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

Thomas Grabs<sup>1,2</sup>, Kevin H. Bishop<sup>1,3</sup>, Hjalmar Laudon<sup>4</sup>, Steve W. Lyon<sup>2,5</sup>, Jan Seibert<sup>1,2,6</sup>

<sup>1</sup>Department of Earth Sciences, Uppsala University, Uppsala, Sweden

<sup>2</sup>Department of Physical Geography and Quaternary Geology, Stockholm University, Stockholm, Sweden

<sup>3</sup>Department of Aquatic Sciences and Assessment, SLU, Uppsala, Sweden

<sup>4</sup>Department of Forest Ecology and Management, SLU, Umeå, Sweden

<sup>5</sup>Bert Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden

<sup>6</sup>Department of Geography, University of Zurich, Zurich, Switzerland

Correspondence to:

Thomas Grabs ([thomas.grabs@geo.uu.se](mailto:thomas.grabs@geo.uu.se))  
Earth Sciences  
Uppsala University  
Villavägen 16  
752 36 Uppsala, SWEDEN  
Phone: +46 (0)18 471 25 21

## 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<sup>2</sup> 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. ~~Exports-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, ~~Near-stream-Buffer-Zone~~, 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 (Cirimo 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

79 horizons become hydrologically connected to the stream. If the soil water in the newly  
80 connected soil horizons is chemically different from lower horizons, then this can result  
81 in the substantial shifts of stream water chemistry observed during flow episodes.

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

96 | To assess the hydrological and chemical variability of the riparian zone across a  
97 | landscape, we recently established a Riparian Observatory in Krycklan (ROK). The ROK  
98 | is a unique study design for monitoring the interaction between soil and stream water  
99 | chemistry based on 13 riparian plots located in the 67 km<sup>2</sup> Krycklan catchment. We  
100 | analyzed hydrometric and total organic carbon (TOC) concentrations observed during 9  
101 | sampling occasions in 2008 and 2009 along with continuous groundwater and streamflow

102 measurements. TOC was chosen over other solutes because several studies have  
103 recognized the RZ as the dominant TOC source (Hinton et al., 1998; Fiebig et al., 1990;  
104 Bishop et al., 1990; Dosskey and Bertsch, 1994) and because TOC is a key controlling  
105 factor for stream water quality (Hruška et al., 2003; Shafer et al., 1997; Erlandsson et al.,  
106 2008) that is sensitive to climatic change (Köhler et al., 2009). Moreover, the assessment  
107 of riparian TOC exports can provide much needed insights into the mechanisms that  
108 control contributions of inland waters to the global carbon cycle (Öquist et al., 2009;  
109 Battin et al., 2009; Cole et al., 2007).

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

## 121 **2. Study design**

### 122 **2.1 Location**

123 Riparian groundwater tables and soil water chemistry were monitored in the 67  
124 km<sup>2</sup> boreal Krycklan catchment, which lies within the Vindeln Experimental Forests (64°

125 14°N, 19° 46'E) about 50 km northwest of Umeå, Sweden (Figure 1). The catchment is  
126 underlain by poorly weathered gneissic bedrock covered with sediment deposits at lower  
127 elevations and moraine (glacial till) deposits at higher elevations. The till deposits are  
128 hydrologically characterized by a sharp decrease of hydraulic conductivity with depth  
129 (Bishop, 1991). Most streams have their headwaters in the till parts of the catchment  
130 where the combination of gentle topography and less permeable substrate has led to the  
131 formation of some small lakes, wetlands and ~~paludified-hydromorphic~~ riparian  
132 ~~hydromorphic-peat~~ soils. In the sedimentary parts of the catchment, several higher order  
133 streams become more defined in the landscape as channels within deeply eroded ravines  
134 bordered by mineral riparian soils (mostly gley). With increasing terrain slope or  
135 increasing distance from the stream, hydromorphic (mineral or organic) soils give way to  
136 well-drained podzols (spodosols), which represent the dominant soil type in Krycklan.

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

142 Based on records from 1980 to 2008 the mean annual air temperature in the  
143 catchment is 1.7 °C and the mean annual precipitation is 612 mm, of which  
144 approximately half falls as snow (Laudon et al., 2011). About half of the precipitation  
145 leaves the catchment as evapotranspiration and the other half flows out as surface water  
146 through the stream network (Köhler et al., 2008). Each year a large spring flood (freshet)

147 occurs and marks the end of the average 168 days of snow coverage. This spring flood is  
148 the dominant hydrological event in the year with peak flow values between 8 and 12 mm  
149 day<sup>-1</sup> (Laudon et al., 2011). Streamflow has been monitored continuously since 1980 at a  
150 thin 90° V-notch weir in a heated dam house located at the outlet of the 50 ha Svartberget  
151 catchment (Figure 1c).

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

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

168

## 169 **2.2 Riparian observatory in Krycklan (ROK)**

170 The ROK consists of 13 soil profiles located in the riparian zone (Figure 1) that  
171 have been instrumented at five depths (15 cm, 30 cm, 45 cm, 60 cm, 75 cm). The sites  
172 were located based on an initial terrain analysis of 1 m resolution airborne light detection  
173 and ranging (LiDAR) data and subsequent field visits to distribute sites across a range of  
174 potentially different wetness conditions. Ten sites were placed in the till part, two in the  
175 sedimentary part and one site was placed at the transition between the till and the  
176 sedimentary part of the catchment. Placing the majority of the sites in the till part was  
177 motivated by a detailed riparian soil survey (Blomberg, 2009). Data from the survey  
178 showed that sedimentary riparian soils were mineral soils with no or only very shallow  
179 organic horizons while most till riparian soils had thick peat horizons ( $\geq 30$  cm). All sites  
180 were installed in October 2007 and have been operational since then. Each site was  
181 constructed by excavating an approximately 1 m deep and 1 m wide pit 1-2 m from the  
182 stream. Pairs of ceramic cup suction lysimeters (K100 suction cups, UMS<sup>®</sup>, pore size  $1\pm$   
183  $0.1\ \mu\text{m}$ ) were inserted at each of the 5 depth intervals in the upslope face of the pit 30 cm  
184 horizontally into the pit face. During back-filling of the pit, shallow groundwater wells  
185 made from perforated PVC pipes (sealed at the bottom) were installed at the center of the  
186 pit (Figure 2). These wells were equipped with TruTrack<sup>®</sup> capacitance rods to record  
187 hourly groundwater table positions. Thus, at each site in the ROK, it was possible to  
188 monitor water table position continuously and to extract groundwater or soil water for  
189 chemical analysis. Each installation was documented by noting site characteristics  
190 including signs of variable groundwater tables as well as the thickness of the organic

191 horizon. Based on the organic horizon thickness the soils at each ROK site were further  
192 classified as organic, mineral-organic or mineral soils. Organic soils were peat (O-  
193 horizon thickness  $\geq 30$  cm), mineral soils were gley without organic matter (O-horizon  
194 thickness  $\leq 0.5$  cm) while all other soils were classified as organic-mineral (gley with  
195 shallow O-horizons).

### 196 **2.3 Soil water TOC measurements**

197 Soil water samples were extracted manually from all suction lysimeters at the 13  
198 ROK sites at 9 individual sampling occasions; in 2008 once per month from May to  
199 October and on three occasions (June, August and September) in 2009. Prior to sampling,  
200 the suction lysimeters were flushed by extracting up to 50 ml of water which were  
201 discarded. After flushing, soil water samples were extracted during a period of 24-48  
202 hours and collected in acid-washed and pre-evacuated (pressure -1 bar) Milli-Q<sup>®</sup> rinsed  
203 Duran glass bottles. The samples were kept dark and cool until they were sub-sampled  
204 and frozen for later analysis. The time from sampling to freezing was typically less than  
205 24 hours. Soil water TOC was measured by a Shimadzu TOC-5000 using catalytic  
206 combustion. The TOC values of the water samples extracted from lysimeter pairs were  
207 individually analyzed and then averaged to obtain a single TOC concentration for each of  
208 the 5 levels monitored at each site on every sampling occasion.

209 It should be noted that suction lysimeters filter out particles of diameters larger  
210 than 1  $\mu\text{m}$ . It has also been shown that boreal surface waters usually carry negligible  
211 amounts of particulate organic carbon (POC) making dissolved organic carbon (DOC) the  
212 dominant fraction (~95 %) of TOC (Laudon et al., 2011). Consequently, the riparian soil

213 water TOC concentrations presented in this study are directly comparable to dissolved  
214 organic carbon (DOC) concentrations in the adjacent streams.

### 215 **3. Combined analysis of hydrometric observations and** 216 **TOC concentrations**

#### 217 **3.1 Lateral flow profiles**

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

$$229 \quad q(z_{Gw}) = k_0 \cdot e^{b(z_{Gw} - z_0)} \quad (1)$$

230 The mathematical derivation of such a lateral flow profile can also be illustrated  
231 using Darcy's law. The derivation (Equation 2) is valid under the assumptions that (1) the  
232 transmissivity feedback concept (Bishop et al., 2011) coupled with Darcian flow is  
233 applicable, (2) hydraulic gradients  $dh/dl$  [-] are time-invariant and (3) specific discharge  
234 rates are spatially homogenous. These assumptions are similar to those adopted by

235 Seibert et al. (2009), who derived an analytical expression for their suggested riparian  
 236 profile flow-concentration integration model (RIM). The specific discharge from a  
 237 hillslope with an area  $A_c$  [m<sup>2</sup>] flowing into the stream along a stream segment of  
 238 length  $L$  [m] can be estimated based on Darcy's law.  $A_c$  and  $L$  can be combined into  
 239 specific lateral contributing area  $a_c = A_c/L$  [m] (Beven and Kirkby, 1979) and  
 240 groundwater fluxes from below 1 m depth ( $z_{base} = -1$  m) are assumed to be negligible, i.e.  
 241  $q(z \leq z_{base}) \approx 0$ .

$$242 \quad q(z_{Gw}) = \frac{K \cdot dh/dl}{a_c} \cdot \int_{z_{base}}^{z_{Gw}} e^{b(z-z_0)} dz = \frac{K \cdot dh/dl}{b \cdot a_c} \cdot e^{b(z_{Gw}-z_0)} = k_0 \cdot e^{b(z_{Gw}-z_0)} \quad (2)$$

243 To reduce scatter in the groundwater-streamflow relationships, hourly discharge  
 244 records were binned at 1 cm groundwater levels intervals across the total depth profile (1  
 245 m). In addition periods with surface flow (defined as periods when measured  
 246 groundwater tables were above the soil surface, see [Table 2 Table 1](#)) were removed from  
 247 the time series of groundwater levels. These periods were removed because surface flow  
 248 violates the assumption of matrix flow when fitting flow profiles. Surface flow occurred  
 249 intermittently and mainly at sites adjacent to wetlands.

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

255 
$$q(z) = k_0 \cdot \left| \frac{z - z_{base}}{z_{base}} \right| \quad (3)$$

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

263

264 **3.2 Flow-weighted TOC concentrations and specific riparian TOC**  
265 **export rates**

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

277 In total 13% of the data were missing due to sample contamination, too little  
 278 sample volume or equipment malfunctioning. The most complete dataset was collected in  
 279 August 2009 (3% missing data) while most gaps occurred in May 2008 (25% missing  
 280 data). For most profiles more than 4 of 5 concentrations were available. Profiles with  
 281 many missing values (between 2 of 5 and 5 of 5 concentrations measured per campaign)  
 282 were located at relatively dry sites R1, R4 and R9. At a single occasion (site R4 in  
 283 September 2008) no water at all could be extracted from the profile. A missing value was  
 284 estimated by the average TOC concentration  $\overline{c_{TOC}(z^*)}$  of all measurements at the  
 285 corresponding depth  $z^*$  [m] multiplied by a scaling factor, which was calculated as the  
 286 average of the  $n$  ratios of observed TOC concentrations  $c_{TOC}(z, t)$  available at the time  $t$  of  
 287 sampling to the TOC concentrations  $\overline{c_{TOC}(z)}$  at the corresponding depths averaged  
 288 across all 9 samplings (Equation 4). For the single occasion at site R4 in September 2008  
 289 when all concentration data were missing an average concentration profile was assumed  
 290 (i.e., the scaling factor was set to 1).

$$291 \quad c_{TOC}^*(z, t) = \frac{1}{n} \cdot \sum_{i=1}^n \frac{c_{TOC}(z, t)}{c_{TOC}(z)} \cdot \overline{c_{TOC}(z^*)} \quad (4)$$

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

297 
$$\omega(z) = \frac{dq/dz}{k_0} = b \cdot e^{b(z-z_0)} \quad (5)$$

298 
$$\omega(z) = \frac{dq/dz}{k_0} = 1 \quad (6)$$

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

303 
$$c_{TOC,q}(t) = \frac{\int_{z_{base}}^{z_{Gw}} \omega(z) \cdot c_{TOC}(t, z) dz}{\int_{z_{base}}^{z_{Gw}} \omega(z) dz} \quad (7)$$

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

307 
$$l_{TOC}(t) = q(t) \cdot c_{TOC,q}(t) \cdot 3.65 \quad (8)$$

#### 308 **4. Landscape and regression analysis**

309 We performed a landscape analysis to derive riparian zone characteristics for each  
 310 site in the ROK based on a quaternary deposits map (1:100,000, Geological Survey of  
 311 Sweden, Uppsala, Sweden) (Figure 1) and on terrain indices calculated from a 5 m  
 312 resolution digital elevation model (DEM) derived from LiDAR data. The terrain indices  
 313 were computed using the open source software SAGA GIS (Conrad, 2007; Böhner et al.,  
 314 2008) and comprise specific upslope contributing area ( $a_c$ , as a surrogate for shallow

315 groundwater flow accumulation), slope ( $\tan \beta$ , as a surrogate for local drainage), and the  
316 topographic wetness index (Beven and Kirkby, 1979) (TWI, as a surrogate for shallow  
317 groundwater table position). Upslope contributing area was calculated using a multiple  
318 direction flow accumulation method ( $MD\infty$ ) (Seibert and McGlynn, 2007). Slope was  
319 computed based on the derivate of a polynomial surface that was locally fitted to the  
320 DEM (Zevenbergen and Thorne, 1987). The stream network was derived using the  
321 “Channel Network” module in SAGA GIS (Conrad, 2007; Böhner et al., 2008) and an  
322 initiation threshold area of 5 ha calculated using the  $MD\infty$  method. To account for  
323 artificially excavated ditches, several streams were set to start at the beginning of ditches  
324 that had been identified in the field even if the accumulated area was below the initiation  
325 threshold area.

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

$$332 \quad TWI = \ln\left(\frac{a_c}{\tan \beta}\right) \quad (9)$$

333 | To evaluate correlations ~~spearman-Spearman~~ rank correlation coefficients,  $r_s$ ,  
334 were computed between observed TOC concentrations and the derived terrain indices  
335 (slope, upslope contributing area and TWI). Preliminary results indicated that TWI and

336 soil depth were the major explanatory variables. For quantification, three different  
337 regression models to predict log-transformed average TOC concentrations at specified  
338 depths and landscape positions (characterized by log-transformed TWI values) were  
339 established using robust, multiple linear regression (Venables and Ripley, 2002). Robust  
340 regression methods can be effectively applied to heteroskedastic datasets including  
341 potential outliers and allow a considerably more robust estimation of parameters than  
342 standard regression methods. The three regression models were established using TOC  
343 values measured at different depths and locations in the till parts of the catchment. For  
344 each site and depth the average TOC value of all 9 sampling occasions was calculated.  
345 The tested regression models relied on TWI and soil depth as the only predictor variables.

## 346 **5. Results**

### 347 **5.1 Hydrometric observations and soil water TOC concentrations**

348 Soil water TOC concentrations as well as soil classes (organic, mineral-organic  
349 and mineral soils) were related to riparian groundwater levels and parent material (till or  
350 sediment deposits). Organic soils were located on till deposits at relatively humid or wet  
351 positions ( $-0.45 < \bar{z}_{Gw}$ ) in the RZ whereas mineral-organic soils were located on till  
352 deposits at relatively dry positions ( $\bar{z}_{Gw} < -0.45$ ) in the RZ. RZs on sediment deposits  
353 were mineral with exception of site R11. Soil water TOC concentrations varied from 3 to  
354 97 mg l<sup>-1</sup> at organic soils, from 1 to 43 mg l<sup>-1</sup> at mineral-organic and from 1 to 19 mg l<sup>-1</sup>  
355 at mineral soils (excluding site R11) ([Table 2](#)[Table 1](#)). Site R11 was excluded because it  
356 was organic peat at the transition between till and sedimentary deposits with TOC  
357 concentrations (4 – 46 mg l<sup>-1</sup>). R11 had a lower maximum concentrations compared with  
358 other organic (peat) soils and higher minimum concentrations compared with mineral

359 soils. Average concentration profiles in till soils showed generally higher TOC  
360 concentrations at sites with more superficial water tables (Figure 3), as was reported by  
361 Lyon et al. (2011). For most TOC concentration profiles in till soils, TOC concentrations  
362 also increased towards the soil surface.

363 RZs in the till parts were ordered with increasing median groundwater table  
364 positions ( $\bar{z}_{Gw}$ ) and further grouped into relatively dry mineral-organic ( $\bar{z}_{Gw} \leq -0.45m$ ),  
365 humid organic ( $-0.45 < \bar{z}_{Gw} \leq -0.15m$ ) and wet organic ( $\bar{z}_{Gw} > -0.15m$ ) soils (Figure 3).  
366 The wettest riparian till site (R8) was situated near the outlet of the Kallkällsmyren  
367 headwater wetland ( $\bar{z}_{Gw} = -0.03m$ ) while the relatively driest riparian till site (R4) was  
368 found on a gley-podzol ( $\bar{z}_{Gw} = -0.62m$ ). Relatively low groundwater levels at the  
369 mineral-organic RZs (such as R4) could in part be explained by low upslope  
370 contributions of water (indicated by the low values of lateral contributing area, [Table](#)  
371 [2Table 1](#)) and effective drainage related to terrain slope ([Table 2Table 1](#)) in conjunction  
372 with stony soils or ditching. Average TOC concentration-depth gradients (assuming  
373 exponential decrease with depth) in the till part of the catchment (Figure 3) were, with  
374 respect to different groundwater table positions, steepest at humid locations (50% less  
375 TOC per 53 cm increase in depth) followed by those at wet locations (50% less TOC per  
376 96 cm increase in depth). TOC concentration-depth profiles at the mineral-organic  
377 locations, on the other hand, showed hardly any increases in soil water TOC  
378 concentrations towards the soil surface. Temporal variability of TOC concentrations  
379 measured in soils underlain by till (expressed by the standard deviation) increased with  
380 increasing TOC concentrations and with more superficial positions in the soil profiles

381 (Figure 3). Site R9 deviated from this pattern; here average TOC concentrations slightly  
382 increased between 0.75 m to 0.45 m depth but then decreased between 0.45 m and 0.15 m  
383 depth.

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

## 398 **5.2 Flow-weighted TOC concentrations and *specifispecific*** 399 ***riparian TOC export rates***

400 For all ROK sites, except for site R14, exponentially shaped lateral flow profiles  
401 could be fit reasonably well to the binned observation data (Figure 4). This allowed  
402 derivation of corresponding depth dependant flow-weights (curved grey lines in Figure  
403 3). Flow-weighted concentrations  $c_{TOCq}$  for each site and sampling occasion (Figure 5b)

404 were computed consecutively from the continuous TOC profiles and flow-weights  
405 | (Equation 5). Specific [riparian](#) TOC export rates for a particular day,  $l_{TOC}$ , which were  
406 | calculated from specific discharge values  $q$  and flow-weighted concentrations  $c_{TOCq}$   
407 | (Equation 6), ranged from 2 to 285 kg ha<sup>-1</sup> y<sup>-1</sup> (per unit of laterally contributing area) and  
408 | varied strongly with discharge conditions (Figures 5c and 5d). It should be noted that the  
409 | specific [riparian](#) export rates were calculated on a daily basis but that their unit was  
410 | expressed as flux per year to facilitate comparison with other values published in  
411 | scientific literature (where fluxes are often calculated on a yearly basis).

412         The shapes of the distributions of average soil water TOC concentrations (Figure  
413 5a) varied because of changing soil water TOC concentrations at the 9 sampling  
414 occasions. Variations of calculated flow-weighted TOC concentrations (Figure 5b) and  
415 | specific [riparian](#) TOC export rates (Figure 5c), on the other hand, reflected the combined  
416 | effect of temporally variable TOC concentrations and variable specific discharge and  
417 | groundwater conditions (Figure 5d). In both 2008 and 2009 average values of TOC  
418 | concentrations  $c_{TOC}$  across each profile were slightly higher in August and September  
419 | compared to values in June (Figure 5a). A slight trend of average TOC concentrations  
420 | increasing from spring to fall was visible in 2008. There were only three sampling  
421 | occasions in 2009 which were too few to detect any trend.

422         It is noteworthy that changes mainly occurred at organic soils whereas mineral  
423 and mineral-organic soils exhibited only small temporal variations of TOC in absolute  
424 terms. This was also confirmed when comparing median groundwater tables to (1) flow-  
425 weighted TOC ( $c_{TOCq}$  values obtained by combining average TOC concentration profiles  
426 with median groundwater tables) and (2) potential variations of flow-weighted TOC

427 concentrations (minimum and maximum  $c_{TOC,q}$  when combining all observed TOC  
428 concentration profiles with 10<sup>th</sup> percentile and 90<sup>th</sup> percentile groundwater positions)  
429 (Figure 6a). Potential variations of flow-weighted TOC concentrations at each site  
430 increased with increasingly organic soils and increasingly shallow median groundwater  
431 positions.

### 432 **5.3 Landscape and regression analysis**

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

439 Regression models to predict average TOC concentrations at the various depths  
440 were developed for the ROK sites in the till parts of the catchment. ROK sites in the  
441 sedimentary part were not included because (1) independent field surveys had shown that  
442 most RZs in the sedimentary part were mineral gleys (Blomberg, 2009) and (2) because  
443 there were only three ROK sites in the sedimentary part. Regression fits for TOC  
444 concentrations in the till part were visually evaluated by plotting predicted against  
445 observed average TOC concentrations (Figure 7). ~~Only For simplicity, only~~ TWI was  
446 selected for regression modeling since it correlated more with observed average TOC  
447 concentrations ( $r_s = 0.67$ ) than slope and laterally contributing area ( $r_s = -0.65$  and  $r_s =$   
448  $0.58$  respectively). Since linear robust regression models were fit on logarithmically  
449 transformed variables, plots were generated for the variables at the logarithmic scale

450 (Figures 7a, c, e) and at the original scale (Figures 7b, d, f). Robust regression with depth  
451 as the only predictor (mean absolute error of 12 mg l<sup>-1</sup> TOC) variable failed to capture the  
452 variability of the average TOC concentrations (Figures 7a, b). When using only TWI as  
453 predictor variable the spectrum of average TOC concentrations was mostly covered  
454 (mean absolute error of 9 mg l<sup>-1</sup> TOC). Observed average TOC concentrations, however,  
455 scattered considerably when compared to relatively low or high predicted average TOC  
456 concentrations (Figures 7c, d), which is a sign of heteroskedasticity. Observed average  
457 TOC concentrations were best predicted by a multi-linear regression model based on  
458 depth and TWI as predictors (mean absolute error of 8 mg l<sup>-1</sup> TOC) (Figures 7e, f).  
459 Although the visual comparison of predicted against observed average TOC  
460 concentrations still revealed a lot of scatter, points were distributed more randomly  
461 around the 1:1 line with fewer apparent clusters than in the regression models based on  
462 single predictor variables.

## 463 **6. Discussion**

### 464 **6.1 Hydrometric observations and soil water TOC concentrations**

465 The range of riparian soil water TOC concentrations (from 1 mg l<sup>-1</sup> to 97 mg l<sup>-1</sup>,  
466 [Table 2](#)[Table 1](#)) measured in this study was almost twice as wide as the range of stream  
467 TOC concentrations at Krycklan (Buffam et al., 2007) and other boreal Swedish  
468 catchments (Laudon et al., 2004a; Temnerud and Bishop, 2005). The dominant sources of  
469 [stream](#) TOC in Krycklan are organic riparian soils, together with headwater wetlands and  
470 not the TOC mobilized from podsols at hillslopes draining into the RZ (Bishop et al.,  
471 1990; Laudon et al., 2011). This corresponds to findings in other catchments with high  
472 TOC levels (> 10 mg l<sup>-1</sup>) (Hinton et al., 1998; Fiebig et al., 1990; Bishop et al., 2004;

473 Dosskey and Bertsch, 1994). Differential mixing of riparian soil waters from different  
474 soil horizons as conceptualized in the RIM (Seibert et al., 2009) model is a mechanism  
475 that could explain Much of some of the observed-temporal variability of stream TOC  
476 concentrations observed in this and similar catchments as presented by other authors  
477 (Köhler et al., 2009; Bishop et al., 2004). ~~(Temmerud et al., 2007; Buffam et al., 2007) can~~  
478 ~~be related to the differential mixing of riparian soil waters from different soil horizons as~~  
479 ~~conceptualized in the RIM model.~~ For this simple model to be scalable to entire stream  
480 networks, much the considerable spatial variability in stream ~~DOC-TOC~~ would need to  
481 derive from variability in lateral exports from different types of RZs and wetlands along  
482 the stream network, ~~together with their temporally varying hydrological connectivity to~~  
483 ~~the stream.~~ And, indeed, there seemed to be sufficient spatial variation in RZ types to  
484 explain some of the spatial variation in stream TOC concentrations at Krycklan. While  
485 the existence of different RZ types does not prove the RIM concept, it is a necessary  
486 prerequisite for upscaling RIM from single hillslopes or small headwaters to a spatially  
487 distributed representation of riparian TOC exports at the catchment scale.~~the range of soil~~  
488 ~~water TOC concentrations as well as the variety of concentration profile shapes and water~~  
489 ~~table positions observed at the ROK sites (Figure 3) indicate that a single representative~~  
490 ~~lumped conceptualization of chemistry or flow pathways in the RZ (e.g. Seibert et al.,~~  
491 ~~2009; Bishop et al., 2004; Boyer et al., 1996; Köhler et al., 2009) is not appropriate for~~  
492 ~~predicting the spatio-temporal variability of stream TOC concentrations.~~ By the same  
493 token, the range of soil water TOC concentrations as well as the variety of concentration  
494 profile shapes and water table positions observed at the ROK sites (Figure 3) indicate that  
495 a single representative lumped conceptualization of chemistry or flow pathways in the RZ

496 (e.g. Seibert et al., 2009; Bishop et al., 2004; Boyer et al., 1996; Köhler et al., 2009) can  
497 be inappropriate for predicting the spatio-temporal variability of stream TOC  
498 concentrations. This appears to be true even when considering only the RZs in the till part  
499 of the Krycklan catchment (Figure 3), which one otherwise might easily and mistakenly  
500 think of as being rather homogenous when one does not have the type of spatial detail in  
501 TOC concentration measurements that could be obtained with the ROK. ~~there seemed to~~  
502 ~~be sufficient variation in the RZ to explain spatially variable stream TOC. This would be~~  
503 ~~a necessary prerequisite for developing a spatially distributed representation of RZ flow~~  
504 ~~and concentration relationships.~~

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

517 Despite the overall variability of observed concentration-depth profiles, some  
518 common patterns emerged, especially for sites located in the till parts of the catchment

519 | where the ROK instrumentation was concentrated. Here, varying soil wetness conditions  
520 | appeared to ~~control~~ influence the total amount of soil water TOC as well as the shape of  
521 | the TOC concentration profiles. Organic matter has not built up in drier, more organic-  
522 | poor (mineral) till soils to the same degree as on more humid (organic-rich) till soils,  
523 | giving lower levels of TOC and less pronounced vertical gradients in TOC (Figure 3).

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

534 |         Although we found organic soils mostly in RZs underlain by till whereas  
535 | sedimentary substrate seemingly implied mineral soils, the apparent link between parent  
536 | substrate (till or sedimentary material), soil organic matter (in this case mostly peat) and  
537 | soil water TOC has yet to be explained. Soil moisture is often not a limiting factor for  
538 | peat formation in the sedimentary parts as groundwater levels are similarly close to the  
539 | ground surface as for till sites, which suggests that varying hydraulic properties of the  
540 | substrate are probably not a sufficient explanation. Other potential factors that might  
541 | substantially influence riparian peat formation and, subsequently, riparian soil water TOC

542 concentrations include differing substrate erodibility or ionic composition of soil- or  
543 groundwater (Almendinger and Leete, 1998; Nilsson et al., 1991; Giesler et al., 1998).  
544 One additional ROK site (R13, not shown on map) was destroyed after being buried  
545 under sediments from a fourth order stream during spring flood 2008. This event  
546 highlights fluvial processes as an additional factor that might hinder the accumulation of  
547 organic matter in sedimentary RZs close to high order streams. At the 67 km<sup>2</sup> catchment  
548 scale, the presence of mineral riparian soils in the lower part of ~~the~~that catchment is  
549 another potential explanation for the observed downstream decreases in stream TOC  
550 concentrations in Krycklan (Ågren et al., 2007) that does not rely directly on the spatial  
551 distribution of wetlands.

552 Temporal variations of soil water TOC concentrations are potentially influenced  
553 by a multitude of interacting factors (Kalbitz et al., 2000) including soil temperature  
554 (Freeman et al., 2001), antecedent wetness (Köhler et al., 2009), soil frost (Haei et al.,  
555 2010), atmospheric deposition (Monteith et al., 2007) or atmospheric CO<sub>2</sub> concentrations  
556 (Freeman et al., 2004), runoff rates and combinations of these factors (Erlandsson et al.,  
557 2008). The time period of data monitored in this study was too short to disentangle the  
558 long and short term interactions of controlling factors. The temporal variability of soil  
559 water TOC concentration observed in this study (indicated by black horizontal lines,  
560 Figure 3), however, can be interpreted as a measure of the sensitivity of the soil solution  
561 response to a change of one or more external factors. Mineral and mineral-organic RZs at  
562 dry till or sedimentary locations appeared less susceptible to change over short periods  
563 than organic RZs at humid or wet till locations (Figure 5). At wet RZs, temporal changes  
564 in soil water chemistry were directly transferred to surface water systems because all soil

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565 horizons (in particular organic-rich surficial horizons) were saturated most of the time  
566 (i.e., hydrologically connected). At humid RZs, temporal changes in soil water chemistry  
567 in the transiently saturated part of the profile (delimited by grey, dotted horizontal lines,  
568 Figure 3) were only propagated to surface waters when these horizons had become  
569 saturated (i.e., hydrologically connected). It thus appeared (when neglecting potential  
570 effects of laterally expanding or shrinking discharge areas) that (1) very wet or  
571 permanently saturated RZs influenced surface water chemistry more through  
572 biogeochemical variations in the soil water while (2) humid or transiently saturated RZs  
573 influenced surface water chemistry more as a result of interplay between biogeochemical  
574 *and* hydrological variations.

## 575 **6.2 Flow-weighted TOC concentrations and specific riparian TOC** 576 **export rates**

577 The RIM concept (Winterdahl et al., 2011b; Seibert et al., 2009) was used to  
578 calculate riparian TOC export rates. RIM only accounts for riparian TOC exported by  
579 lateral subsurface flows through a single, chemostatic soil profile. Consequently, other  
580 potential flow pathways (such as groundwater recharge to the streambed or overland  
581 flow) and biogeochemical processes during transport through the RZ were not taken into  
582 account. The effect of alternative flow pathways which could partially bypass the RZ was  
583 not assessed in detail, though other studies have confirmed the strong relationship  
584 between stream flow and riparian groundwater levels (Seibert et al., 2002). However,  
585 periods of potential overland flow as indicated by groundwater levels above surface were  
586 relatively limited at most ROK sites (Table 1). This also agrees with the transmissivity  
587 feedback mechanism (Bishop, 1991; Bishop et al., 2011), which implies that even during

588 relatively high discharge conditions most runoff reaches the stream as shallow subsurface  
589 flow rather than as overland flow. That 1991 study also examined lateral versus vertical  
590 hydraulic gradients during stream events and concluded that on two till hillslopes in the  
591 vicinity of the ROK, upwelling groundwater is not a major factor as lateral subsurface  
592 flow is the dominant flow component.

593 In contrast to the transmissivity feedback mechanism (Bishop, 1991; Laudon et  
594 al., 2004b; Nyberg et al., 2001; Kendall et al., 1999; Rodhe, 1989) the two ~~other~~  
595 additional assumptions (constant hydraulic gradients and homogeneous specific  
596 discharge) that underlie the derivation of lateral flow profiles have been less intensively  
597 studied in the past. Heterogeneous land cover and topography, for instance, might  
598 influence the timing, magnitude and direction of hydraulic gradients in the RZ (Bishop,  
599 1994; Vidon and Smith, 2007; Rodhe and Seibert, 2011) as well as the spatial variability  
600 of specific discharge rates (Temnerud et al., 2007; Lyon et al., in press).

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

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

619           Overall, TOC exports from different riparian soil profiles in this study (2 – 285 kg  
620  $\text{ha}^{-1} \text{yr}^{-1}$ ), even if only sustained for a day, covered the entire range of annual stream TOC  
621 exports (3 – 250  $\text{kg ha}^{-1} \text{yr}^{-1}$ ) observed in other cold temperate or boreal regions in the  
622 world (Temnerud et al., 2007; Dawson et al., 2004; Hope et al., 1994), which highlights  
623 the considerable spatial variability of RZs within a single catchment. Organic soils at  
624 humid or wet riparian till locations clearly emerged as hot spots with a considerable  
625 [potential to control on](#) spatial and temporal variations of [riparian](#) TOC exports to streams  
626 (Figure 5 and Figure 6a). Variations of TOC exports from wet RZs were largely related to  
627 changes in soil water TOC concentrations while variations in TOC exports from humid  
628 RZs were related to changing groundwater tables ([which were correlated to streamflow](#)  
629 [conditions as illustrated by figures 4 and 5](#)) and varying soil water TOC concentrations.  
630 TOC exports from humid RZs were thus controlled by processes in the transiently  
631 saturated part of the soil column (Figure 3) [as other authors have previously explained for](#)

632 | a single site within this study area (Seibert et al., 2009; Winterdahl et al., 2011a; Bishop  
633 | et al., 1990). In this study, vertical changes of TOC concentrations with depth in the  
634 | transiently saturated zone of these humid RZs varied approximately between -1.3 and  
635 | +2.5 mgTOC l<sup>-1</sup> cm<sup>-1</sup> (determined from measurements at 15 and 30 cm depth).  
636 | Conversely, mineral-organic soils at dry till RZs or mineral soils at RZs underlain by  
637 | sediments exhibited only relatively little changes in soil water TOC related attributes  
638 | (Figure 3).

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

### 650 | **6.3 Landscape and regression analysis**

651 | The TWI appeared appropriate for predicting groundwater tables in RZs located  
652 | in both till and sedimentary parts of the catchment (Figure 6). On the other hand, the TWI  
653 | was found suitable for predicting TOC-related RZ attributes only in the till parts of the  
654 | catchment, where TOC was also considerably more variable than in the sedimentary parts

655 (Figure 7). In the till areas combining TWI and depth allowed prediction of the spatial  
656 variability of average TOC concentrations both at different riparian landscape positions  
657 and at different depths (Figure 7e and Figure 7f). This is an important step forward  
658 compared to previous studies relying on a single riparian soil profile to represent the  
659 entire RZ in a catchment (Seibert et al., 2009; Köhler et al., 2009). This opens up  
660 possibilities for representing the spatial variability of stream TOC using the RIM  
661 approach. The poor fit when using a regression model based on depth as single predictor  
662 variable further underlined the need to account for the RZ heterogeneity in the landscape.  
663 Upscaling carbon-related attributes of the RZ such as soil water TOC concentrations or  
664 soil carbon storages based on the TWI is a promising approach that is sufficiently general  
665 to be transferred to other catchments in cold climates.

666 In addition to spatially variable TOC concentrations and groundwater tables,  
667 however, the temporal variability in both lateral flows and TOC profiles must be  
668 explicitly accounted for to fully simulate dynamic riparian carbon exports. Since  
669 groundwater tables (Figure 6b) and flow pathways can be related to topography (Grabs et  
670 al., 2009; Grabs et al., 2010; Lyon et al., 2011), topographic landscape analysis is an  
671 approach for upscaling hillslope scale hydrological understanding to the landscape scale.  
672 Temporal variations of concentration depth profiles, however, also need to be addressed.  
673 We have made a start, but in contrast to water fluxes, soil solution chemistry may depend  
674 on other factors than just the water balance, so a further refinement could be to  
675 incorporate additional information including antecedent conditions, varying temperature  
676 (Köhler et al., 2009; Winterdahl et al., 2011a) or measures of biological activity. The  
677 effect of temporal variations of TOC concentrations on flow weighted TOC

678 | concentrations and specific riparian TOC export rates is strongest in organic RZs (Figures  
679 | 5b, 5c, 6a and 6c), which are also the dominant sources of stream water TOC in  
680 | Krycklan. Here, the assumption of time-invariant average TOC concentration depth  
681 | profiles (assuming average TOC concentration depth profiles) would result in  
682 | substantially underestimated ranges of flow-weighted TOC concentrations (solid error  
683 | bars in Figures 6a and 6c) compared to the potentially wide ranges assuming temporally  
684 | varying flow-weighted TOC concentrations (dotted error bars in Figures 6a and 6c).

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

## 693 | **7. Conclusions**

694 |         In this study we documented the importance of accounting for heterogeneity of  
695 | riparian zones with respect to vertical distributions of lateral flow and TOC  
696 | concentrations at the landscape scale and their combined role in regulating lateral riparian  
697 | TOC exports to streams. ~~This~~ The marked heterogeneity of riparian zones also indicated  
698 | that lumped representations of riparian zones ~~are probably inadequate~~ at the catchment  
699 | scale can be overly simplistic and highlights the need both for more distributed RZ

700 | representations and more studies of variability in the riparian zone of other landscapes.  
701 | We further showed that topographic landscape analysis can provide the necessary basis to  
702 | upscale riparian zone processes (e.g., vertical profiles of TOC and lateral flow) from the  
703 | plot to the catchment scale, which is a prerequisite for distributed RZ representations. The  
704 | usefulness of topographic indices seemed to be consistent with the idea that topography  
705 | has influenced water flows and soil moisture over millennia and thereby also soil  
706 | development and paludification. The interplay of varying lateral flow pathways and  
707 | heterogeneity of riparian zones can be expected to be similarly crucial for transport  
708 | processes involving other key parameters of water quality such as nitrate or heavy metals.  
709 | While lateral subsurface flow is the major transport pathway through the riparian zones of  
710 | Krycklan, alternative pathways such as overland flow or groundwater recharge to streams  
711 | can be more important in other catchments. Based on our analysis of hydrometric data  
712 | and TOC measurements, riparian zones along the stream network contribute differently to  
713 | the observed variability of stream water TOC. In particular, we found that organic  
714 | riparian zones with peat soils and shallow groundwater tables fluctuating within the upper  
715 | 40-50 cm of the soil column were hotspots that controlled most of the temporal  
716 | variability of riparian TOC exports to streams. The spatial variability of riparian-derived  
717 | TOC ~~exports~~ in streams, on the other hand, appeared to be influenced by ~~the an~~ upstream  
718 | mosaic of mineral, mineral-organic and organic riparian zones along ~~of~~ the stream  
719 | network.

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727  
728

729 **References**

- 730 Ågren, A., Buffam, I., Jansson, M., and Laudon, H.: Importance of seasonality and small  
731 streams for the landscape regulation of dissolved organic carbon export, *Journal of*  
732 *Geophysical Research G: Biogeosciences*, 112, G03003, doi:10.1029/2006JG000381,  
733 2007.
- 734 Almendinger, J. E., and Leete, J. H.: Peat characteristics and groundwater geochemistry  
735 of calcareous fens in the Minnesota River Basin, USA, *Biogeochemistry*, 43, 17-41,  
736 doi:10.1023/A:1005905431071, 1998.
- 737 Battin, T. J., Luysaert, S., Kaplan, L. A., Aufdenkampe, A. K., Richter, A., and Tranvik,  
738 L. J.: The boundless carbon cycle, *Nature Geoscience*, 2, 598-600, 2009.
- 739 Berggren, M., Laudon, H., and Jansson, M.: Hydrological Control of Organic Carbon  
740 Support for Bacterial Growth in Boreal Headwater Streams, *Microbial Ecology*, 57, 170-  
741 178, 2009.
- 742 Beven, K. J., and Kirkby, M. J.: A physically based, variable contributing area model of  
743 basin hydrology, *Hydrological Sciences Bulletin*, 24, 43-69,  
744 doi:10.1080/02626667909491834, 1979.
- 745 Bishop, K., Lee, Y. H., Pettersson, C., and Allard, B.: Terrestrial sources of  
746 methylmercury in surface waters: The importance of the riparian zone on the Svartberget  
747 Catchment, *Water, Air, & Soil Pollution*, 80, 435-444, doi:10.1007/bf01189693, 1995.
- 748 Bishop, K., Seibert, J., Köhler, S., and Laudon, H.: Resolving the Double Paradox of  
749 rapidly mobilized old water with highly variable responses in runoff chemistry,  
750 *Hydrological Processes*, 18, 185-189, 2004.
- 751 Bishop, K., Seibert, J., Nyberg, L., and Rodhe, A.: Water storage in a till catchment. II:  
752 Implications of transmissivity feedback for flow paths and turnover times, *Hydrological*  
753 *Processes*, 25, 3950-3959, 10.1002/hyp.8355, 2011.
- 754 Bishop, K. H., Grip, H., and O'Neill, A.: The origins of acid runoff in a hillslope during  
755 storm events, *Journal of Hydrology*, 116, 35-61, 1990.
- 756 Bishop, K. H.: Episodic increases in stream acidity, catchment flow pathways and  
757 hydrograph separation, University of Cambridge, UK, 246 pp., 1991.
- 758 Bishop, K. H.: Return flow in till hillslopes, Dep. of Forest Ecology, Swedish University  
759 of Agricultural Sciences: Final report of a project funded by the Swedish Geological  
760 Survey, Umeå, 36, 1994.
- 761 Blomberg, M.: Can a high-resolution digital elevation model predict the thickness of the  
762 organic soil layer in the riparian soil?, M.Sc., Department of Aquatic Sciences and  
763 Assessment, Swedish University of Agricultural Sciences, Uppsala, Sweden, 54 pp.,  
764 2009.

- 765 Böhner, J., Blaschke, T., and Montanarella, L.: SAGA: System for an automated  
766 geographical analysis, in: *Hamburger Beiträge zur Physischen Geographie und*  
767 *Landschaftsökologie*, edited by: Schickhoff, U., and Böhner, J., Institute of Geography,  
768 University of Hamburg, Hamburg, 2008.
- 769 Boyer, E. W., Hornberger, G. M., Bencala, K. E., and McKnight, D.: Overview of a  
770 simple model describing variation of dissolved organic carbon in an upland catchment,  
771 *Ecological Modelling*, 86, 183-188, 1996.
- 772 Buffam, I., Laudon, H., Temnerud, J., Morth, C. M., and Bishop, K.: Landscape-scale  
773 variability of acidity and dissolved organic carbon during spring flood in a boreal stream  
774 network, *J. Geophys. Res.*, 112, G01022, doi:10.1029/2006jg000218, 2007.
- 775 Cirimo, C. P., and McDonnell, J. J.: Linking the hydrologic and biogeochemical controls  
776 of nitrogen transport in near-stream zones of temperate-forested catchments: a review,  
777 *Journal of Hydrology*, 199, 88-120, 1997.
- 778 Cole, J., Prairie, Y., Caraco, N., McDowell, W., Tranvik, L., Striegl, R., Duarte, C.,  
779 Kortelainen, P., Downing, J., Middelburg, J., and Melack, J.: Plumbing the Global  
780 Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget, *Ecosystems*,  
781 10, 172-185, doi:10.1007/s10021-006-9013-8, 2007.
- 782 Conrad, O.: SAGA - Entwurf, Funktionsumfang und Anwendung eines Systems für  
783 Automatisierte Geowissenschaftliche Analysen, Ph.D., Physical Geography, University  
784 of Göttingen, Göttingen, 221 pp., 2007.
- 785 Cory, N., Laudon, H., Köhler, S., Seibert, J., and Bishop, K.: Evolution of soil solution  
786 aluminum during transport along a forested boreal hillslope, *Journal of Geophysical*  
787 *Research*, 112, G03014, doi:10.1029/2006jg000387, 2007.
- 788 Dawson, J. J. C., Billett, M. F., Hope, D., Palmer, S. M., and Deacon, C. M.: Sources and  
789 sinks of aquatic carbon in a peatland stream continuum, *Biogeochemistry*, 70, 71-92,  
790 2004.
- 791 Dosskey, M. G., and Bertsch, P. M.: Forest Sources and Pathways of Organic Matter  
792 Transport to a Blackwater Stream: A Hydrologic Approach, *Biogeochemistry*, 24, 1-19,  
793 1994.
- 794 Dunne, T., and Black, R. D.: Partial area contributions to storm runoff in a small New  
795 England watershed, *Water Resources Research*, 6, 1296-1311, 1970.
- 796 Erlandsson, M., Buffam, I., Folster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G. A.,  
797 and Bishop, K.: Thirty-five years of synchrony in the organic matter concentrations of  
798 Swedish rivers explained by variation in flow and sulphate, *Global Change Biology*, 14,  
799 1191-1198, doi:10.1111/j.1365-2486.2008.01551.x, 2008.
- 800 Esseen, P.-A., Ehnström, B., Ericson, L., and Sjöberg, K.: Boreal Forests, *Ecological*  
801 *Bulletins*, 16-47, 1997.

- 802 Fiebig, D. M., Lock, M. A., and Neal, C.: Soil water in the riparian zone as a source of  
803 carbon for a headwater stream, *Journal of Hydrology*, 116, 217-237, doi:10.1016/0022-  
804 1694(90)90124-G, 1990.
- 805 Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., and Fenner, N.: Export of  
806 organic carbon from peat soils, *Nature*, 412, 785-785, 2001.
- 807 Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M.  
808 A., Sleep, D., Hughes, S., and Hudson, J.: Export of dissolved organic carbon from  
809 peatlands under elevated carbon dioxide levels, *Nature*, 430, 195-198, 2004.
- 810 Giesler, R., Högberg, M., and Högberg, P.: Soil Chemistry and Plants in Fennoscandian  
811 Boreal Forest as Exemplified by a Local Gradient, *Ecology*, 79, 119-137, 1998.
- 812 Grabs, T., Seibert, J., Bishop, K., and Laudon, H.: Modeling spatial patterns of saturated  
813 areas: A comparison of the topographic wetness index and a dynamic distributed model,  
814 *Journal of Hydrology*, 373, 15-23, doi:10.1016/j.jhydrol.2009.03.031, 2009.
- 815 Grabs, T. J., Jencso, K. G., McGlynn, B. L., and Seibert, J.: Calculating terrain indices  
816 along streams - a new method for separating stream sides *Water Resources Research*, 46,  
817 W12536, doi:10.1029/2010WR009296, 2010.
- 818 Haei, M., Öquist, M. G., Buffam, I., Ågren, A., Blomkvist, P., Bishop, K., Ottosson  
819 Löfvenius, M., and Laudon, H.: Cold winter soils enhance dissolved organic carbon  
820 concentrations in soil and stream water, *Geophys. Res. Lett.*, 37, L08501,  
821 doi:10.1029/2010gl042821, 2010.
- 822 Hill, A.: Ground water flow paths in relation to nitrogen chemistry in the near-stream  
823 zone, *Hydrobiologia*, 206, 39-52, 1990.
- 824 Hinton, M. J., Schiff, S. L., and English, M. C.: Sources and flowpaths of dissolved  
825 organic carbon during storms in two forested watersheds of the Precambrian Shield,  
826 *Biogeochemistry*, 41, 175-197, doi:10.1023/A:1005903428956, 1998.
- 827 Hooper, R. P., Aulenbach, B. T., Burns, D. A., McDonnell, J., Freer, J., Kendall, C., and  
828 Beven, K.: Riparian control of stream-water chemistry: implications for hydrochemical  
829 basin models, in: *International Association of Hydrological Sciences, Publication*, 248,  
830 *Proceedings of the HeadWater'98 Conference*, Mean/Merano, Italy, 451-458, 1998.
- 831 Hope, D., Billett, M. F., and Cresser, M. S.: A review of the export of carbon in river  
832 water: Fluxes and processes, *Environmental Pollution*, 84, 301-324, doi:10.1016/0269-  
833 7491(94)90142-2, 1994.
- 834 Hruška, J., Köhler, S., Laudon, H., and Bishop, K.: Is a universal model of organic  
835 acidity possible: Comparison of the acid/base properties of dissolved organic carbon in  
836 the boreal and temperate zones, *Environmental Science & Technology*, 37, 1726-1730,  
837 doi: 10.1021/es0201552, 2003.

- 838 Jansson, R., Laudon, H., Johansson, E., and Augspurger, C.: The importance of  
839 groundwater discharge for plant species number in riparian zones, *Ecology*, 88, 131-139,  
840 doi:10.1890/0012-9658(2007)88[131:TIOGDF]2.0.CO;2, 2007.
- 841 Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E., and  
842 Marshall, L. A.: Hydrologic connectivity between landscapes and streams: Transferring  
843 reach-and plot-scale understanding to the catchment scale, *Water Resources Research*,  
844 45, W04428, doi:10.1029/2008wr007225, 2009.
- 845 Kalbitz, K., Solinger, S., Park, J. H., Michalzik, B., and Matzner, E.: Controls on the  
846 dynamics of dissolved organic matter in soils: a review, *Soil Science*, 165, 277-304,  
847 2000.
- 848 Kendall, K. A., Shanley, J. B., and McDonnell, J. J.: A hydrometric and geochemical  
849 approach to test the transmissivity feedback hypothesis during snowmelt, *Journal of*  
850 *Hydrology*(Amsterdam), 219, 188-205, 1999.
- 851 Kirchner, J. W.: A double paradox in catchment hydrology and geochemistry,  
852 *Hydrological Processes*, 17, 871-874, 2003.
- 853 Klaminder, J., Bindler, R., Laudon, H., Bishop, K., Emteryd, O., and Renberg, I.: Flux  
854 Rates of Atmospheric Lead Pollution within Soils of a Small Catchment in Northern  
855 Sweden and Their Implications for Future Stream Water Quality, *Environmental Science*  
856 *& Technology*, 40, 4639-4645, doi:10.1021/es0520666, 2006.
- 857 Köhler, S., Buffam, I., Jonsson, A., and Bishop, K.: Photochemical and microbial  
858 processing of stream and soil water dissolved organic matter in a boreal forested  
859 catchment in northern Sweden, *Aquatic Sciences - Research Across Boundaries*, 64, 269-  
860 281, doi:10.1007/s00027-002-8071-z, 2002.
- 861 Köhler, S., Buffam, I., Laudon, H., and Bishop, K.: Intra- and interannual variability of  
862 total organic carbon in two contrasting boreal landscape elements., *Geophysical*  
863 *Research-Biogeosciences*, 113, G03012, G03012, doi:10.1029/2007JG000629, 2008.
- 864 Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H., and Laudon, H.: Dynamics of stream  
865 water TOC concentrations in a boreal headwater catchment: Controlling factors and  
866 implications for climate scenarios, *Journal of Hydrology*, 373, 44-56,  
867 doi:10.1016/j.jhydrol.2009.04.012, 2009.
- 868 Laudon, H., Köhler, S., and Buffam, I.: Seasonal TOC export from seven boreal  
869 catchments in northern Sweden, *Aquatic Sciences-Research Across Boundaries*, 66, 223-  
870 230, 2004a.
- 871 Laudon, H., Seibert, J., Köhler, S., and Bishop, K.: Hydrological flow paths during  
872 snowmelt: congruence between hydrometric measurements and oxygen 18 in meltwater,  
873 soil water, and runoff, *Water Resources Research*, 40, W03102, 2004b.

- 874 Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and  
875 Köhler, S.: Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal  
876 Streams: The Role of Processes, Connectivity, and Scaling, *Ecosystems*, 14, 880-893,  
877 doi:10.1007/s10021-011-9452-8, 2011.
- 878 Lyon, S. W., Grabs, T., Laudon, H., Bishop, K. H., and Seibert, J.: Variability of  
879 groundwater levels and total organic carbon in the riparian zone of a boreal catchment, *J.*  
880 *Geophys. Res.*, 116, G01020, doi:10.1029/2010JG001452, 2011.
- 881 Lyon, S. W., Nathanson, M., Spans, A., Grabs, T., Laudon, H., Temnerud, J., Bishop, K.  
882 H., and Seibert, J.: Specific discharge variability in a boreal landscape, *Water Resources*  
883 *Research*, in press.
- 884 McClain, M. E., Boyer, E. W., Dent, C. L., Gergel, S. E., Grimm, N. B., Groffman, P. M.,  
885 Hart, S. C., Judson, W. H., Johnston, C. A., Mayorga, E., McDowell, W. H., and Pinay,  
886 G.: Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and  
887 Aquatic Ecosystems, *Ecosystems*, 6, 301-312, 2003.
- 888 McGlynn, B. L., and McDonnell, J. J.: Quantifying the relative contributions of riparian  
889 and hillslope zones to catchment runoff, *Water Resources Research*, 39, 1310,  
890 doi:10.1029/2003wr002091, 2003.
- 891 McGlynn, B. L., and Seibert, J.: Distributed assessment of contributing area and riparian  
892 buffering along stream networks, *Water Resources Research*, 39, 1082, 2003.
- 893 Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Hogasen, T.,  
894 Wilander, A., Skjelkvale, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopacek, J.,  
895 and Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric  
896 deposition chemistry, *Nature*, 450, 537-540, 2007.
- 897 Nilsson, C., Grelsson, G., Dynesius, M., Johansson, M. E., and Sperens, U.: Small Rivers  
898 Behave Like Large Rivers: Effects of Postglacial History on Plant Species Richness  
899 Along Riverbanks, *Journal of Biogeography*, 18, 533-541, 1991.
- 900 Nyberg, L., Stähli, M., Mellander, P.-E., and Bishop, K. H.: Soil frost effects on soil  
901 water and runoff dynamics along a boreal forest transect: 1. Field investigations,  
902 *Hydrological Processes*, 15, 909-926, doi:10.1002/hyp.256, 2001.
- 903 Ocampo, C. J., Sivapalan, M., and Oldham, C.: Hydrological connectivity of upland-  
904 riparian zones in agricultural catchments: Implications for runoff generation and nitrate  
905 transport, *Journal of Hydrology*, 331, 643-658, doi:10.1016/j.jhydrol.2006.06.010, 2006.
- 906 Öquist, M. G., Wallin, M., Seibert, J., Bishop, K., and Laudon, H.: Dissolved Inorganic  
907 Carbon Export Across the Soil/Stream Interface and Its Fate in a Boreal Headwater  
908 Stream, *Environmental Science & Technology*, 43, 7364-7369, doi: 10.1021/es900416h,  
909 2009.

- 910 Rodhe, A.: On the generation of stream runoff in till soils, *Nordic Hydrology*, 20, 1-8,  
911 1989.
- 912 Rodhe, A., and Seibert, J.: Groundwater dynamics in a till hillslope: flow directions,  
913 gradients and delay, *Hydrological Processes*, 25, 1899-1909, doi:10.1002/hyp.7946,  
914 2011.
- 915 Seibert, J., Bishop, K., Rodhe, A., and McDonnell, J.: Groundwater dynamics along a  
916 hillslope: A test of the steady state hypothesis, *Water Resources Research*, 39, 101029,  
917 doi:10.1029/2002WR001404, 2002.
- 918 Seibert, J., and McGlynn, B. L.: A new triangular multiple flow direction algorithm for  
919 computing upslope areas from gridded digital elevation models, *Water Resources*  
920 *Research*, 43, W04501, doi:10.1029/2006WR005128, 2007.
- 921 Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., and Bishop, K.: Linking  
922 soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration  
923 Model, *Hydrological Earth System Sciences*, 13, 2287-2297, doi:10.5194/hess-13-2287-  
924 2009, 2009.
- 925 Serrano, I., Buffam, I., Palm, D., Brännäs, E., and Laudon, H.: Thresholds for survival of  
926 brown trout during the spring flood acid pulse in streams high in dissolved organic  
927 carbon, *Transactions of the American Fisheries Society*, 137, 1363-1377,  
928 doi:10.1577/T07-069.1, 2008.
- 929 Shafer, M. M., Overdier, J. T., Hurley, J. P., Armstrong, D., and Webb, D.: The influence  
930 of dissolved organic carbon, suspended particulates, and hydrology on the concentration,  
931 partitioning and variability of trace metals in two contrasting Wisconsin watersheds  
932 (U.S.A.), *Chemical Geology*, 136, 71-97, doi:10.1016/S0009-2541(96)00139-8, 1997.
- 933 Temnerud, J., and Bishop, K.: Spatial variation of streamwater chemistry in two Swedish  
934 boreal catchments: Implications for environmental assessment, *Environmental Science &*  
935 *Technology*, 39, 1463-1469, 2005.
- 936 Temnerud, J., Seibert, J., Jansson, M., and Bishop, K.: Spatial variation in discharge and  
937 concentrations of organic carbon in a catchment network of boreal streams in northern  
938 Sweden, *Journal of Hydrology*, 342, 72-87, doi:10.1016/j.jhydrol.2007.05.015, 2007.
- 939 Venables, W. N., and Ripley, B. D.: *Modern Applied Statistics with S*, Fourth ed.,  
940 Springer, New York, 2002.
- 941 Vidon, P., and Smith, A. P.: Upland controls on the hydrological functioning of riparian  
942 zones in glacial till valleys of the Midwest, *Journal of the American Water Resources*  
943 *Association*, 43, 1524-1539, 2007.
- 944 Wallin, M., Buffam, I., Öquist, M., Laudon, H., and Bishop, K.: Temporal and spatial  
945 variability of dissolved inorganic carbon in a boreal stream network: Concentrations and  
946 downstream fluxes, *J. Geophys. Res.*, 115, G02014, doi:10.1029/2009jg001100, 2010.

- 947 Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., and Bishop, K.: Riparian  
948 soil temperature modification of the relationship between flow and dissolved organic  
949 carbon concentration in a boreal stream, *Water Resour. Res.*, 47, W08532,  
950 doi:10.1029/2010WR010235, 2011a.
- 951 Winterdahl, M., Temnerud, J., Futter, M., Löfgren, S., Moldan, F., and Bishop, K.:  
952 Riparian Zone Influence on Stream Water Dissolved Organic Carbon Concentrations at  
953 the Swedish Integrated Monitoring Sites, *AMBIO: A Journal of the Human Environment*,  
954 40, 920-930, doi:10.1007/s13280-011-0199-4, 2011b.
- 955 Zackrisson, O.: Influence of Forest Fires on the North Swedish Boreal Forest, *Oikos*, 29,  
956 22-32, 1977.
- 957 Zevenbergen, L. W., and Thorne, C. R.: Quantitative analysis of land surface topography,  
958 *Earth Surface Processes and Landforms*, 12, 47-56, doi:10.1002/esp.3290120107, 1987.
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962 **Table 1:** Site characteristics (minimum and maximum in each column are shown as bold numbers).

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

**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

964 **Figure texts**

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**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.

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**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).

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**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  $\omega$  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  $\pm 1$  standard deviation) and the range of temporal variability of groundwater positions is indicated by dotted grey horizontal lines (10<sup>th</sup> and 90<sup>th</sup> 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 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> row respectively). The lower 4<sup>th</sup> row contains sites underlain by sediment deposits.

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**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 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> row respectively). The lower 4<sup>th</sup> row contains sites underlain by glaciofluvial sediment deposits.

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**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.

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1009 **Figure 6:** Links between median groundwater positions  $z_{GW}$ , median flow-weighted TOC profile  
1010 | concentrations ( $c_{TOC,q}$ ) and the topographic wetness index (TWI). In the **upper-left** plot (a) median flow-  
1011 | weighted  $c_{TOC,q}$  values (from 9 sampling occasions in 2008-2009) are plotted against median  $z_{GW}$  values.  
1012 | The middle plot (b) compares median  $z_{GW}$  values against the TWI whereas the **lower-right** plot (c) compares  
1013 | median  $c_{TOC,q}$  values against the TWI. Vertical error bars show the 10<sup>th</sup> and 90<sup>th</sup> percentile groundwater  
1014 | positions (b) respectively the potential range of flow-weighted TOC concentrations (a and c) assuming  
1015 | average profile concentrations (solid lines) or changing profile concentrations (dotted lines). Circles  
1016 | represent sites located in the till parts and triangles represent sites located in the sedimentary part of the  
1017 | catchment. Organic sites are colored black, mineral sites are white and mineral-organic sites are grey. Site  
1018 | numbers are plotted next to the circles and triangles. Only site numbers are shown and “R” prefixes used in  
1019 | the text (preceding the site digits) were omitted for better readability.

1020

1021 **Figure 7:** Modeled versus predicted average TOC concentrations (empty circles) for 10 riparian monitoring  
1022 | sites and 5 different depths (15, 30, 45, 60 and 75 cm below the surface) in the till part of the catchment. In  
1023 | the upper row log-transformed TOC concentrations are shown. Three regression models for TOC were  
1024 | tested using depth (first column), TWI (middle column) as well as using both depth and TWI as predictors  
1025 | (right column).

1026

1027 **Figure 8:** Temporal variability as function of riparian zone wetness for different quantities (schematic  
1028 | figure).

1029