

# Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments

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## Abstract

Boreal regions store most of the global terrestrial carbon, which can be transferred as dissolved organic carbon (DOC) to inland waters with implications for both aquatic ecology and carbon budgets. Headwater riparian zones (RZ) are important sources of DOC, and often just a narrow 'dominant source layer' (DSL) within the riparian profile is responsible for most of the DOC export. Two important questions arise: how long boreal RZ could sustain lateral DOC fluxes as the sole source of exported carbon and how its hydromorphological variability influences this role. We estimate theoretical turnover times by comparing carbon pools and lateral exports in the DSL of 13 riparian profiles distributed over a 69 km<sup>2</sup> catchment in northern Sweden. The thickness of the DSL was  $36 \pm 18$  (average  $\pm$  SD) cm. Thus, only about one-third of the 1-m-deep riparian profile contributed 90% of the lateral DOC flux. The 13 RZ exported  $8.7 \pm 6.5$  g C m<sup>-2</sup> year<sup>-1</sup>, covering the whole range of boreal stream DOC exports. The variation could be explained by local hydromorphological characteristics including RZ width ( $R^2 = 0.90$ ). The estimated theoretical turnover times were hundreds to a few thousands of years, that is there is a potential long-lasting supply of DOC. Estimates of net ecosystem production in the RZ suggest that lateral fluxes, including both organic and inorganic C, could be maintained without drawing down the riparian pools. This was supported by measurements of stream DO<sup>14</sup>C that indicated modern carbon as the predominant fraction exported, including streams disturbed by ditching. The transfer of DOC into boreal inland waters from new and old carbon sources has a major influence on surface water quality and global carbon balances. This study highlights the importance of local variations in RZ hydromorphology and DSL extent for future DOC fluxes under a changing climate.

**Keywords:** carbon 14, carbon cycling, climate change, ditching, hydromorphology, isotopic measurement, organic matter, primary production, total organic carbon, turnover time

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## Introduction

Boreal peatlands and permafrost regions store most of the world's terrestrial carbon (Post *et al.*, 1982; Gorham, 1991; Tarnocai *et al.*, 2009) and export large amounts of organic carbon to inland waters (Battin *et al.*, 2009). In the aquatic environment, dissolved organic carbon (DOC) plays a key role in food web interactions and biodiversity (Williamson *et al.*, 1999; Karlsson *et al.*, 2012), water acidification status (Erlandsson *et al.*, 2011; Valinia *et al.*, 2014), and mobilization of toxic metals and organic pollutants (Shafer *et al.*, 1997; Dawson *et al.*, 2009). DOC also interferes in water treatment processes (Lavonen *et al.*, 2013). A large proportion of the

terrestrial DOC inputs to inland waters is lost by emission to the atmosphere as carbon dioxide (CO<sub>2</sub>) or buried in aquatic sediments before reaching the oceans (Cole *et al.*, 2007; Aufdenkampe *et al.*, 2011). This implies that headwaters have higher DOC concentrations and exports than downstream waters (Wolock *et al.*, 1997; Ågren *et al.*, 2007). The influence of small headwater catchments on large biogeochemical cycles and in the geochemistry of larger aquatic networks is widely recognized (Bormann & Likens, 1967; Peterson *et al.*, 2001; Temnerud & Bishop, 2005).

The link between the terrestrial and the aquatic environments in boreal headwaters is dominated by organic matter-rich riparian zones (RZ) and wetlands. The potential for organic matter accumulation in RZ is caused by both high productivity due to high nutrient availability (Jansson *et al.*, 2007) and low degradation

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limited by shallow groundwater tables that create anoxic conditions. The result is a transition in the soil configuration from mineral podzols in upslope areas to organic histosols in the near-stream RZ, typical of boreal regions (Chesworth, 2008). This pattern is not homogeneous because the RZ extent is spatially variable depending on the local hydromorphology (Grabs *et al.*, 2012; Kuglerová *et al.*, 2014). Constraining the size of the RZ and its contribution to stream DOC exports is important to shed light on catchment biogeochemical processes and the global carbon cycle because the riparian zone is often the main source of DOC entering streams independent of upslope conditions (Fiebig *et al.*, 1990; Dosskey & Bertsch, 1994; Bishop *et al.*, 1995; Hinton *et al.*, 1998; Fölster, 2001; Köhler *et al.*, 2009; Löfgren & Zetterberg, 2011; Strohmeier *et al.*, 2013; Dick *et al.*, 2014). The apparent disconnection between RZ and upslopes is revealed by a typical low vertical transfer of carbon from upland topsoils (Fröberg *et al.*, 2006; Sierra *et al.*, 2013), which suggests that only a limited amount of carbon from upslope makes it to the RZ. Supporting this idea, comparisons among upslope, RZ, and stream DOC quality show similar organic matter composition in RZ and stream in contrast to upslope (Sanderman *et al.*, 2009; Maehder, 2012).

Lateral DOC fluxes from RZ to streams are limited to only a fraction of the total RZ volume. The exponential decrease in hydraulic conductivity with depth (Bishop, 1991; Nyberg, 1995) implies that lateral fluxes are often shallow and converge to a relatively narrow layer in the riparian soil profile (Schiff *et al.*, 1998). This is a common phenomenon in till soils worldwide (McDonnell *et al.*, 1998; McGlynn & McDonnell, 2003b; Seibert *et al.*, 2003) and dominant in the boreal region (Rodhe, 1989; Bishop *et al.*, 2011). If DOC concentrations are constant or decline with depth, most lateral DOC fluxes occur within this layer of predominant flowpaths (Hinton *et al.*, 1998). We termed this layer in the RZ profile as the 'dominant source layer' (DSL) and attempt for the first time to quantify its spatial extent.

Some authors have defined the RZ as a near-infinite DOC source into streams (McGlynn & McDonnell, 2003a; Sanderman *et al.*, 2009). The concept that the majority of DOC in run-off originates from a narrow RZ layer (the DSL) leads to the question of, if not infinitely, how long this source can possibly sustain the current lateral DOC fluxes. Typically, stream DOC exports in boreal catchments vary between 2 and 10 g m<sup>-2</sup> year<sup>-1</sup> (Ågren *et al.*, 2007). Furthermore, RZ are spatially variable. This raises the additional question as to how the RZ variability influences its role as contributor of DOC to stream run-off. Both questions are relevant in the context of climate change: forecasted warmer soils and wetter conditions in boreal regions

will tend to increase DOC fluxes (Futter *et al.*, 2009; Köhler *et al.*, 2009; Larsen *et al.*, 2011), although some studies have shown long-term declines (Striegl *et al.*, 2005). Additionally, anthropogenically disturbed sites by drainage may affect RZ oxygenation and thus DOC fluxes (Åström *et al.*, 2001). This can cause a decline in the riparian carbon pools (Moore *et al.*, 2013), which can be revealed by isotopic measurements of carbon age that help to identify sources and processes controlling DOC mobilization (Schiff *et al.*, 1997).

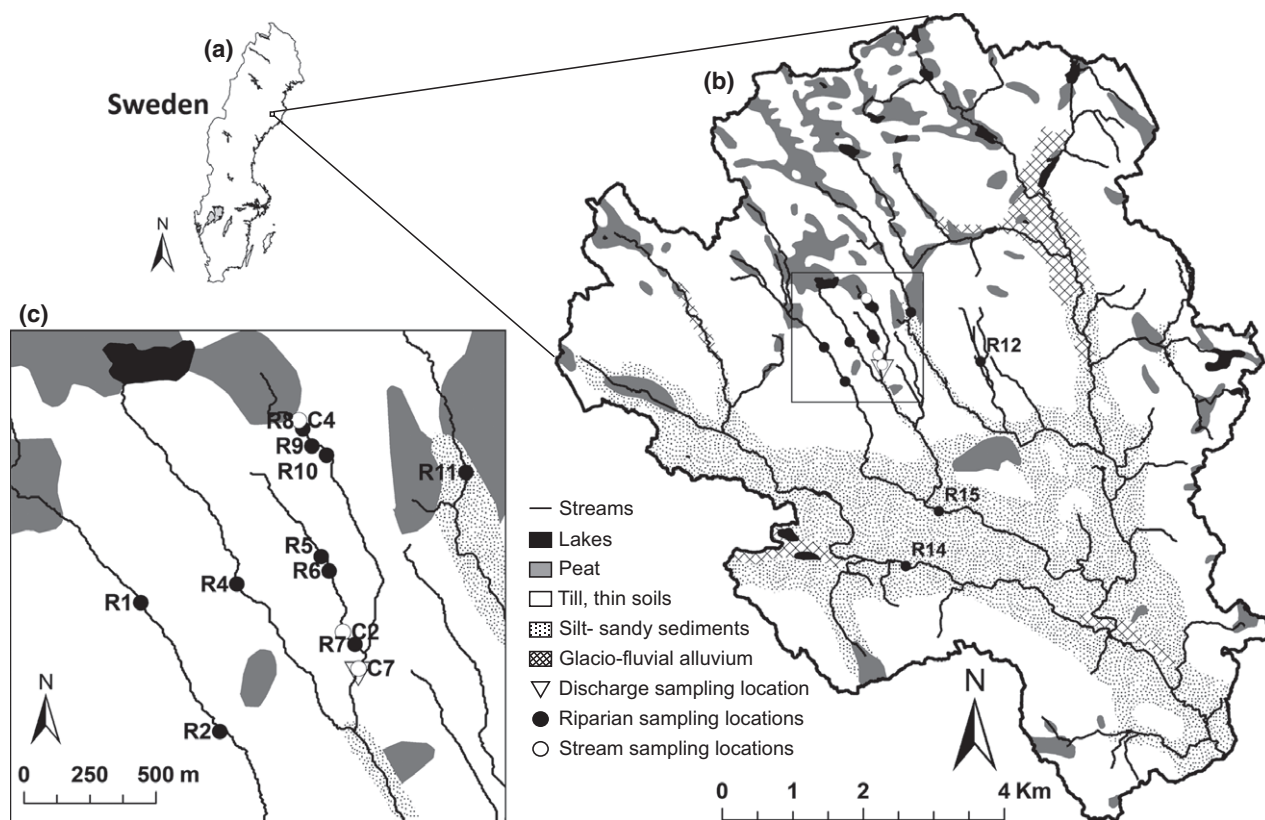
This study estimates the theoretical turnover time of DOC in 13 riparian profiles distributed over a 69 km<sup>2</sup> boreal catchment in northern Sweden by comparing the size of the potential sources in relation to the potential exports from the DSL. Therefore, the main objective was to quantitatively evaluate the timescale of riparian carbon pools' potential to sustain lateral DOC fluxes. The studied profiles cover a wide range in wetness conditions and soil types, so we also aimed to investigate the architecture of these RZ with a focus on how physical variables control spatial differences in lateral DOC fluxes and carbon pools. Finally, measurements of DO<sup>14</sup>C in stream waters were used to distinguish the mobilization of recently produced carbon relative to old carbon from the riparian pools. Thus, this study evaluates the potential from both new and old carbon sources in RZ to be transferred as DOC into surface waters in boreal catchments.

## Materials and methods

### Overview and approach

Thirteen RZ located in a boreal catchment (Fig. 1) were assessed for theoretical turnover times of DOC using field observations during the two hydrologically ordinary years 2008 (344 mm) and 2009 (326 mm), that is annual run-offs were close to the long-term mean 1981–2012 (324 mm). Theoretical turnover times were defined and calculated as the time period over which current annual lateral DOC export rates could theoretically be sustained if all carbon in the riparian pools was eventually available for mobilization. We assume that all carbon originates in the RZ with a negligible contribution from the upslope area. This approach is appropriate to test the plausibility of whether the RZ alone can sustain DOC exports.

The riparian flow-concentration integration model (RIM) approach (Bishop *et al.*, 2004; Seibert *et al.*, 2009) was used to estimate lateral DOC fluxes. RIM can be either used as a model at the catchment scale to explain stream chemical variability (Winterdahl *et al.*, 2011a,b) or, as in this study, at the soil profile scale to quantify lateral fluxes from RZ to streams. This has been shown for DOC (Köhler *et al.*, 2009; Ågren *et al.*, 2010), dissolved inorganic carbon (DIC) (Öquist *et al.*, 2009), aluminium (Cory *et al.*, 2007), nitrogen (Petroni *et al.*, 2007), lead (Klaminder *et al.*, 2006), methylmercury (Bishop *et al.*,



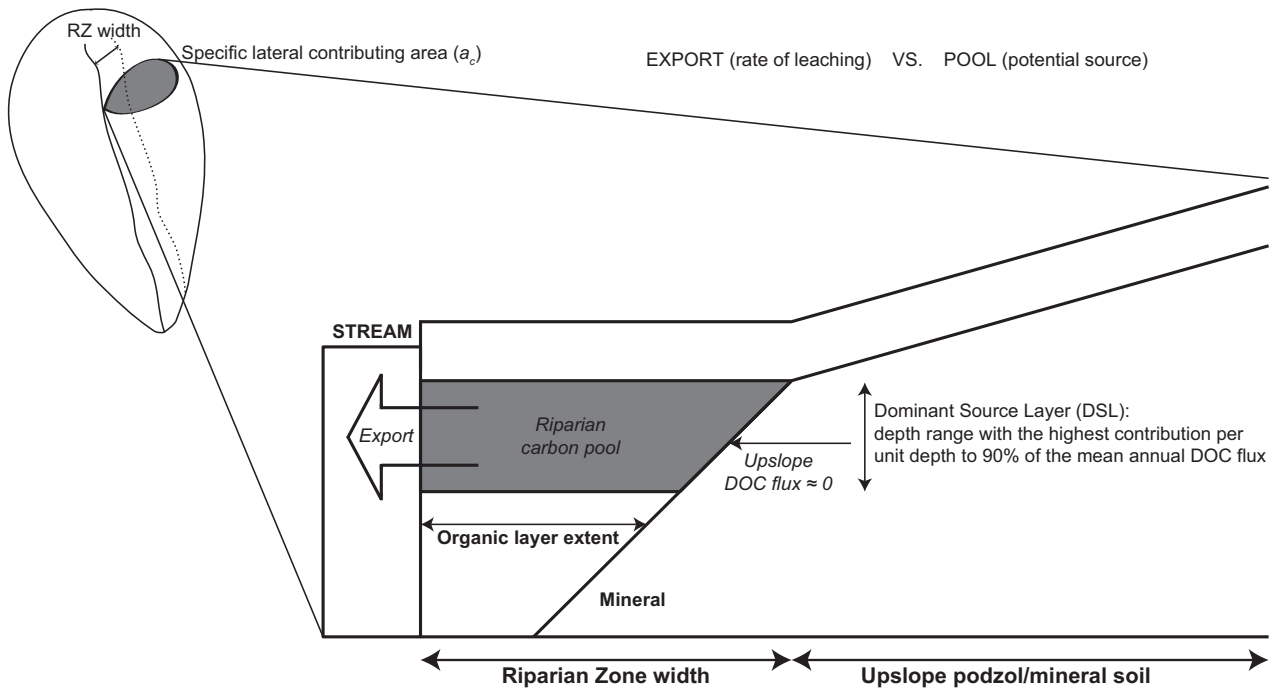
**Fig. 1** Location of the Krycklan catchment ( $64^{\circ}12'N$   $19^{\circ}52'E$ ) within Sweden (a). In (b): shape of the Krycklan catchment. In (c): zoom to the highlighted square in (b).

1995), and base cations (Ledesma *et al.*, 2013). The combination of lateral water flows and soil water chemistry in the RZ is the basis of the method, and it is analogous to the way in which riverine fluxes are estimated. Under the assumption that all water passes the RZ before discharging into the stream, the relationship between observed groundwater tables in the RZ and specific discharge in the stream allows the calculation of a potential lateral flow profile. Lateral flow is assumed to occur only in saturated soil layers, that is below the groundwater table. Chemical concentrations of solutes, measured at different depths in the RZ, are interpolated both in space and in time to generate time series of concentration profiles. Concentration profiles are then multiplied by the potential lateral flow profile to estimate riparian lateral fluxes. The step size for numerical integration in space was 0.1 cm. The RIM calculations of DOC fluxes for each of the 13 riparian profiles studied identified a 'dominant source layer' (DSL). The DSL was defined as the depth range with the highest contribution per unit depth to 90% of the mean annual DOC flux. A conceptual diagram of the approach is shown in Fig. 2, and an overview of all symbols and abbreviations can be found in Table S1.

#### Catchment characterization

The Krycklan Catchment Study (KCS,  $64^{\circ} 12'N$   $19^{\circ} 52'E$ ) includes the upper  $69 \text{ km}^2$  of the Krycklan catchment ( $121 \text{ km}^2$ ), which is located approximately 50 km north-west

from the Swedish city of Umeå and 60 km west from the Baltic Sea (Fig. 1). KCS comprises 18 partially nested subcatchments that have been intensively monitored since 2002 (Laudon *et al.*, 2013), including the Svartberget catchment ( $0.47 \text{ km}^2$ ) that has been studied for over 30 years. The area is characterized by a subarctic climate with a mean temperature of  $1.8^{\circ}\text{C}$  and averages in January and June of  $-9.5^{\circ}\text{C}$  and  $11.9^{\circ}\text{C}$ , respectively (1981–2012). The catchment receives a mean precipitation of  $632 \text{ mm year}^{-1}$  (1981–2012), half of which falls as snow. Approximately 50% of the water input contributes to run-off and 50% is lost by evapotranspiration. The 4- to 6-week period of spring flood (April–May) contributes between 40% and 60% of the total annual run-off. Forests dominate the land use (87%), with lower proportions of peat-dominated wetlands (9%), arable lands (3%), and lakes (1%). Tree volume is dominated by boreal stands of scots pine (*Pinus sylvestris*, 63%), common in dry upslope podzols, and Norway spruce (*Picea abies*, 27%), common in wetter low-lying areas towards histosol RZ, where deciduous stands (10%) of mainly birch (*Betula* spp.) are found. *Sphagnum* spp. mosses and *Vaccinium* spp. are common in peat-dominated areas including wetlands and RZ. A differentiation regarding soil deposits is usually made between upper parts of the KCS underlain by Quaternary deposits of glacial till and downstream parts underlain by glacio-fluvial sediments dominated by silt deposits formed by a postglacial river delta (Fig. 1). These two areas will be named hereafter as till and sediment.



**Fig. 2** Conceptual diagram of the approach used to estimate the theoretical turnover time of dissolved organic carbon (DOC) in the riparian profiles. Within the dominant source layer (DSL), the total mass of carbon in the riparian pool is compared with the total export rate of DOC. The DOC input from upslope areas is assumed to be negligible.

Most of the headwater streams were straightened and deepened, or they are a consequence of ditching occurring 50 to 150 years ago. These practices were common to improve drainage and thereby forest productivity in large areas across Fennoscandia.

#### Riparian Observatory in Krycklan (ROK)

The Riparian Observatory in Krycklan (ROK, Grabs *et al.*, 2012; Ledesma *et al.*, 2013) was established in 2007 and includes 13 instrumented riparian soil profiles, also referred as sites hereafter (Fig. 1). Each site consists of two ceramic cup suction lysimeters (nominal filter pore size  $1 \pm 0.1 \mu\text{m}$ ) at each of five equally distributed soil depths (15, 30, 45, 60, and 75 cm) and a perforated PVC tube equipped with an automatic waterlogging device. Thus, soil water chemistry and groundwater levels can be monitored. Ten of the profiles were located in the till area of the catchment, two were in the sediment area, and one was in the transition between till and sediment areas (Fig. 1, Table 1). Ground vegetation in the sites is dominated by *Sphagnum* spp. and *Vaccinium* spp. (Table S2) and trees by Norway spruce. The ROK sites were classified following Grabs *et al.* (2012) and Ledesma *et al.* (2013) according to parent material and median groundwater table in four classes: (i) till-dry, (ii) till-humid, (iii) till-wet, and (iv) sediment (Table 1). Note that site R11 located in the transition between till and sediment was classified here as till-wet because of shallow groundwater tables and relatively high carbon content for sediment sites.

#### Discharge measurements

To date, there is one reliable continuous long-term discharge measurement location within the Krycklan catchment, with uncertainty estimated to be below 5% (Laudon *et al.*, 2007). Specific discharge is assumed to be the same all over the catchment and therefore commonly used to calculate fluxes (Ågren *et al.*, 2007; Wallin *et al.*, 2010; Ledesma *et al.*, 2013). The discharge measurement point is located at the outlet of stream site C7 (Fig. 1) and consists of a 90° V-notch weir within a heated hut. Established stage-discharge rating curves are used to calculate daily discharge values from the water levels monitored at the weir. The discharge time series includes the two years of this study.

#### Lateral water and DOC fluxes and DSL size

Riparian soil water samples were manually collected from suction lysimeters at the 13 ROK sites on 8 field campaigns (June to October in 2008 and June to September in 2009) using acid-washed Milli-Q rinsed Duran glass bottles (Grabs *et al.*, 2012). The samples were kept dark and cool prior to being subsampled within 24 h and frozen for future chemical analysis. Soil water organic carbon was measured as total organic carbon (TOC) by a Shimadzu TOC-5000 using catalytic combustion, although the water passed through the 1- $\mu\text{m}$  pore-size lysimeter when being collected. A total of 90 samples collected during the summer of 2013 from sites R2, R5, and R10 (Fig. 1; Table 1) were analysed for both TOC and

**Table 1** Characteristics of the 13 riparian profiles including median modelled groundwater table ( $z_{Gw}$ ) (2008–2009), mean soil organic carbon content (SOCC), topographic wetness index (TWI), specific lateral contributing area ( $a_c$ ), and riparian zone width (RZ width)

Site	Parent material	Class	Median $z_{Gw}$ (cm)	SOCC (%)	TWI	$a_c$ (m)	RZ width (m)
R4	Till	Till-dry	−59	4	4.2	8.2	3.3
R12	Till	Till-dry	−62	5	3.6	2.5	2.3
R1	Till	Till-dry	−53	17	8.0	157.2	12.0
R9	Till	Till-dry	−50	14	4.7	16.3	3.1
R7	Till	Till-humid	−48	50	6.0	27.4	38.8
R10	Till	Till-humid	−27	52	7.7	114.1	16.3
R6	Till	Till-humid	−17	38	8.3	230.6	39.0
R5	Till	Till-humid	−17	38	5.6	20.0	17.1
R2	Till	Till-wet	−13	45	11.1	1480.9	40.4
R8	Till	Till-wet	−8	52	8.6	181.4	90.6
R11	Till-Sediment	Till-wet	−6	32	9.1	127.3	17.0
R15	Sediment	Sediment	−58	2	4.9	5.3	10.0
R14	Sediment	Sediment	−2	3	9.2	53.0	2.0

DOC (after 0.45  $\mu\text{m}$  filtration). No statistically significant difference between pairs was observed using Wilcoxon test for nonparametric data (Fig. S3). This suggests that TOC is effectively equivalent to DOC in riparian soil water, as it was previously shown for the streams in Krycklan and other Swedish catchments (Laudon *et al.*, 2004; Ågren *et al.*, 2007). Therefore, the term DOC is used here.

The total number of samples available for this study was 725, and the total number of campaign concentrations (mean of the lysimeter pairs) was 458, that is 88% of the total 520 possible concentrations (eight campaigns, 13 sites, five depths). Thus, campaign concentrations are the result of averaging the measurements of the two lysimeters at a single depth and time. Missing values of a single lysimeter were estimated by multiplying its replicate by the average of the ratios of both lysimeter measures for the other campaigns. When both lysimeter measures were missing, an average of the rest of the campaigns was used (Grabs *et al.*, 2012).

Campaign concentrations were linearly interpolated in time (2008–2009) to obtain daily time series of DOC concentrations at each depth and site. Despite relatively few sampling occasions, these covered the period of the year when riparian DOC concentrations vary, usually from lowest in spring to highest in early autumn (Clark *et al.*, 2005; Grabs *et al.*, 2012). Subsequently, DOC concentrations were linearly interpolated in space assuming a 1-m riparian soil depth to obtain daily continuous DOC concentration ( $C_{DOC}$ ,  $\text{mg l}^{-1}$ ) profiles for each site. Concentrations between 15 cm and the surface were assumed to be constant and equal to the concentration at 15 cm. Analogously, concentrations between 75 cm and 100 cm were assumed to be equal to the concentration at 75 cm.

Hourly groundwater tables ( $obs\ z_{Gw}$ , cm) measured at the automatic loggers of the 13 ROK sites were fit to corresponding specific discharge ( $q$ ,  $\text{l m}^{-2}$ ) at C7 by linear regression with log-transformed specific discharge. Thus, a model equation could fit a curve for each site describing the relation between observed groundwater levels and specific discharge [Eqn (1)] (Grabs *et al.*, 2012).

$$q = e^{b \cdot ((obs\ z_{Gw} - h_0) + a)} \quad (1)$$

The equation contains an offset parameter ( $h_0$ , cm), a flow parameter ( $a$ , cm), and an exponential parameter describing the water flux curve ( $b$ ,  $\text{cm}^{-1}$ ). Eqn (1) was used to back-calculate daily modelled groundwater tables ( $z_{Gw}$ , cm) because of gaps in the observations, which were recorded from May 2008 to September 2009. Site R14 had low variation in groundwater levels, and therefore, a mean of the observations was assumed for every day in the two-year study period. The parameter  $b$  at site R14 was assumed to be the same as for site R15 based on their similar soil properties (Ledesma *et al.*, 2013). Overland flow was disregarded (Grabs *et al.*, 2012; Ledesma *et al.*, 2013), that is  $z_{Gw} > 0$  cm was set to 0 cm, because surface run-off has been rarely observed in the area (Bishop *et al.*, 1995). Lateral flow profiles were defined by flow-weights ( $w$ , dimensionless), which describe the incremental lateral specific groundwater discharge rates, that is a proxy to the water flux at each integrated depth. Flow-weights were calculated at every integrated depth using the exponential parameter  $b$  describing the water flux curve [Eqn (2)]. The step size for numerical integration across the soil profile was set to  $\Delta z = 0.1$  cm. Total flow-weights ( $W$ , dimensionless) were defined as the integration of all flow-weights below  $z_{Gw}$  for a specific day and site [Eqn (3)].

$$w = e^{(z \cdot b)} \quad (2)$$

$$W = \sum_{z=-100\text{ cm}}^{z=z_{Gw}} w \quad (3)$$

A mass per centimetre of soil layer normalized to lateral contributing area ( $f_{DOC}$ ,  $\text{mg m}^{-2} \text{cm}^{-1}$ ) for the 731-day period 2008–2009 was calculated using daily values of specific discharge, DOC concentrations, and flow-weights [Eqn (4)].

$$f_{DOC}(z) = \sum_{day=1}^{day=731} \frac{C_{DOC} \cdot w}{W} \cdot q \quad (4)$$

The total DOC flux normalized to lateral contributing area ( $F_{DOC}$ ,  $\text{mg m}^{-2}$ ) from every riparian profile could then be

calculated with Eqn (5). The reported annual lateral DOC fluxes in the 13 riparian profiles (hereafter termed potential or estimated) were obtained by dividing Eqn (5) by 2 because annual run-off in 2008 and 2009 differed only slightly ( $\pm 5\%$ ).

$$F_{DOC} = \sum_{z=-100 \text{ cm}}^{z=0 \text{ cm}} f_{DOC}(z) \cdot \Delta z \quad (5)$$

Analogously, lateral flow ( $f_{flow}$ , dimensionless) contributions were determined from Eqn (6). Only soil depths below the daily modelled groundwater table, that is  $z < z_{Gwr}$ , were considered to contribute to flow when using Eqns (4) and (6). This was based on the RIM assumption that lateral flow only occurs in saturated soils below the groundwater table (Seibert *et al.*, 2009).

$$f_{flow}(z) = \sum_{day=1}^{day=731} \tau \quad (6)$$

The mean annual mass exported from every integrated depth per metre of stream bank ( $E_{DOC}$ ,  $\text{mg m}^{-1} \text{cm}^{-1} \text{year}^{-1}$ ) [Eqn (7)] was calculated based on the specific lateral contributing area ( $a_c$ ,  $\text{m}^2 \text{m}^{-1}$ ) (Fig. 2). This area represents the combined riparian and upslope areas that contribute to flow to a specific location along the stream, and it is normalized to 1-m stream bank (Grabs *et al.*, 2010). The value of  $a_c$  was computed for every ROK site by applying the multiple deterministic infinite-directional triangular facets flow algorithm (Seibert & McGlynn, 2007) in combination with the Stream Index Division Equations (SIDE) algorithm (Grabs *et al.*, 2010) in a hydrologically corrected, 5-m resolution Digital Elevation Model (DEM).

$$E_{DOC}(z) = \frac{f_{DOC}(z)}{2} \cdot a_c \quad (7)$$

#### Riparian carbon pools and theoretical turnover times

Representative pits of the existing ROK sites were excavated in August 2008 for soil characterization of the locations installed the previous year. Soil samples were collected with small spades or using peat samplers. At site R15, the soil was collected using bulk density cylinders. Samples were stored in plastic bags with ziplocks to hinder air intrusion. The soil mass was measured immediately after the field day and the samples were stored in a cooling room for later analyses. For each site, 2–5 samples at different depths were analysed for soil organic carbon content (SOCC, %) by combustion. Soil organic carbon content profiles were estimated by linear interpolation between observations analogously to soil water DOC concentration profiles. Bulk density ( $\rho_b$ ,  $\text{g m}^{-3}$ ) was available from two different sets of samples collected in 2007 and 2012 distributed all over the Krycklan catchment ( $N = 145$ ). These samples were extracted at different depths from both organic and mineral soils. A logarithmic function described the relationship between carbon content and bulk density ( $R^2 = 0.83$ ; Fig. S4). This equation was used to estimate bulk density profiles from soil organic carbon content of the samples presented here. Subsequently, specific carbon pools per square metre of RZ (SCPs,  $\text{g m}^{-2}$ ) over a 1-m soil profile were calculated for

every integrated soil depth ( $\Delta z = 0.001 \text{ m}$ ) at each ROK site using Eqn (8). SCPs representing the 13 riparian sites were estimated with Eqn (9).

$$SCP(z) = SOCC \cdot \rho_b \cdot \Delta z \quad (8)$$

$$SCP = \sum_{z=-1 \text{ m}}^{z=0 \text{ m}} SCP(z) \quad (9)$$

We also estimated the total amount of RZ carbon per metre of stream bank. This total carbon pool (TCP,  $\text{g m}^{-1}$ ) was calculated accounting for the lateral extent of the organic layer in every integrated depth and normalized to a 1-m stream bank [Eqns (10) and (11)].

$$TCP(z) = SCP(z) \cdot OL_x \quad (10)$$

$$TCP = \sum_{z=-1 \text{ m}}^{z=0 \text{ m}} TCP(z) \quad (11)$$

Organic layer widths ( $OL_x$ , m) (Fig. 2) were estimated by interpolating and averaging organic layer depths measured in the field at multiple distances in four transects parallel to the local topographic slope direction as a proxy for the local water flow direction. The transects were located 2 and 4 m upstream and 2 and 4 m downstream of the instrumented ROK sites. The organic layer width could be at maximum the RZ width of that specific site. RZ widths were determined based on field observations similar to the method by McGlynn & Seibert (2003), using soil type changes from organic/transitional soils to podzols as the main criterion. RZ widths in sites R14 and R15 were determined, respectively, from the extent of continuous vegetation and from change in slope because no well-developed soils exist in the sediment area where these two profiles are located.

Theoretical turnover times were estimated assuming that there are no inputs of carbon to the DSL and that all DSL carbon is eventually soluble to DOC (Fig. 2). Theoretical turnover times ( $TT$ , years) at every integrated depth were calculated with Eqn (12). The reported estimates were calculated as the mean value of all theoretical turnover times within the identified DSL in every site.

$$TT(z) = \frac{TCP(z)}{E_{DOC}(z)} \quad (12)$$

#### Influence of local hydromorphological conditions

We used a combination of simple and multiple linear regression and hierarchical partitioning analyses to compare the variation of estimated annual DOC fluxes [Eqn (5) divided by 2] with five independent variables: median  $z_{Gwr}$ , computed values of topographic wetness index ( $TWI$ , dimensionless),  $SCP$ ,  $TCP$  and observed RZ width. R8 was excluded in the simple linear regression analysis of the RZ width because the local contributing area at this site includes large parts of mire. Thereby, the RZ width at R8 is disproportionately large when based on the criterion of changes from histosols/transitional soils to podzols. Riparian profiles in the sediment areas R14 and R15 (Table 1, Fig. 1) were excluded in the linear regression

analyses for median  $z_{Gw}$  and  $TWI$  because of differences in soil properties compared to till soils. A hierarchical partitioning analysis (Chevan & Sutherland, 1991; Mac Nally, 2002), excluding R8, R14, and R15, was performed to separate the total independent contribution and the joint influence of every predictor in a multiple linear regression model where the estimated DOC flux was the response variable. A randomization test was carried out to examine which of the five variables would be statistically significant to retain in the model.

The sensitivity of theoretical turnover times was assessed for uncertainties in the parameters  $a_c$ ,  $z_{Gw}$ , and organic layer width. We quantified the influence of  $a_c$  by calculating three values of theoretical turnover times for each ROK site using  $a_c$  from the likely ROK position ( $a_{c0}$ ) as well as  $a_c$  from the closest upstream ( $a_{c+1}$ ) and downstream grid cells ( $a_{c-1}$ ) in the DEM. Choosing  $a_c$  values from the two closest five-by-five metre grid cells also matched the estimated accuracy of  $\pm 5$  m of the site positions (which was obtained from repeated GPS measurements) and the spacing of the transects used for measuring organic layer widths. This analysis was not performed at site R8 because it is located at the head of a stream and only the most likely position was used. Note that the values of  $a_c$  presented in Table 1 correspond to those at the most likely positions. The influence of uncertainties in the modelled groundwater tables was assessed by varying  $z_{Gw} \pm 1.96$  standard errors of the residuals of the model used to back-calculate  $z_{Gw}$  at each site. Organic layer widths were varied according to the standard error of the four field measurements of RZ width at each site (supporting information).

#### Carbon in stream run-off: isotopic measurements

To assess the source of DOC in stream water, that is to evaluate whether recently produced carbon or old carbon from the riparian pools is predominantly mobilized to the aquatic environment, stream water samples were analysed for  $DO^{14}C$ . Water samples ( $N = 28$ ) were collected during two separate years (1999 and 2007) from three streams within KCS (C2,  $N = 12$ ; C4,  $N = 10$ ; and C7,  $N = 6$ ; Fig. 1). Both C2 and C7 were deepened in the 1920s; thus, at these streams, older carbon sources could be exposed to enhanced decomposition leading to a contribution of DOC from older carbon sources. After collection, filtered samples were acidified to pH 4.0 and stored in amber glass. Samples were then evaporated to dryness in a freeze-drier, combusted to  $CO_2$ , and purified in an offline vacuum glass line.  $\delta^{13}C$  was analysed in a split sample by continuous flow isotope ratio mass spectrometry with a precision of  $\pm 0.3\%$ . Purified  $CO_2$  was sent to Isotracer in 1999 and to University of California, Irvine, in 2007 for analysis of  $^{14}C$  by tandem accelerator mass spectrometry. Precision was  $\pm 0.9$  pMC (percentage of modern carbon) in 1999 and  $\pm 0.8$  pMC in 2007. All  $^{14}C$  values were corrected using the measured  $\delta^{13}C$ . The pMC units represent the proportion of radiocarbon atoms present in a sample compared to that in the year 1950 (Stuiver & Polach, 1977). Thus, a pMC larger than 100 indicates the presence of carbon with elevated  $^{14}C$  from atmospheric weapons testing and thus a significant contribution of carbon younger than 49 and 57 years old for the

samples collected in 1999 and 2007, respectively. Given that organic matter sources created in the postatmospheric weapons testing interval have a range of  $^{14}C$  activities corresponding to the changing atmospheric  $^{14}C-CO_2$ , present-day DOC with a pMC  $>100$  indicates that a majority of the DOC must have been derived from carbon fixed and released after 1950, commonly referred as modern.

## Results

### Lateral water and DOC fluxes and DSL size

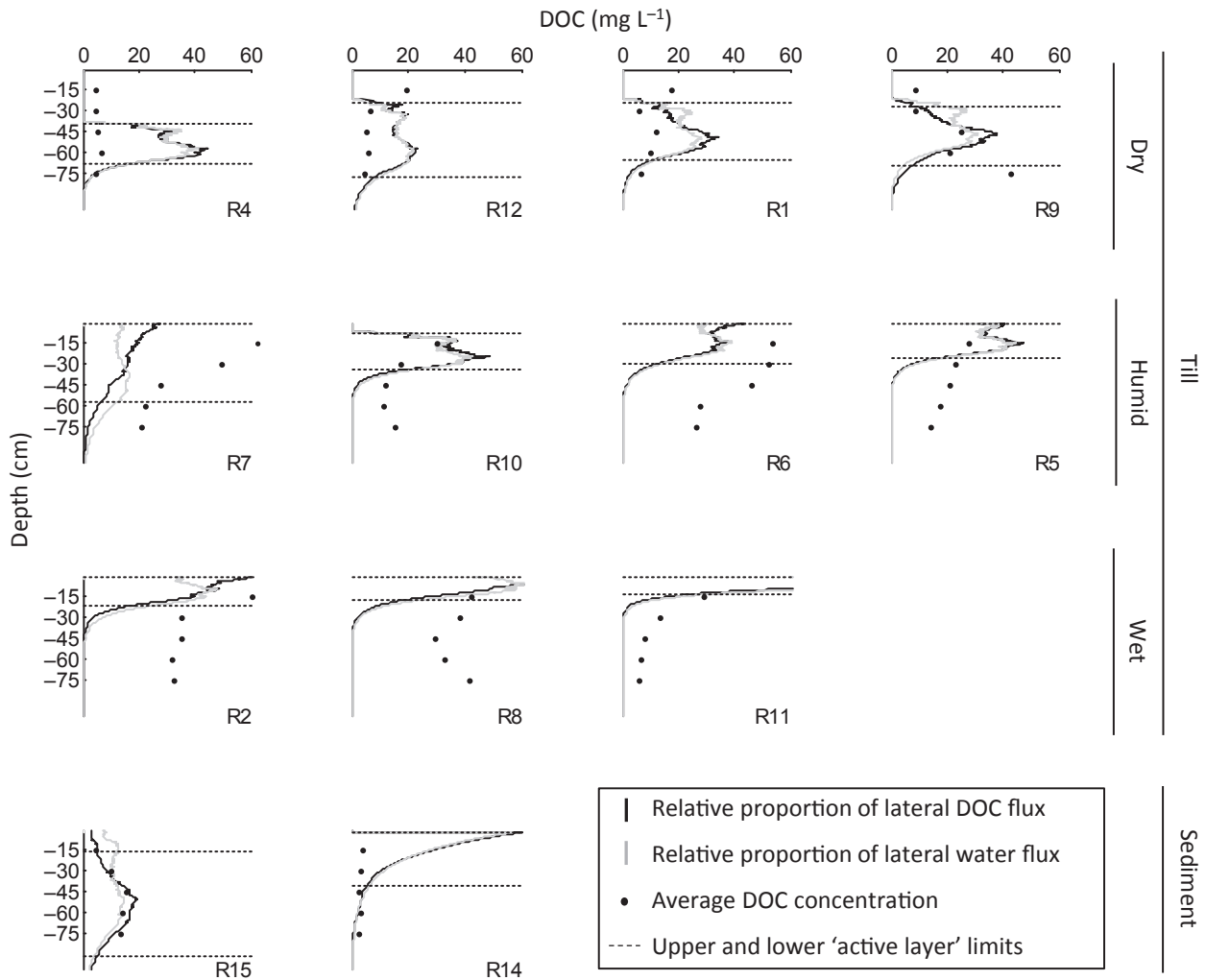
The DSL thickness varied from 13 to 75 cm with a mean value of  $35.9 \pm 17.6$  ( $\pm$ SD) cm (Table 2). Sites with deeper  $z_{Gw}$  and larger variations in  $z_{Gw}$  had broader DSL (see for example sites R7, R12, and R15 in Fig. 3) compared to sites with more shallow  $z_{Gw}$  that had narrower DSL (see for example R2, R8, and R11). This was also revealed by the significant relationship between median  $z_{Gw}$  and DSL thickness ( $R^2 = 0.51$ ; Fig. S5). In general, estimated lateral DOC fluxes (Table 2) followed estimated lateral flow, as indicated by their relative proportions within the riparian profile (Fig. 3), and varied widely ( $8.7 \pm 6.5$   $g\ m^{-2}\ year^{-1}$ ). Till-wet sites had the highest potential fluxes ( $15.1 \pm 5.3$   $g\ m^{-2}\ year^{-1}$ ) followed by till-humid sites ( $12.1 \pm 5.3$   $g\ m^{-2}\ year^{-1}$ ). Till-dry ( $3.7 \pm 2.4$   $g\ m^{-2}\ year^{-1}$ ) and sediment sites ( $2.6 \pm 2.1$   $g\ m^{-2}\ year^{-1}$ ) showed lower fluxes.

### Riparian carbon pools and theoretical turnover times

The mean specific carbon pool per square metre of RZ (SCP) for the 13 ROK sites was  $61.7 \pm 27.5$   $kg\ m^{-2}$

**Table 2** For every riparian profile, thickness of the dominant source layer (DSL), potential mean annual dissolved organic carbon flux (2008–2009), specific carbon pool per square metre of riparian zone (SCP), and total carbon pool in a 1-m stream bank (TCP)

Site	DSL thickness (cm)	DOC flux ( $g\ m^{-2}\ year^{-1}$ )	SCP ( $kg\ m^{-2}$ )	TCP ( $kg\ m^{-1}$ )
R4	28.6	2.0	34.6	93
R12	53.1	2.1	57.1	78
R1	40.9	3.4	86.6	694
R9	42.3	7.1	90.9	157
R7	56.5	15.5	48.5	1186
R10	26.2	6.6	22.9	319
R6	28.8	17.6	82.8	2743
R5	25.0	8.7	82.8	1213
R2	21.4	20.6	70.7	2718
R8	17.8	14.7	30.5	2738
R11	12.7	10.0	108.0	1836
R15	74.8	4.1	29.2	292
R14	38.0	1.2	57.1	114



**Fig. 3** Relative lateral dissolved organic carbon (DOC) and water flux proportions in the 13 riparian profiles for the two-year period 2008–2009. The upper and lower limits of the dominant source layer (DSL) and the average DOC concentrations at the measured depths are also displayed.

(Table 2). This is in line with literature values for peatland areas including wetlands and histosols (Table 3). No differences between site classes were observed, and the estimates were not related with the mean soil organic carbon content or the DOC fluxes. In contrast, the variability in total carbon pool per metre of stream bank (*TCP*) was consistent with the variability observed in the estimated DOC fluxes ( $R^2 = 0.80$ ; Table 2). These current fluxes could be maintained for hundreds to a few thousands of years according to the theoretical turnover time estimates, although there was a large variation between and within ROK sites (Table 4).

*Influence of local hydromorphological conditions*

Excluding sedimentary sites R14 and R15, *TWI* and median  $z_{Gw}$  each individually explained about 50% of

the variation in potential DOC fluxes (Fig. S6). We found RZ width to be a powerful predictor, explaining about 90% of the variation in potential DOC fluxes (Fig. 4), excluding the mire site R8 from the analysis. The relation between potential DOC fluxes and *TCP* was good ( $R^2 = 0.80$ ), but there was no relation with *SCP*. The hierarchical partitioning analysis (Table 5) showed a high joint influence between the five explanatory variables in a multiple regression model that explained 93% of the variation in the estimated DOC fluxes. RZ width had the highest independent effect and was the only variable statistically significant to be retained in the model, as indicated by the randomization test.

The considerable small-scale variation of  $a_c$  derived from the DEM impacted estimated theoretical turnover times considerably more than uncertainties in  $z_{Gw}$  and



**Table 3** Mean soil carbon pools and standard deviations (when available) in different ecosystem types and in the riparian zones of this study (in bold)

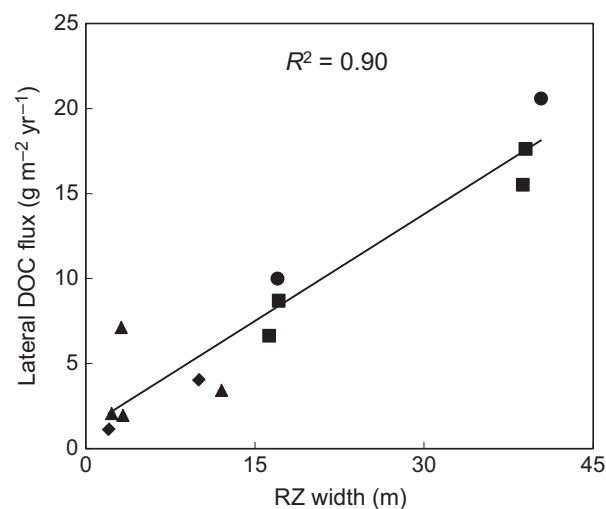
Type/location	Pool (kg C m <sup>-2</sup> )	Observations	Reference
Global soil organic carbon pool	10	World's soil carbon density	Post <i>et al.</i> (1982)
Boreal forests	14.9 ± 8.59	First 60 to 230 cm of soil profile	Schlesinger (1977)
Podzols in permafrost region	24.7 ± 20.2	First 100 cm of soil profile	Tarnocai <i>et al.</i> (2009)
<b>Till and sediment RZ</b>	<b>61.7 ± 27.5</b>	<b>First 100 cm of soil profile</b>	<b>This study</b>
Global wetlands	63.3 ± 49.9	Total carbon mass divided by total area	Mitsch & Gosselink (2007)
Swamps and marshes	68.6 ± 47.43	First 60 to 290 cm of soil profile	Schlesinger (1977)
Histosols in permafrost region	69.6 ± 56.9	First 100 cm of soil profile	Tarnocai <i>et al.</i> (2009)

**Table 4** Theoretical turnover times (TT) of dissolved organic carbon in the riparian profiles with sensitivity analysis for uncertainties in specific lateral contributing areas ( $a_c$ )

Site	TT <sub>0</sub> (years)	TT <sub>+1</sub> (years)	TT <sub>-1</sub> (years)	RSD
R4	832	615	841	17%
R12	6873	544	346	143%
R1	618	1253	38854	161%
R9	587	465	55	76%
R7	2533	1513	2188	25%
R10	215	130	199	25%
R6	313	579	187	56%
R5	2853	3697	5201	30%
R2	25	2923	9256	116%
R8	236	–	–	–
R11	247	1007	935	57%
R15	12264	167	463	161%
R14	1278	467	4189	99%

The subscripts 0, +1, and –1 indicate, respectively, turnover times calculated using  $a_c$  at the most likely grid cell position, the upstream neighbouring grid cell position, and the downstream neighbouring grid cell position. RSD is the relative standard deviation of TT<sub>0</sub>, TT<sub>+1</sub>, and TT<sub>-1</sub> for each site. The analysis was not carried out for site R8, located at the head of a stream.

organic layer widths (Table 4, Table S7). Even when looking at single sites, computed  $a_c$  values could vary markedly within only 5 m around the location of the site. The uncertainty in  $a_c$  is related to the inaccuracy of the measured GPS coordinates ( $\pm 5$  m). Consequently, theoretical turnover times were highly sensitive to changes in  $a_c$  (Table 4), which is directly caused by the estimation method [see Eqns (7) and (12)]. Theoretical turnover times were, in general, shortest at 'hot spots', characterized by relatively high values of  $a_c$ , and longest at 'cold spots', characterized by relatively low values of  $a_c$ . Looking at all 37 calculated theoretical turnover time values for the sensitivity analysis of  $a_c$ , the 10th percentile (160 years), median (618 years), and 90th percentile (7350 years) were still in the order of hundreds to a few thousands of years. The sensitivity

**Fig. 4** Simple linear regression model to predict potential lateral dissolved organic carbon fluxes in the riparian sites from riparian zone widths. Triangles represent till-dry sites, squares represent till-humid sites, circles represent till-wet sites, and diamonds represent sediment sites. Note that site R8 is not included.**Table 5** Hierarchical partitioning analysis and randomization test results using median ground water table ( $z_{Gw}$ ), topographic wetness index (TWI), specific carbon pool per square metre of riparian zone (SCP), total carbon pool in a 1-m stream bank (TCP), and riparian zone (RZ) width as explanatory variables and estimated lateral dissolved organic carbon fluxes as response variable in a multiple linear regression model

Variable	<i>I</i>	<i>J</i>	<i>I</i> (%)	Z score
Median $z_{Gw}$	0.11	0.31	12.0	–0.04
TWI	0.12	0.33	13.0	0.22
SCP	0.02	0.02	2.1	–0.74
TCP	0.29	0.50	31.2	1.40
RZ width	0.39	0.50	41.7	<b>2.86</b>

*I* indicates the independent fraction explained by each variable and *J* the joint effect of each variable together with the other variables. *I* (%) indicates the percentage distribution of independent effects. In bold, the significant variables ( $\alpha = 0.05$ ) to be retained in the model.

to uncertainties in  $z_{Gw}$  and organic layer widths (Table S7) using relative standard deviations of the three values of theoretical turnover times for each ROK site was on average 3% and 16%, respectively, considerably lower than for  $a_c$  (80%). Therefore, theoretical turnover times fell within the same order of magnitude.

#### Carbon in stream run-off: isotopic measurements

The results from the  $DO^{14}C$  analyses of stream water samples are shown in Table 6. All mean values for the three sites in both 1999 and 2007 are larger than 100 pMC, indicating that the majority of the organic carbon found in the aquatic system was of recent origin, that is fixed from the atmosphere after 1950.

### Discussion

By applying a simple hydrological approach that compares the size of the carbon pools with the rate of leaching in 13 riparian soil profiles, we have shown that there is a potential long-term transfer of DOC from boreal RZ into streams.

#### Lateral water and DOC fluxes in relation to DSL size

Estimated DOC fluxes varied significantly between riparian profiles, and spanned the whole range of reported values for the streams in the Krycklan catchment, from ca 2 to 10  $g\ m^{-2}\ year^{-1}$  (Ågren *et al.*, 2007; Köhler *et al.*, 2008). The variation in our riparian estimate ranged from around 2  $g\ m^{-2}\ year^{-1}$ , similar to values given for temperate forests, to around 20  $g\ m^{-2}\ year^{-1}$ , similar to upper-end values given for organic matter-rich wetlands (Hope *et al.*, 1994). This re-emphasizes the need to account for RZ heterogeneity with regard to DOC source areas, as previously shown when estimating DOC fluxes during single sampling days (Grabs *et al.*, 2012).

We demonstrate that 90% of the potential DOC flux could have originated from an approximately 36 cm thick layer in the RZ soil profile, the dominant source layer DSL. This strengthens the idea that the mobilization of solutes to streams is limited to only a fraction of

the total near-stream soil volume (Schiff *et al.*, 1998; Palmer *et al.*, 2001). DSL thickness was related to groundwater tables: relatively wet RZ with shallow and relatively stable groundwater table positions had relatively shallow and narrow DSL layers (Fig. 3; Fig. S5). The opposite was true for relatively dry RZ with deeper and more variable groundwater tables. This is in accordance with our previously suggested conceptual view (Grabs *et al.*, 2012), in which temporal variability of groundwater tables is related to riparian zone wetness. The estimated lateral DOC fluxes were strongly related to estimated lateral water fluxes (Fig. 3), similar to what it is usually seen in the assessment of riverine fluxes (Hinton *et al.*, 1997; Ledesma *et al.*, 2012).

#### Riparian carbon pools and theoretical turnover times

The variation in specific carbon pools per square metre of RZ (SCPs) had no statistical relation to variations in  $z_{Gw}$ , site class, or soil organic carbon content. For example, the mire site R8 had a mean soil organic carbon content of 52% and a SCP of 31  $kg\ m^{-2}$ ; whereas site R14 had a mean soil organic carbon content of 3% and a SCP of 57  $kg\ m^{-2}$ . This counterintuitive observation can be explained by the inverse relationship of soil organic carbon content and bulk density in the soil (Fig. S4). In the given example, the mean bulk density in R8 was 0.06  $g\ cm^{-3}$ , similar to other peat areas in northern Sweden (Waddington & Roulet, 2000), while the mean bulk density in R14 was 1.6  $g\ cm^{-3}$ , which is similar to forested mineral soils (Tamminen & Starr, 1994). Thus, the large range in soil organic carbon content between sites (2–52%) translates into a much reduced range in SCP (23–108  $kg\ m^{-2}$ ). On the contrary, marked differences between sites and site classes were observed in the total carbon pool per metre of stream bank (TCP). This is due to the close relation between TCP and RZ width [Eqn (10)], which has a wide range between sites (2–91 m).

Theoretical turnover time estimates here represent how long it would take to empty the riparian carbon pools of the DSL at the current constant rate of leaching denoted by the estimated exports (Fig. 2) and should not be perceived as a proxy for age of the organic

**Table 6** Stream sampling sites data including corresponding riparian profiles draining upstream the sampling point, land cover type proportions, and  $DO^{14}C$  information for 1999 and 2007 (note that there were no data for C7 in 2007)

Site	Name	Stream order	Riparian sites	Area (km <sup>2</sup> )	Forest (%)	Wetland (%)	N samples in 1999	$DO^{14}C$ (pMC) in 1999	N samples in 2007	$DO^{14}C$ (pMC) in 2007
C2	Västrabäcken	1	R5–R7	0.12	100.0	0.0	5	106.0 ± 4.0	7	108.3 ± 2.0
C4	Kallkällsmyren	1	R8	0.18	55.9	44.1	3	107.6 ± 2.7	7	111.6 ± 1.2
C7	Kallkällsbäcken	2	R5–R10	0.47	82.0	18.0	6	101.4 ± 2.6	0	–

carbon in the pool. The estimates for all our 13 RZ indicate that there is a potential long-lasting supply of DOC (Table 4). In other words, the current rate of DOC export could be maintained for hundreds to a few thousands of years by only mining the current riparian carbon pools.

#### *Influence of local hydromorphological conditions*

The total carbon pool in the RZ normalized to a 1-m stream bank (TCP) explained 80% of the variation in the potential DOC fluxes. This relates to several interconnected processes. A larger lateral extent of the carbon pools, and thereby a wider RZ, is an indicator of persistent wet conditions (i.e. higher groundwater levels) which usually show higher soil water DOC concentrations (Lyon *et al.*, 2011) and will have increased potential DOC fluxes. This is indicated by the correlation between median  $z_{Gw}$  and estimated DOC fluxes (Fig. S6), similar to the findings by Grabs *et al.* (2012). Furthermore, it implies longer flowpaths of the water in organic-rich layers along its way to the stream. Potentially, this leads to a larger DOC mobilization and flux, although longer residence times would also increase the opportunity for mineralization (Battin *et al.*, 2008). We suggest a conceptual diagram showing the interplay of these factors (Fig. 5a), which was supported by the large joint effects of the parameters used to predict potential DOC fluxes (Table 5). RZ width was the best predictor, explaining 90% of the variability in all profiles if site R8 was excluded (Fig. 4). These results suggest that potential DOC fluxes from RZ in boreal forests could be predicted using high-resolution soil maps that differentiate histosols/transitional soils from podzols. DOC fluxes in boreal catchments are primarily controlled by local hydromorphological characteristics of RZ, as opposed to minerogenic elements such as base cations which are controlled by landscape element types, that is open water, peatlands, upland forest till soils, and lowland sediments (Ledesma *et al.*, 2013).

Specific lateral contributing area ( $a_c$ ) exhibited a strong spatial variability but matched fairly well with locations of small springs and small concentrated near-surface flows observed in the field. We therefore argue that even though predicting the theoretical turnover time for a specific point in the RZ is highly uncertain, predicting the theoretical turnover time range for a RZ reach is a comparatively reliable estimate of the natural variability that one would expect at the considered reach based on the RIM assumptions. The large variability further stresses the importance of accounting for RZ heterogeneity when trying to scale up local findings to the catchment scale.

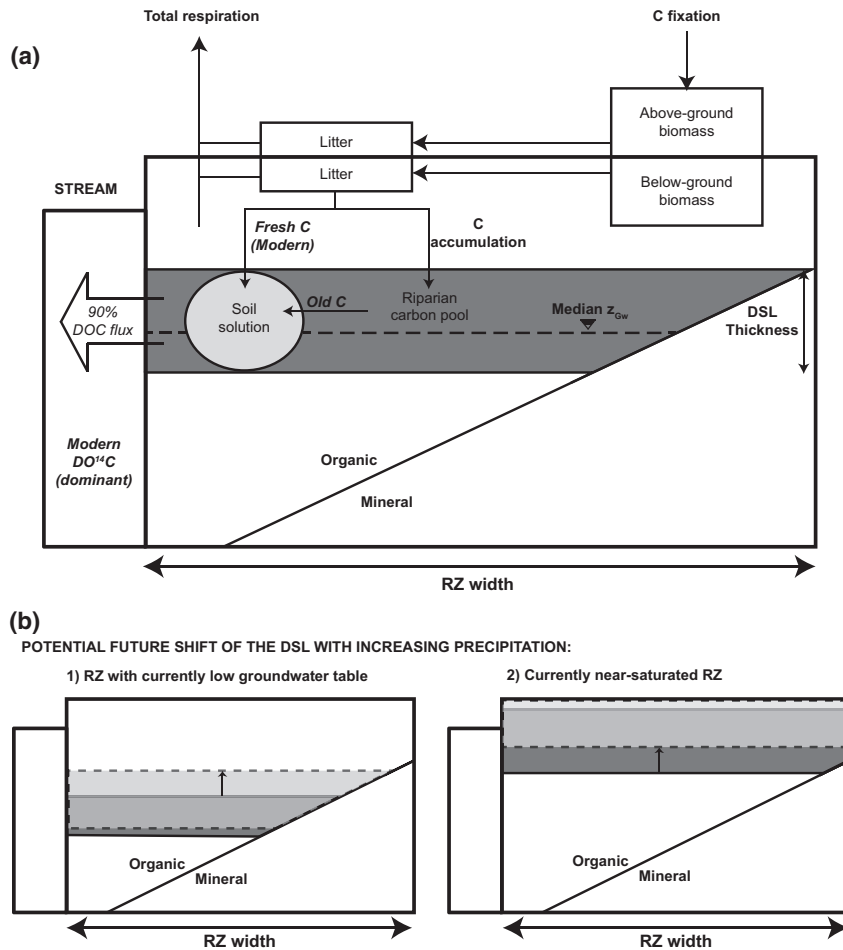
Other sources of uncertainty involve the hydrological simplifications of the RIM approach, including exclusively lateral Darcian flow below the groundwater table, horizontal water flux in the direction of the hydraulic gradient, and all lateral flow discharges into the stream (Köhler *et al.*, 2009; Seibert *et al.*, 2009; Grabs *et al.*, 2012; Ledesma *et al.*, 2013). These assumptions imply that flows that potentially bypass the RZ (e.g. overland flow, upward flows, upwelling of deep groundwater into the stream bed) are disregarded. Surface run-off has been rarely observed in the area (Bishop *et al.*, 1995), although it could be relatively important in the surroundings of site R8 (Laudon *et al.*, 2007; Ledesma *et al.*, 2013). All these flowpaths would bypass the DSL and therefore would tend to increase the theoretical turnover time.

#### *Carbon in stream run-off: recent production or ancient carbon mobilization?*

Our estimates of the size of the riparian carbon pools suggest that the DSL could maintain lateral DOC exports for hundreds to a few thousands of years assuming that: (i) all carbon in the pools is eventually soluble, (ii) there are no inputs of carbon into the system, and (iii) all decomposition in the RZ releases only DOC to the soil water. However, it is critical to consider that: (i) in the short-term, not all of the organic carbon in the riparian pool is available for mobilization into the solution, (ii) there is an annual production of new organic carbon contributed mainly by below-ground biomass in the RZ, together with a minor component of upslope DOC, and (iii) not all of the carbon decomposition is released as DOC as some is released as CO<sub>2</sub> and methane (Moore & Dalva, 2001). In relation to (iii), we estimated upslope sources of DIC to be 0.8 g C m<sup>-2</sup> year<sup>-1</sup> within the subcatchment where our site R5 is located (data from Cory *et al.*, 2007). Öquist *et al.* (2009) estimated the lateral DIC flux in a RZ similar to R5 to be 3.2 g C m<sup>-2</sup> year<sup>-1</sup> (November 2003 to October 2004,  $q = 330$  mm). Assuming that the difference is due to carbon oxidation within the RZ, 2.4 g m<sup>-2</sup> year<sup>-1</sup> of inorganic C would have originated here. Thus, in site R5, the theoretical turnover time would be around 20% lower accounting for the decomposition of carbon as CO<sub>2</sub>, as the DOC flux was equal to 8.7 g C m<sup>-2</sup> year<sup>-1</sup>.

Taking into account the points discussed above, we suggest that the DOC exported to the stream is made up by (i) a component of old carbon limited by the solubility of the riparian pool and (ii) a component of recent carbon limited by the net fixation from the atmosphere (Fig. 5a).

The easily soluble fraction of carbon pools is larger in organic soils relative to mineral soils because of



**Fig. 5** (a): Conceptual diagram of the interplay between hydromorphological factors controlling riparian lateral dissolved organic carbon (DOC) fluxes and how recent vs. old carbon is mobilized. Higher lateral DOC fluxes will be found in riparian zones (RZ) with more superficial dominant source layers (DSL), which would generally imply shallower groundwater levels, longer RZ widths, and larger riparian carbon pools that lead to longer transit distances of the water in organic-rich layers. The annual input of carbon available for export (via the soil solution) or storage (soil accumulation) is given by the difference between the carbon fixed from the atmosphere and the total respiration. DOC in the soil solution will be made up by a fraction of modern carbon from production (mainly from microbial degradation of below-ground biomass litter) and a fraction of old carbon that is solubilized from older carbon stored in the riparian pool. Stream  $DO^{14}C$  measurements suggest that the input of modern carbon from primary production is quantitatively more important than the mining of old carbon from the riparian carbon store. (b): Potential future shift of the DSL with increasing precipitation. Future DSL position is represented within the dashed lines. In RZ with currently low groundwater tables, the DSL will be expanded activating new carbon pools for drainage. In currently near-saturated RZ, the DSL will be reduced by concentration of flowpaths in the top soil.

stronger DOC sorption affinity to mineral phases (McDowell & Wood, 1984; Borken *et al.*, 2011; Huang *et al.*, 2013). Neff & Hooper (2002) estimated that the size of the easily mobile fraction that could become readily available for DOC export could be as much as 40% of the total pool in highly organic tundra soils. Organic matter solubility is influenced by multiple factors including dissolved oxygen content, pH, metal binding, humic charge, ionic strength, and dominant anion present (Herbert & Bertsch, 1995; Lofts *et al.*, 2001; Clark *et al.*, 2006; Kleber & Johnson, 2010). As many of these factors are interdependent, none may

individually explain changes in DOC solution at different sites (Löfgren *et al.*, 2010). Large enough and lasting trends in the mentioned chemical driving factors are not expected in the catchment given the nutrient-poor acid soils, the homogeneous geology, and the comparably slow and small predicted recovery from acidification. Changes in temperature and oxygen content that in turn are driven by soil water content might, however, have profound consequences on DOC processing in the RZ. The latter factors make it difficult to predict carbon mobilization from riparian carbon pools using static approaches, such as the one used here.

It is worth analysing whether the annual net production of carbon sustained by microbial degradation of litter in the RZ is enough to maintain the fluxes as predicted here. *Sphagnum* spp.-dominated systems, similar to the RZ presented here, have a mean annual gross production of about  $200 \text{ g C m}^{-2} \text{ year}^{-1}$  (Granath *et al.*, 2014). However, the vertical losses of respired carbon as DIC also need to be taken into account. These can be revealed in terms of net ecosystem production (NEP), which is the estimated carbon available for storage or export given by the difference between gross primary production (GPP) and total respiration (including both below- and above-ground respiration) (Chapin *et al.*, 2006). It is important to mention that old forests such as the forest in the Krycklan catchment tend to accumulate carbon in the biomass very slowly (Schlesinger, 1997; Jonsson *et al.*, 2007), so almost all NEP would be available for soil storage or lateral transfer as DOC or DIC. In a neighbouring spruce forest catchment with similar characteristics to the near-stream low-lying areas in KCS, the NEP for a 7-year period was  $120 \text{ g C m}^{-2} \text{ year}^{-1}$  (Grelle, 1997; Öquist & Laudon, 2008). When comparing this number with our DOC fluxes estimates, the NEP needs to be corrected because of our assumption of all carbon originating in the RZ with negligible contributions from upslope areas. For this, we used sites R4, R5, and R6, which belong to headwater catchments with low, intermediate, and high estimated DOC fluxes, respectively (Table 2). Roughly, these RZ account, respectively, for 5%, 10%, and 20% of the total catchment area. Thus, only accounting for the RZ, the corresponding NEP would be 6, 12, and  $24 \text{ g C m}^{-2} \text{ year}^{-1}$ , respectively. This would be enough to support the calculated DOC fluxes in the three riparian profiles (Table 2), and potentially even the lateral DIC flux, which also contributes to the lateral carbon losses (Leith *et al.*, 2014). The total DOC + DIC lateral flux at R5 (including only the DIC generated in the RZ as calculated above) would be  $11.1 \text{ g C m}^{-2} \text{ year}^{-1}$ , close to the NEP estimate of  $12 \text{ g C m}^{-2} \text{ year}^{-1}$ .

The potential for errors from NEP estimates (Waddington & Roulet, 2000) and the site-to-site variation (Schulze *et al.*, 1999) imply that these figures should be seen as rough comparisons and complementary lines of evidence should be used too. Isotopic measurements of carbon age can help to identify sources and processes controlling DOC exports. Our  $^{14}\text{C}$  data from stream samples indicate that DOC is predominantly modern, that is fixed from the atmosphere after the year 1950, suggesting that indeed recent production in the riparian system could be enough to support the lateral DOC exports (Fig. 5a). Nevertheless, this does not imply that old carbon is not being mobilized. Water samples contain a mixture of carbon from different sources, and

isotopic measurements provide information of the mean  $^{14}\text{C}$  activity in the mixture. Particularly, in RZ where the DSL extends below rooting depths, it is likely that old carbon is being exported (see for example till-dry sites in Fig. 3). However, according to our results, in this type of RZ, the amount of carbon exported per unit of area is significantly lower than that from relatively wetter RZ and thus contributes less to the total DOC found in a stream water sample. Moreover, it is unlikely that in-stream production contributes significant amounts of modern carbon because DOC fluxes are high and streams in the catchment are dominated by allochthonous dissolved organic matter (Berggren *et al.*, 2010). Recent carbon has also been observed in streams from similar catchments in the United Kingdom (Palmer *et al.*, 2001; Billett *et al.*, 2007; Rowe *et al.*, 2014) and Canada (Schiff *et al.*, 1998).

#### *Implications for ditching, future climate, and global carbon cycle*

In the larger context, carbon has been accumulated in boreal regions after the end of the last glacial period for about 6000 to 10000 years. These carbon pools were exposed to more oxygen in many headwater streams in Fennoscandia as a consequence of ditching to improve drainage and forest productivity during the early 20th century.  $\text{DO}^{14}\text{C}$  data show that organic carbon is predominantly younger than the time when those activities were carried out, even in Västrabäcken (C2) and Kallkällsbäcken (C7) (Fig. 1; Table 6), both deepened around 100 years ago. These findings for disturbed boreal RZ contrast with those of disturbed tropical peatlands, where significant amounts of old carbon are lost via run-off promoting the collapse of carbon storages (Moore *et al.*, 2013).

The climatic and hydrological conditions during the two-year period presented here were close to the long-term means for the area and therefore representative of the current conditions. An increase in both temperature and precipitation is forecasted in boreal regions (IPCC, 2007). Lateral DOC fluxes are highly sensitive to precipitation (Öquist *et al.*, 2014) and will increase together with increasing precipitation due to the close relationship with annual lateral flow fluxes (Fig. 3). The current range in run-off data in the Krycklan catchment covers  $\pm 50\%$  of the mean annual (1981–2012). Under wetter conditions, predominant flowpaths might permanently switch to upper soil layers with higher DOC concentrations, potentially leading to a higher increase in DOC fluxes relative to the increase in run-off. This would tend to reduce the theoretical turnover times estimated here. The extent of this reduction will depend on the current groundwater table position because the carbon

pool that is the effective source of the lateral DOC flux would shift together with the DSL (Fig. 5b). In RZ with currently low groundwater table levels, the area that is exposed to drainage could spread, activating new pools. In sites that are already near saturation, the DSL could be reduced by concentration of flowpaths in the top layer, which would reduce the effective pool and theoretical turnover times. High frequency measurements of stream and RZ soil water chemistry combined with hydrometric measurements at fine spatial resolution are needed to make topography-based, quantitative predictions on which of the two processes will dominate in the future. This will be of interest for further investigations under global change.

The increasing trends in DOC concentrations in boreal surface waters have been related to increasing DOC production linked to higher temperature and precipitation (Christ & David, 1996; Hongve *et al.*, 2004; Lepistö *et al.*, 2008; Ledesma *et al.*, 2012), including streams in the Krycklan catchment (Köhler *et al.*, 2009; Oni *et al.*, 2013). Our comparison of the organic carbon supply storage in the RZ and the potential DOC export, in addition to the  $\text{DO}^{14}\text{C}$  measurements, suggests that DOC production can be enough to sustain DOC exports in the foreseeable future and to support observed increasing DOC trends because of climate-related increasing productivity. Wu & Roulet (2014) suggested that NEP will decrease in the future in peatlands due to a relatively larger increase in total respiration with respect to the increase in GPP from carbon fixation (Fig. 5a). This change could shift the predominant source of carbon in the streams from recently fixed carbon to old carbon in the riparian pools as NEP will be no longer enough to support the exports. However, Wania *et al.* (2009) predicted an increase in NEP in boreal peatlands and permafrost regions under future climate conditions. It is therefore difficult at this stage to infer potential future changes of the results presented here under such uncertain forecasts.

We demonstrate the large potential of boreal RZ to transfer DOC into inland waters from both new and old carbon sources, which then has a major influence on surface water quality. The most important findings of this study can be summarized in four points. (i) A narrow layer ( $36 \pm 18$  cm) within the riparian soil profile, the 'dominant source layer' DSL, is the source of most of the potential terrestrial DOC flux exported to streams. (ii) The RZ width appears to control these DOC fluxes, which vary heterogeneously along the stream bank. (iii) There is a potential long-lasting supply of DOC (on the order of hundreds to a few thousands of years) from the riparian carbon pools in the DSL at the current rate of leaching. (iv) Rough estimates of NEP and isotopic measurements suggest that the

modern carbon found in stream run-off can be supported by recent primary production in the riparian system. Thus, despite the large store of carbon in the RZ, the dynamic allocation of new carbon from riparian production through the DSL is what controls the output of DOC. This is influenced by the riparian architecture due to the interaction of flowpaths and source areas of carbon. These findings are important for global carbon balances given the increasing recognition of the influence of inland waters in the global carbon cycle (Tranvik *et al.*, 2009; Wallin *et al.*, 2013), and the key role of RZ as sources of DOC into the aquatic environment.

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### Supporting Information

Additional Supporting Information may be found in the online version of this article:

**Table S1** Overview of symbols and abbreviations (in order of appearance in the text)

**Table S2** Percentage of 0.5 m × 0.5 m plots where the specified ground vegetation species were present in the riparian zone (August 2013)

**Figure S3** Wilcoxon test for differences between TOC and DOC in 90 samples collected during summer 2013 in riparian profiles R2, R5, and R10.  $\text{Prob} > |Z| = 0.81$  indicates no significant differences between group pairs.

**Figure S4** Relationship between carbon content and bulk density in soil samples collected during 2007 and 2012 within the Krycklan catchment ( $N = 145$ ).

**Figure S5** Relationship between median modelled groundwater table ( $z_{Gw}$ ) (as depth to groundwater table from the surface) and dominant source layer (DSL) thickness in the 13 riparian profiles in Krycklan.

**Figure S6** Simple linear regression models to predict lateral DOC fluxes in the ROK sites from (a) median modelled groundwater tables ( $z_{Gw}$ ) (as depth to groundwater table from the surface); and (b) topographic wetness indexes (TWI).

**Table S7** Sensitivity of theoretical turnover times (TT) of DOC in the riparian profiles to uncertainties in groundwater tables ( $z_{Gw}$ ) and organic layer widths ( $OL_x$ )