundwater table intersects the soil surface. While the adjusted lateral flow profile at site R14 could not be experimentally confirmed, this choice had only a negligible effect on the calculation of specific riparian TOC export rates due to the nearly constant TOC concentration profile (see following sections).

3.2 Flow-weighted TOC concentrations and specific riparian TOC export rates

Specific TOC export rates (i.e. the flux of TOC exported through a ROK soil profile normalized by laterally contributing area) were computed using the riparian profile flow-concentration integration modeling (RIM) approach (Seibert et al., 2009). For this, 117 (13 sites, 9 occasions) vertically continuous TOC concentration profiles were generated by interpolating linearly between measured soil water TOC concentrations observed during a given sampling occasion at each of the 5 depth intervals for each ROK site. To extrapolate TOC concentrations above the most superficial pair of suction lysimeters (15 cm), TOC concentrations were assumed to be the same as the average measured at the most superficial pair of lysimeters. Correspondingly, to extrapolate TOC concentrations below the lowest pair of suction lysimeters (75 cm) TOC concentrations were assumed to be the same as observed at the deepest lysimeter.

In total 13% of the data were missing due to sample contamination, too little sample volume or equipment malfunctioning. The most complete dataset was collected in

August 2009 (3% missing data) while most gaps occurred in May 2008 (25% missing data). For most profiles more than 4 of 5 concentrations were available. Profiles with many missing values (between 2 of 5 and 5 of 5 concentrations measured per campaign) were located at relatively dry sites R1, R4 and R9. At a single occasion (site R4 in September 2008) no water at all could be extracted from the profile. A missing value was estimated by the average TOC concentration $\overline{c_{TOC}(z^*)}$ of all measurements at the corresponding depth z^* [m] multiplied by a scaling factor, which was calculated as the average of the *n* ratios of observed TOC concentrations $c_{TOC}(z,t)$ available at the time t of sampling to the TOC concentrations $\overline{c_{TOC}(z)}$ at the corresponding depths averaged across all 9 samplings (Equation 4). For the single occasion at site R4 in September 2008 when all concentration data were missing an average concentration profile was assumed (i.e., the scaling factor was set to 1).

$$c^*_{TOC}(z,t) = \frac{1}{n} \cdot \sum_{i=1}^{n} \frac{c_{TOC}(z,t)}{\overline{c_{TOC}(z)}} \cdot \overline{c_{TOC}(z^*)} \qquad (4)$$

After establishing the continuous TOC concentration profiles, flow-weights $\omega(z)$, [-] which are values proportional to the incremental lateral specific groundwater discharge rates $dq(z)/dz$, were derived for each ROK site using the exponential lateral flow profile (Equation 1) except site R14 for which the linear lateral flow profile (Equation 3) was used.

$$\omega(z) = \frac{dq/dz}{k_0} = b \cdot e^{b(z-z0)} \qquad (5)$$

$$\omega(z) = \frac{dq/dz}{k_0} = 1 \qquad (6)$$

Flow-weighted TOC concentrations $c_{TOC,q}(t)$ were subsequently computed for each ROK site and sampling occasion by juxtaposing flow-weights and continuous TOC profiles and integrating over the part of the profile that was below the groundwater table ($z \leq z_{Gw}$) at the time of sampling (Equation 7).

$$c_{TOC.q}(t) = \int_{z_{base}}^{z_{Gw}} \omega(z) \cdot c_{TOC}(t,z)dz \Bigg/ \int_{z_{base}}^{z_{Gw}} \omega(z)dz \quad (7)$$

Finally, specific riparian TOC export rates l_{TOC} [kg ha^{-1} y^{-1}] were obtained by multiplying the flow-weighted TOC concentrations with specific discharge and applying a conversion factor to express the result in [kg ha^{-1} y^{-1}] (Equation 8).

$$l_{TOC}(t) = q(t) \cdot c_{TOC,q}(t) \cdot 3.65 \qquad (8)$$

4. Landscape and regression analysis

We performed a landscape analysis to derive riparian zone characteristics for each site in the ROK based on a quaternary deposits map (1:100,000, Geological Survey of Sweden, Uppsala, Sweden) (Figure 1) and on terrain indices calculated from a 5 m resolution digital elevation model (DEM) derived from LiDAR data. The terrain indices were computed using the open source software SAGA GIS (Conrad, 2007; Böhner et al., 2008) and comprise specific upslope contributing area (a_c, as a surrogate for shallow groundwater flow accumulation), slope ($\tan\beta$, as a surrogate for local drainage), and the topographic wetness index (Beven and Kirkby, 1979) (TWI, as a surrogate for shallow groundwater table position). Upslope contributing area was calculated using a multiple direction flow accumulation method (MD∞) (Seibert and McGlynn, 2007). Slope was computed based on the derivate of a polynomial surface that was locally fitted to the DEM (Zevenbergen and Thorne, 1987). The stream network was derived using the “Channel Network” module in SAGA GIS (Conrad, 2007; Böhner et al., 2008) and an initiation threshold area of 5 ha calculated using the MD∞ method. To account for artificially excavated ditches, several streams were set to start at the beginning of ditches that had been identified in the field even if the accumulated area was below the initiation threshold area.

Side-separated lateral contributing areas to all ROK sites and along the entire stream network were quantified using the SIDE algorithm by Grabs et al. (2010). Lateral contributing areas were divided by the grid-resolution (5 m) to obtain specific contributing area values (a_c). Local TWI values were calculated for the RZs on both sides of the stream as the logarithm of specific (side-separated) contributing area a_c divided by local slope $\tan\beta$ (Equation 9).

$$TWI = \ln\left(\frac{a_c}{\tan\beta}\right) \qquad (9)$$

To evaluate correlations Spearman rank correlation coefficients, r_s, were computed between observed TOC concentrations and the derived terrain indices (slope, upslope contributing area and TWI). Preliminary results indicated that TWI and soil depth were the major explanatory variables. For quantification, three different regression models to predict log-transformed average TOC concentrations at specified depths and landscape positions (characterized by log-transformed TWI values) were established using robust, multiple linear regression (Venables and Ripley, 2002). Robust regression methods can be effectively applied to heteroskedastic datasets including potential outliers and allow a considerably more robust estimation of parameters than standard regression methods. The three regression models were established using TOC values measured at different depths and locations in the till parts of the catchment. For each site and depth the average TOC value of all 9 sampling occasions was calculated. The tested regression models relied on TWI and soil depth as the only predictor variables.

5. Results

5.1 Hydrometric observations and soil water TOC concentrations

Soil water TOC concentrations as well as soil classes (organic, mineral-organic and mineral soils) were related to riparian groundwater levels and parent material (till or sediment deposits). Organic soils were located on till deposits at relatively humid or wet positions ($-0.45 < \bar{z}_{Gw}$) in the RZ whereas mineral-organic soils were located on till deposits at relatively dry positions ($\bar{z}_{Gw} < -0.45$) in the RZ. RZs on sediment deposits were mineral with exception of site R11. Soil water TOC concentrations varied from 3 to 97 mg l^{-1} at organic soils, from 1 to 43 mg l^{-1} at mineral-organic and from 1 to 19 mg l^{-1} at mineral soils (excluding site R11) (Table 1). Site R11 was excluded because it was organic peat at the transition between till and sedimentary deposits with TOC concentrations (4 – 46 mg l^{-1}). R11 had a lower maximum concentrations compared with other organic (peat) soils and higher minimum concentrations compared with mineral soils. Average concentration profiles in till soils showed generally higher TOC concentrations at sites with more superficial water tables (Figure 3), as was reported by

Lyon et al. (2011). For most TOC concentration profiles in till soils, TOC concentrations also increased towards the soil surface.

RZs in the till parts were ordered with increasing median groundwater table positions ($\bar{z}_{Gw}$) and further grouped into relatively dry mineral-organic ($\bar{z}_{Gw} \leq -0.45m$), humid organic ($-0.45 < \bar{z}_{Gw} \leq -0.15m$) and wet organic ($\bar{z}_{Gw} > -0.15m$) soils (Figure 3). The wettest riparian till site (R8) was situated near the outlet of the Kallkällsmyren headwater wetland ($\bar{z}_{Gw} = -0.03m$) while the relatively driest riparian till site (R4) was found on a gley-podzol ($\bar{z}_{Gw} = -0.62m$). Relatively low groundwater levels at the mineral-organic RZs (such as R4) could in part be explained by low upslope contributions of water (indicated by the low values of lateral contributing area, Table 1) and effective drainage related to terrain slope (Table 1) in conjunction with stony soils or ditching. Average TOC concentration-depth gradients (assuming exponential decrease with depth) in the till part of the catchment (Figure 3) were, with respect to different groundwater table positions, steepest at humid locations (50% less TOC per 53 cm increase in depth) followed by those at wet locations (50% less TOC per 96 cm increase in depth). TOC concentration-depth profiles at the mineral-organic locations, on the other hand, showed hardly any increases in soil water TOC concentrations towards the soil surface. Temporal variability of TOC concentrations measured in soils underlain by till (expressed by the standard deviation) increased with increasing TOC concentrations and with more superficial positions in the soil profiles (Figure 3). Site R9 deviated from this pattern; here average TOC concentrations slightly increased between 0.75 m to 0.45 m depth but then decreased between 0.45 m and 0.15 m depth.

RZs in the sedimentary parts were mineral (R14 and R15) and organic (R11) and differed from RZs in the till parts with respect to accumulation of organic matter because it was unrelated to groundwater table position. This observation is consistent with the results from a more detailed riparian soil survey (Blomberg, 2009) indicating that RZs in the sedimentary parts are predominantly mineral gley soils. In other words, paludification of these RZs did not occur even in the presence of almost permanently saturated soils at site R14. ($\bar{z}_{Gw} > -0.02m$). Median groundwater table positions at sites R11 and R15 were -0.03 m and-0.51 m respectively. Mineral RZs had relatively low TOC concentrations and no characteristic shape to the vertical profile of TOC whereas the organic RZ exhibited a similar TOC concentration-depth gradient as seen in organic RZs in the till parts. TOC concentration depth gradients varied from positive (site R15) to negative (site R11) and to almost zero (Site R14). Temporal variability of TOC concentrations at the mineral RZs in the sedimentary parts was low and comparable to the variability in mineral-organic till soils (Figure 3).

5.2 Flow-weighted TOC concentrations and specific riparian TOC export rates

For all ROK sites, except for site R14, exponentially shaped lateral flow profiles could be fit reasonably well to the binned observation data (Figure 4). This allowed derivation of corresponding depth dependant flow-weights (curved grey lines in Figure 3). Flow-weighted concentrations $c_{TOC\,q}$ for each site and sampling occasion (Figure 5b) were computed consecutively from the continuous TOC profiles and flow-weights (Equation 5). Specific riparian TOC export rates for a particular day, l_{TOC}, which were calculated from specific discharge values q and flow-weighted concentrations $c_{TOC\,q}$

(Equation 6), ranged from 2 to 285 kg ha^{-1} y^{-1} (per unit of laterally contributing area) and varied strongly with discharge conditions (Figures 5c and 5d). It should be noted that the specific riparian export rates were calculated on a daily basis but that their unit was expressed as flux per year to facilitate comparison with other values published in scientific literature (where fluxes are often calculated on a yearly basis).

The shapes of the distributions of average soil water TOC concentrations (Figure 5a) varied because of changing soil water TOC concentrations at the 9 sampling occasions. Variations of calculated flow-weighted TOC concentrations (Figure 5b) and specific riparian TOC export rates (Figure 5c), on the other hand, reflected the combined effect of temporally variable TOC concentrations and variable specific discharge and groundwater conditions (Figure 5d). In both 2008 and 2009 average values of TOC concentrations c_{TOC} across each profile were slightly higher in August and September compared to values in June (Figure 5a). A slight trend of average TOC concentrations increasing from spring to fall was visible in 2008. There were only three sampling occasions in 2009 which were too few to detect any trend.

It is noteworthy that changes mainly occurred at organic soils whereas mineral and mineral-organic soils exhibited only small temporal variations of TOC in absolute terms. This was also confirmed when comparing median groundwater tables to (1) flow-weighted TOC ($c_{TOC\,q}$ values obtained by combining average TOC concentration profiles with median groundwater tables) and (2) potential variations of flow-weighted TOC concentrations (minimum and maximum $c_{TOC\,q}$ when combining all observed TOC concentration profiles with 10th percentile and 90th percentile groundwater positions) (Figure 6a). Potential variations of flow-weighted TOC concentrations at each site increased with increasingly organic soils and increasingly shallow median groundwater positions.

5.3 Landscape and regression analysis

Median groundwater table positions correlated to the TWI (Figure 6b) at all ROK sites, and the corresponding median flow-weighted TOC concentrations of all ROK except site R14 sites correlated to the TWI and median groundwater table positions (Figure 6a, c). While the shallow median groundwater table position at R14 coincided with the highest TWI value, flow-weighted TOC concentrations were largely overestimated for this mineral RZ.

Regression models to predict average TOC concentrations at the various depths were developed for the ROK sites in the till parts of the catchment. ROK sites in the sedimentary part were not included because (1) independent field surveys had shown that most RZs in the sedimentary part were mineral gleys (Blomberg, 2009) and (2) because there were only three ROK sites in the sedimentary part. Regression fits for TOC concentrations in the till part were visually evaluated by plotting predicted against observed average TOC concentrations (Figure 7). For simplicity, only TWI was selected for regression modeling since it correlated more with observed average TOC concentrations (r_s = 0.67) than slope and laterally contributing area (r_s= -0.65 and r_s = 0.58 respectively). Since linear robust regression models were fit on logarithmically transformed variables, plots were generated for the variables at the logarithmic scale (Figures 7a, c, e) and at the original scale (Figures 7b, d, f). Robust regression with depth as the only predictor (mean absolute error of 12 mg l^{-1} TOC) variable failed to capture the variability of the average TOC concentrations (Figures 7a, b). When using only TWI as predictor variable the spectrum of average TOC concentrations was mostly covered (mean absolute error of 9 mg l^{-1} TOC). Observed average TOC concentrations, however, scattered considerably when compared to relatively low or high predicted average TOC concentrations (Figures 7c, d), which is a sign of heteroskedasticity. Observed average TOC concentrations were best predicted by a multi-linear regression model based on depth and TWI as predictors (mean absolute error of 8 mg l^{-1} TOC) (Figures 7e, f). Although the visual comparison of predicted against observed average TOC concentrations still revealed a lot of scatter, points were distributed more randomly around the 1:1 line with fewer apparent clusters than in the regression models based on single predictor variables.

6. Discussion

6.1 Hydrometric observations and soil water TOC concentrations

The range of riparian soil water TOC concentrations (from 1 mg l^{-1} to 97 mg l^{-1}, Table 1) measured in this study was almost twice as wide as the range of stream TOC concentrations at Krycklan (Buffam et al., 2007) and other boreal Swedish catchments (Laudon et al., 2004a; Temnerud and Bishop, 2005). The dominant sources of stream TOC in Krycklan are organic riparian soils, together with headwater wetlands and not the TOC mobilized from podsols at hillslopes draining into the RZ (Bishop et al., 1990; Laudon et al., 2011). This corresponds to findings in other catchments with high TOC levels (> 10 mg l^{-1}) (Hinton et al., 1998; Fiebig et al., 1990; Bishop et al., 2004; Dosskey and Bertsch, 1994). Differential mixing of riparian soil waters from different soil horizons as conceptualized in the RIM (Seibert et al., 2009) model is a mechanism that could explain some of the temporal variability of stream TOC concentrations observed in this and similar catchments as presented by other authors (Köhler et al., 2009; Bishop et al., 2004) . For this simple model to be scalable to entire stream networks, much the considerable spatial variability in stream TOC would need to derive from variability in lateral exports from different types of RZs and wetlands along the stream network.. And, indeed, there seemed to be sufficient spatial variation in RZ types to explain some of the spatial variation in stream TOC concentrations at Krycklan. While the existence of different RZ types does not prove the RIM concept, it is a necessary prerequisite for upscaling RIM from single hillslopes or small headwaters to a spatially distributed representation of riparian TOC exports at the catchment scale. By the same token, the range of soil water TOC concentrations as well as the variety of concentration profile shapes and water table positions observed at the ROK sites (Figure 3) indicate that a single representative lumped conceptualization of chemistry or flow pathways in the RZ (e.g. Seibert et al., 2009; Bishop et al., 2004; Boyer et al., 1996; Köhler et al., 2009) can be inappropriate for predicting the spatio-temporal variability of stream TOC concentrations. This appears to be true even when considering only the RZs in the till part of the Krycklan catchment (Figure 3), which one otherwise might easily and mistakenly think of as being rather homogenous when one does not have the type of spatial detail in TOC concentration measurements that could be obtained with the ROK.

All ROK sites except sites R9 and R15 exhibited a trend of increasing soil water TOC concentrations with more superficial soil horizons. As site R9 is located on stony till next to a ditched stream, its soil profile might have been subjected to disturbances despite now being located in a RZ. It is also possible that paludification was less pronounced at this site. At site R15, which lies in the sediment part of Krycklan, neither the mineral riparian gley soils nor the adjacent hillside podzols seem to be likely sources of the observed TOC enriched soil water (up to 19 mg l^{-1} at 60 cm depth) in the lower parts of the profile. TOC enriched water might have however originated (1) from locally buried organic matter in this actively scoured and aggrading flood plain, (2) in the drainage water from a small agriculture field located 50 m upslope or, (3) in hyporheic fluxes between the stream and the RZ. Carbon dating techniques might help to further investigate this question.

Despite the overall variability of observed concentration-depth profiles, some common patterns emerged, especially for sites located in the till parts of the catchment where the ROK instrumentation was concentrated. Here, varying soil wetness conditions appeared to influence the total amount of soil water TOC as well as the shape of the TOC concentration profiles. Organic matter has not built up in drier, more organic-poor (mineral) till soils to the same degree as on more humid (organic-rich) till soils, giving lower levels of TOC and less pronounced vertical gradients in TOC (Figure 3).

The lack of a common discernable TOC concentration-depth profile at the sedimentary sites could be attributed to the small number of sites as well as to an unclear relation between substrate and soil organic matter accumulation. An extrapolation from three sites to the entire RZ in the sedimentary zone would obviously be uncertain especially as two of these were selected as interesting extremes rather than typical sedimentary riparian sites. Observations from an independent riparian soil inventory at Krycklan (Blomberg, 2009) however indicate that most riparian soils in the sedimentary parts of the catchment were mineral gley soils. Based on these observations we would expect TOC concentrations in water outflows from sedimentary RZs to be around 6 mg l^{-1} (average of all TOC concentrations measured at sites R14 and R15).

Although we found organic soils mostly in RZs underlain by till whereas sedimentary substrate seemingly implied mineral soils, the apparent link between parent substrate (till or sedimentary material), soil organic matter (in this case mostly peat) and soil water TOC has yet to be explained. Soil moisture is often not a limiting factor for peat formation in the sedimentary parts as groundwater levels are similarly close to the ground surface as for till sites, which suggests that varying hydraulic properties of the substrate are probably not a sufficient explanation. Other potential factors that might substantially influence riparian peat formation and, subsequently, riparian soil water TOC concentrations include differing substrate erodibility or ionic composition of soil- or groundwater (Almendinger and Leete, 1998; Nilsson et al., 1991; Giesler et al., 1998). One additional ROK site (R13, not shown on map) was destroyed after being buried under sediments from a fourth order stream during spring flood 2008.This event highlights fluvial processes as an additional factor that might hinder the accumulation of organic matter in sedimentary RZs close to high order streams. At the 67 km^2 catchment scale, the presence of mineral riparian soils in the lower part of that catchment is another potential explanation for the observed downstream decreases in stream TOC concentrations in Krycklan (Ågren et al., 2007) that does not rely directly on the spatial distribution of wetlands.

Temporal variations of soil water TOC concentrations are potentially influenced by a multitude of interacting factors (Kalbitz et al., 2000) including soil temperature (Freeman et al., 2001), antecedent wetness (Köhler et al., 2009), soil frost (Haei et al., 2010), atmospheric deposition (Monteith et al., 2007) or atmospheric CO_2 concentrations (Freeman et al., 2004), runoff rates and combinations of these factors (Erlandsson et al., 2008). The time period of data monitored in this study was too short to disentangle the long and short term interactions of controlling factors. The temporal variability of soil water TOC concentration observed in this study (indicated by black horizontal lines, Figure 3), however, can be interpreted as a measure of the sensitivity of the soil solution response to a change of one or more external factors. Mineral and mineral-organic RZs at dry till or sedimentary locations appeared less susceptible to change over short periods than organic RZs at humid or wet till locations (Figure 5). At wet RZs, temporal changes in soil water chemistry were directly transferred to surface water systems because all soil horizons (in particular organic-rich surficial horizons) were saturated most of the time (i.e., hydrologically connected). At humid RZs, temporal changes in soil water chemistry in the transiently saturated part of the profile (delimited by grey, dotted horizontal lines, Figure 3) were only propagated to surface waters when these horizons had become saturated (i.e., hydrologically connected). It thus appeared (when neglecting potential effects of laterally expanding or shrinking discharge areas) that (1) very wet or permanently saturated RZs influenced surface water chemistry more through biogeochemical variations in the soil water while (2) humid or transiently saturated RZs influenced surface water chemistry more as a result of interplay between biogeochemical *and* hydrological variations.

6.2 Flow-weighted TOC concentrations and specific riparian TOC export rates

The RIM concept (Winterdahl et al., 2011b; Seibert et al., 2009) was used to calculate riparian TOC export rates. RIM only accounts for riparian TOC exported by lateral subsurface flows through a single, chemostatic soil profile. Consequently, other potential flow pathways (such as groundwater recharge to the streambed or overland flow) and biogeochemical processes during transport through the RZ were not taken into account. The effect of alternative flow pathways which could partially bypass the RZ was not assessed in detail, though other studies have confirmed the strong relationship between stream flow and riparian groundwater levels (Seibert et al., 2002). However, periods of potential overland flow as indicated by groundwater levels above surface were relatively limited at most ROK sites (Table 1). This also agrees with the transmissivity feedback mechanism (Bishop, 1991; Bishop et al., 2011), which implies that even during relatively high discharge conditions most runoff reaches the stream as shallow subsurface flow rather than as overland flow. That 1991 study also examined lateral versus vertical hydraulic gradients during stream events and concluded that on two till hillslopes in the vicinity of the ROK, upwelling groundwater is not a major factor as lateral subsurface flow is the dominant flow component.

In contrast to the transmissivity feedback mechanism (Bishop, 1991; Laudon et al., 2004b; Nyberg et al., 2001; Kendall et al., 1999; Rodhe, 1989) the two additional assumptions (constant hydraulic gradients and homogeneous specific discharge) that underlie the derivation of lateral flow profiles have been less intensively studied in the past. Heterogeneous land cover and topography, for instance, might influence the timing, magnitude and direction of hydraulic gradients in the RZ (Bishop, 1994; Vidon and Smith, 2007; Rodhe and Seibert, 2011) as well as the spatial variability of specific discharge rates (Temnerud et al., 2007; Lyon et al., in press).

Horizontally changing riparian hydraulic gradients effect calculations in this study to a lesser degree because (1) the magnitude of riparian hydraulic gradients and their possible variation are usually small compared to the associated relative changes of flow (Bishop, 1991) and because (2) slight changes of flow directions in the direct vicinity of streams have little effect on TOC concentrations as long as the flow is not reversed. The possibility of a reversal of flow, i.e. streams recharging water into the RZ, has not been further investigated but can be considered as rather unlikely for the sites in this study.

The use of homogeneous specific discharge rates observed at a single gaging station could introduce a considerable amount of uncertainty in the estimates of lateral flow profiles and riparian TOC exports. The streamflow and groundwater table data were binned to reduce scatter, resulting in scatter plots with little amounts of apparent noise (Figure 4). Still, it can be expected that the uncertainty of lateral flow profiles increases with increasing specific discharge. Potential implications for flow-weighted TOC concentrations and specific riparian export rates depend on the TOC concentration-depth profiles. For relatively constant profiles (such as site R14) the exact shape of the flow profile is of minor importance whereas it can be crucial for sites with strongly curved concentration depth profiles (such as site R7).

Overall, TOC exports from different riparian soil profiles in this study (2 – 285 kg ha^{-1} yr^{-1}), even if only sustained for a day, covered the entire range of annual stream TOC exports (3 – 250 kg ha^{-1} yr^{-1}) observed in other cold temperate or boreal regions in the world (Temnerud et al., 2007; Dawson et al., 2004; Hope et al., 1994), which highlights the considerable spatial variability of RZs within a single catchment. Organic soils at humid or wet riparian till locations clearly emerged as hot spots with a considerable potential to control spatial and temporal variations of riparian TOC exports to streams (Figure 5 and Figure 6a). Variations of TOC exports from wet RZs were largely related to changes in soil water TOC concentrations while variations in TOC exports from humid RZs were related to changing groundwater tables (which were correlated to streamflow conditions as illustrated by figures 4 and 5) and varying soil water TOC concentrations. TOC exports from humid RZs were thus controlled by processes in the transiently saturated part of the soil column (Figure 3) as other authors have previously explained for a single site within this study area (Seibert et al., 2009; Winterdahl et al., 2011a; Bishop et al., 1990). In this study, vertical changes of TOC concentrations with depth in the transiently saturated zone of these humid RZs varied approximately between -1.3 and +2.5 mgTOC l^{-1} cm^{-1} (determined from measurements at 15 and 30 cm depth). Conversely, mineral-organic soils at dry till RZs or mineral soils at RZs underlain by sediments exhibited only relatively little changes in soil water TOC related attributes (Figure 3).

It is noteworthy that TOC exported from the RZ, and in particular its labile fraction, might be subject to additional processes in the hyporheic zone. Although we hypothesize that much of the estimated lateral riparian TOC exports reaches the stream, a part of it might be metabolized in either the hyporheic zone or within the stream itself and transformed to dissolved inorganic carbon (DIC). The low rates of TOC breakdown relative to the short time that water spends in the largely shaded stream channel of the Krycklan streams (Wallin et al., 2010) and measured rates of TOC mineralization (Köhler et al., 2002) indicate, however, that only a few percent of the TOC will be mineralized in the stream. The rate of hyporheic processing of TOC has not, to our knowledge, been quantified in Fennoscandian streams, or been suggested to be a major factor in downstream patterns of TOC (Temnerud et al., 2007).

6.3 Landscape and regression analysis

The TWI appeared appropriate for predicting groundwater tables in RZs located in both till and sedimentary parts of the catchment (Figure 6). On the other hand, the TWI was found suitable for predicting TOC-related RZ attributes only in the till parts of the catchment, where TOC was also considerably more variable than in the sedimentary parts (Figure 7). In the till areas combining TWI and depth allowed prediction of the spatial variability of average TOC concentrations both at different riparian landscape positions and at different depths (Figure 7e and Figure 7f). This is an important step forward compared to previous studies relying on a single riparian soil profile to represent the entire RZ in a catchment (Seibert et al., 2009; Köhler et al., 2009). This opens up possibilities for representing the spatial variability of stream TOC using the RIM approach. The poor fit when using a regression model based on depth as single predictor variable further underlined the need to account for the RZ heterogeneity in the landscape. Upscaling carbon-related attributes of the RZ such as soil water TOC concentrations or soil carbon storages based on the TWI is a promising approach that is sufficiently general to be transferred to other catchments in cold climates.

In addition to spatially variable TOC concentrations and groundwater tables, however, the temporal variability in both lateral flows and TOC profiles must be explicitly accounted for to fully simulate dynamic riparian carbon exports. Since groundwater tables (Figure 6b) and flow pathways can be related to topography (Grabs et al., 2009; Grabs et al., 2010; Lyon et al., 2011), topographic landscape analysis is an approach for upscaling hillslope scale hydrological understanding to the landscape scale. Temporal variations of concentration depth profiles, however, also need to be addressed. We have made a start, but in contrast to water fluxes, soil solution chemistry may depend on other factors than just the water balance, so a further refinement could be to incorporate additional information including antecedent conditions, varying temperature (Köhler et al., 2009; Winterdahl et al., 2011a) or measures of biological activity. The effect of temporal variations of TOC concentrations on flow weighted TOC concentrations and specific riparian TOC export rates is strongest in organic RZs (Figures 5b, 5c, 6a and 6c), which are also the dominant sources of stream water TOC in Krycklan. Here, the assumption of time-invariant average TOC concentration depth profiles (assuming average TOC concentration depth profiles) would result in substantially underestimated ranges of flow-weighted TOC concentrations (solid error bars in Figures 6a and 6c) compared to the potentially wide ranges assuming temporally varying flow-weighted TOC concentrations (dotted error bars in Figures 6a and 6c).

The combined influence of spatial and temporal heterogeneities of groundwater table positions and TOC concentration depths profiles for different RZs could be summarized schematically (Figure 8). Groundwater tables were most variable in relatively dry RZs. However, the variability of groundwater tables implied a high variability in flow-weighted concentrations only at humid or wet organic RZs. This was because the variability of soil water TOC-concentrations was low in mineral and mineral-organic soils, which meant that flow-weighted concentrations did not vary much regardless of the groundwater table variations.

7. Conclusions

In this study we documented the importance of accounting for heterogeneity of riparian zones with respect to vertical distributions of lateral flow and TOC concentrations at the landscape scale and their combined role in regulating lateral riparian TOC exports to streams. The marked heterogeneity of riparian zones also indicated that lumped representations of riparian zones at the catchment scale can be overly simplistic and highlights the need both for more distributed RZ representations and more studies of variability in the riparian zone of other landscapes. We further showed that topographic landscape analysis can provide the necessary basis to upscale riparian zone processes (e.g., vertical profiles of TOC and lateral flow) from the plot to the catchment scale, which is a prerequisite for distributed RZ representations. The usefulness of topographic indices seemed to be consistent with the idea that topography has influenced water flows and soil moisture over millennia and thereby also soil development and paludification. The interplay of varying lateral flow pathways and heterogeneity of riparian zones can be expected to be similarly crucial for transport processes involving other key parameters of water quality such as nitrate or heavy metals. While lateral subsurface flow is the major transport pathway through the riparian zones of Krycklan, alternative pathways such as overland flow or groundwater recharge to streams can be more important in other catchments. Based on our analysis of hydrometric data and TOC measurements, riparian zones along the stream network contribute differently to the observed variability of stream water TOC. In particular, we found that organic riparian zones with peat soils and shallow groundwater tables fluctuating within the upper 40-50 cm of the soil column were hotspots that controlled most of the temporal variability of riparian TOC exports to streams. The spatial variability of riparian-derived TOC in streams, on the other hand, appeared to be influenced by an upstream mosaic of mineral, mineral-organic and organic riparian zones along the stream network.

Acknowledgements

The financial support for this project was partly provided by the Swedish Research Council (VR, grant no. 2005-4289). This study is part of the Krycklan catchment study which is funded by VR, Formas (ForWater), Mistra (Future Forest), SKB and the Kempe Foundation. Special thanks to Julia Paraskova, Magdalena Nyberg the Krycklan crew and many others for excellent field and laboratory work as well as to Claudia Teutschbein for illustrating the design of the riparian monitoring sites (Figure 2).

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Tables

Table 1: Site characteristics (minimum and maximum in each column are shown as bold numbers).

	Groundwater table position (cm)				**TOC concentration ($mg\ l^{-1}$)**			**Substrate**	**Topography**		
Site	10^{th} Percentile	Median	90^{th} Percentile	Above surface [a]	Avg	Min	Max	Parent material, Soil group [d]	Slope	Lateral contributing area (m^2)	TWI
R4 [c]	**-66**	**-62**	**-52**	**0 %**	4	1	7	Till, Mineral-Organic	12.9 %	40.9	4.2
R12	-72	-60	-47	**0 %**	6	3	32	Till, Mineral-Organic	6.8 %	12.5	3.6
R1	-58	-54	-42	**0 %**	10	3	25	Till, Mineral-Organic	8.8 %	**12.5**	**3.3**
R9	-56	-47	-37	**0 %**	18	3	43	Till, Mineral-Organic	**14.0 %**	103.3	5
R7	-35	-28	-23	**0 %**	36	**12**	**97**	Till, Organic	6.4 %	229.4	6.6
R10	-31	-24	-20	**0 %**	16	3	52	Till, Organic	4.3 %	944.7	8.4
R6	-23	-19	-5	4.5 %	**38**	7	88	Till, Organic	5.7 %	**1153.4**	8.3
R5	-19	-15	-10	< 0.1%	19	6	44	Till, Organic	7.4 %	100	5.6
R2 [b]	-15	-8	-5	1.8 %	35	10	76	Till, Organic	**0.6 %**	62.1	7.7
R8 [b]	-9	-3	3	**27.8 %**	30	11	53	Till, Organic	3.3 %	907.4	8.6
R15	-61	-51	-43	**0 %**	9	3	19	Sediment, Mineral	4.7 %	20.8	4.5
R11 [b]	-8	-3	0	9.0 %	12	4	46	Sediment, Organic	1.4 %	545.6	8.9
R14 [b]	**-5**	**-2**	**1**	15.5 %	**3**	**1**	**7**	Sediment, Mineral	1.2 %	725.5	**9.4**

Notes

[a] Percentage of time (relative to the total record length) with groundwater tables positioned above the soil surface.
[b] Adjacent to a wetland.
[c] Soil profile with both spodic (podzol) characteristics in the upper and gley characteristics in the lower part of the profile.
[d] Soil groups: Mineral ≡ gley soil with O-horizon < 5 cm, Mineral-Organic ≡ gley soil with O-horizon ≥ 5 cm and < 30 cm, Organic ≡ peat with O-horizon ≥ 30 cm

Figure texts

Figure 1: Locations of the (numbered) riparian monitoring sites (empty white circles) in the Krycklan catchment (outlined by thin black lines in inset b) and the gauging station (black triangle) at the outlet of Svartberget (outlined by thin black lines in inset c). Streams and lakes are represented by black areas and thin black lines. Parts of the catchment underlain by till are shown as white areas and others underlain by alluvial sediment deposits are marked by the cross-hatched areas respectively while wetlands are highlighted as grey shaded patches. Wetlands and lakes are highlighted as grey patches. Only site numbers are shown and "R" prefixes used in the text (preceding the site digits) were omitted for better readability.

Figure 2: Illustration of an instrumented riparian monitoring site. Pairs of suction lysimeters are installed at 15, 30, 45, 60 and 75 centimeters below the soil surface at a distance of about 2 m from the stream. A perforated PVC tube equipped with an automatic water logging device is located at mid-distance between the stream and the suction lysimeter nest. The schematic coordinate system on the right side of the figure. illustrates the orientation and datum of the z axis (depth, groundwater table) in relation to the x axis (lateral flow, solute concentration).

Figure 3: Average TOC concentrations c_{TOC} (circles) from 9 sampling occasions (2008-2009), interpolated TOC profiles (black lines), median groundwater position (solid, grey horizontal line) and the (dimensionless) weighting functions ώ obtained from lateral flow profiles (light-grey curves) for all 13 sites. The range of temporal variability of TOC concentrations at different depths is represented by horizontal black lines (average concentration ± 1 standard deviation) and the range of temporal variability of groundwater positions is indicated by dotted grey horizontal lines (10th and 90th percentile of groundwater positions). Each subplot contains a site label located in the lower right corner. The subscripts next to each site number in the labels indicate mineral (m), mineral-organic (mo) and organic (o) soil profiles. Rows 1 to 3 represent soil plots underlain by till deposits and sorted according to increasingly shallow average groundwater positions (dry, humid and wet locations in the 1st, 2nd and 3rd row respectively). The lower 4th row contains sites underlain by sediment deposits.

Figure 4: Binned measurements of groundwater level plotted against specific discharge (circles). Fitted, site-specific lateral flow profiles and their respective 95% confidence intervals are shown as thin black lines and (thin) grey shaded areas. Each subplot contains a site label located in the lower right corner. The subscripts next to each site number in the labels indicate mineral (m), mineral-organic (mo) and organic (o) soil profiles. Rows 1 to 3 represent soil plots underlain by till deposits and sorted according to increasingly shallow average groundwater positions (dry, humid and wet locations in the 1st, 2nd and 3rd row respectively). The lower 4th row contains sites underlain by glaciofluvial sediment deposits.

Figure 5: Ranges of average TOC profile concentrations c_{TOC} (a), flow-weighted profile concentrations $c_{TOC\,q}$ (b) and specific TOC export rates l_{TOC} (c) and the specific discharge q (d) at the time of 9 individual sampling occasions (6 in 2008 and 3 in 2009). For each campaign the ranges of TOC-related variables (left y-axis) are illustrated by box plots (contoured by light-shaded lines) and site-specific values (short, dark-shaded horizontal lines). Site specific values from organic till sites are additionally highlighted by asterisks and dots respectively at both ends of the corresponding horizontal lines.

Figure 6: Links between median groundwater positions z_{GW}, median flow-weighted TOC profile concentrations ($c_{TOC\,q}$) and the topographic wetness index (TWI). In the left plot (a) median flow-weighted $c_{TOC\,q}$ values (from 9 sampling occasions in 2008-2009) are plotted against median z_{GW} values. The middle plot (b) compares median z_{GW} values against the TWI whereas the right plot (c) compares median $c_{TOC,\,q}$ values against the TWI. Vertical error bars show the 10^{th} and 90^{th} percentile groundwater positions (b) respectively the potential range of flow-weighted TOC concentrations (a and c) assuming average profile concentrations (solid lines) or changing profile concentrations (dotted lines) . Circles represent sites located in the till parts and triangles represent sites located in the sedimentary part of the catchment. Organic sites are colored black, mineral sites are white and mineral-organic sites are grey. Site numbers are plotted next to the circles and triangles. Only site numbers are shown and “R” prefixes used in the text (preceding the site digits) were omitted for better readability.

Figure 7: Modeled versus predicted average TOC concentrations (empty circles) for 10 riparian monitoring sites and 5 different depths (15, 30, 45, 60 and 75 cm below the surface) in the till part of the catchment. In the upper row log-transformed TOC concentrations are shown. Three regression models for TOC were tested using depth (first column), TWI (middle column) as well as using both depth and TWI as predictors (right column).

Figure 8: Temporal variability as function of riparian zone wetness for different quantities (schematic figure).