Are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest?

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Abstract.

The riparian zone, or near-stream area, plays a fundamental role for the biogeochemistry of headwaters. Here wet, carbon-rich soils can change groundwater chemistry before it enters the stream. In the boreal forest, the riparian zone plays an especially important role in the export of dissolved organic carbon (DOC) to streams. However, the riparian zone is not uniform and spatial variability of riparian groundwater hydrology and chemistry can be large. Terrestrial topographic depressions create hydrological pathways towards focal points in the riparian zone, which we refer to as Discrete Riparian Inflow Points (DRIPs). Combining the chemical function of the riparian zone and the convergence of hydrological pathways, we hypothesize that DRIPs play a disproportionally large role in conveying DOC to small streams. Earlier work has demonstrated that runoff from DRIPs can make up the majority of riparian flow contributions to streams, but so far it is unknown how their groundwater chemistry differs from the rest of the riparian zone. We therefore ask the question: are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest? To answer this question we sampled riparian groundwater during six campaigns across three boreal headwater streams in Sweden. The groundwater wells were distributed in ten DRIP and non-DRIP pairs (60 wells), following transects from upland (20 meters lateral distance from the stream bank) to near stream area (<5 meters lateral distance). The variability in dissolved organic carbon (DOC), pH and electrical conductivity (EC) was analyzed using linear mixed effect models (LMM). We explained the variability using three factors: distance from the stream, seasonality and DRIP/non-DRIP. Our results showed that DRIPs provided DOC rich water (34 mg/l) with relatively low EC (36 µS/cm). The 'non-DRIP' riparian water had on average 40% lower DOC concentrations (20 mg/l) and 45% higher EC (52 µS/cm). Moreover, groundwater chemistry from DRIPs was spatially and temporally relatively homogeneous. In contrast, non-DRIP water transformed distinctly in the last 25 meters to the stream, and chemical variability was also larger between seasons. We concluded that hydrological pathways and spatial variability in riparian groundwater DOC concentrations are linked, and that DRIPs can be seen as important control points in the boreal landscape. Characterizing DRIPs in headwater catchments can be useful for upscaling of carbon inputs in boreal stream ecosystems, and for delineating of hydrologically adapted buffers for forest management practices.

1 Introduction

Headwater streams can be seen as the capillaries of the landscape: although small in appearance, collectively they make up the majority of a stream network. The rich variety in hydrology, biology and chemistry of headwaters is tightly connected to processes in their catchments (Bishop et al., 2008; Hunsaker and Levine, 1995). Lateral groundwater inputs account for a large part of the streamflow of small streams, magnifying groundwater controls on stream CO_2 emissions (Hotchkiss et al., 2015). These controls are governed by groundwater-surface water exchange in the last interface between the landscape and stream ecosystems (Hayashi and Rosenberry, 2002). This near-stream area, so called riparian zone (RZ), holds important functions such as chemical transformation of hillslope water (Cirmo and McDonnell, 1997), thermal regulation (Davies-Colley and Rutherford, 2005) and erosion control (Smith, 1976). A few characteristics of the boreal RZ that leads to its unique ecosystem functions are high groundwater levels, dynamic redox potential, build-up of soil organic matter, and diverse vegetation (Grabs et al., 2012; Kuglerová et al., 2014b; Lidman et al., 2017). In terms of the hydrological role of the RZ, it has been demonstrated that riparian water dominates streamflow generation, instead of event-based water contributions from hillslopes (McGlynn and McDonnell, 2003). Combined with the chemical transformation of water in the riparian zone, stream biogeochemistry is therefore largely controlled by riparian zones (Ledesma et al., 2018b; Lidman et al., 2017). However, RZ's are not homogenous strips surrounding surface waters, but contain an array of heterogeneities in hydrogeology, soil development and vegetation across small spatial scales (Buttle, 2002; Kuglerová et al., 2014b). Moreover, wetness state changes the chemical function of the RZ in time (Vidon, 2017). It is therefore important to further investigate which parts of the riparian zone matter most for element transport, stream flow generation and associated biogeochemical processes.

In hydrological models streamflow generation has often been conceptualized as a diffuse process, which limits the ability to express points of focused groundwater discharges (Briggs and Hare, 2018). Some models, such as the RIM model and DSL concept, have considered the vertical heterogeneity in riparian groundwater fluxes to boreal streams (Ledesma et al., 2015; Seibert et al., 2009). But also longitudinally along streams reaches it is necessary to account for hydrological and biogeochemical heterogeneity within the RZ. For example, permanently saturated riparian areas have been identified as main stream flow generators (Penna et al., 2016), and have been associated with denitrification, as well as retention and transformation of (labile) OM, compared to drier, oxic, riparian soils (Blackburn et al., 2017; Burgin and Groffman, 2012; Ledesma et al., 2018b). In terms of vegetation, groundwater discharge zones are hotspots for diversity (Kuglerová et al., 2014a). Although these studies show that heterogeneity in the saturation or wetness conditions could be good predictor for heterogeneity in soil chemistry, the connection between spatial variability in groundwater chemistry and hydrological pathways within the riparian-upland continuum has not been demonstrated. The hydrological connection between the upslope catchment, riparian zones and consequently the stream network are highly variable: where some parts of the riparian zone only drain small individual hillslopes, others function as main hydrological flow paths funneling subsurface water through riparian input zones (Leach et al., 2017). Combining their chemical signature and hydrological upslope connectivity, contributions of such focused riparian inputs could therefore function as important *control points* in the landscape (Bernhardt et al., 2017). The difficulty is that incorporating these control points into models or practical applications means that they have to be characterized in order to explain stream dynamics. Especially for informing distributed models that overpass catchment scale, determination and characterization of these control points remains one of the challenges for the scientific community (Briggs and Hare, 2018).

For the hydrological characterization of riparian inputs, various approaches can be used across scales. Although subsurface pathways do not entirely follow surface topography (Devito et al., 2005), it has been demonstrated that topographic depressions are a good indicator for accumulation areas of water, ponding, shallow groundwater tables and concentrated flow paths in the near-stream area (Ågren et al., 2014; Jencso et al., 2009; Wallace et al., 2018). As such, topographic models can predict where

along a stream network disproportionally large amounts of groundwater connect with the stream. Mixing models using water temperature and chemistry can further depict whether the topography-based predictions of focused riparian inputs to streams are in line with reality (Leach et al., 2017). These discrete riparian inflow points (DRIPs, Fig. S2), provide continuous flows of subsurface water during low flow periods, but have also been observed to be highly dynamic in their activation during hydrological events (Ploum et al., 2018). Contrary to the incorporation of water from ephemeral streams in perennial stream networks, or the connection of intermittent sections of a stream network (Ågren et al., 2015), DRIPs are dominated by subsurface flowing water and the discharge to the stream is the first exposure to an open channel. A recent study demonstrated temporal dynamics in increasing greenhouse gas evasion from the stream reach in close downstream proximity of DRIPs (Lupon et al., 2019). Also in Arctic systems the presence of riparian wet areas has partially explained stream CO_2 evasion (Rocher-Ros et al., 2019). The latter suggests that both the hydrological fluxes as well as biogeochemical reactions in the stream are associated with the hydrological activity of DRIPs. However, in order to determine whether DRIPs matter for stream biogeochemistry, chemical characterization of the discharging groundwater is needed.

Characterizing groundwater chemistry is an especially challenging task. Previously this challenge has been by-passed by inferring groundwater chemistry from base flow chemistry of streams (Peralta-Tapia et al., 2015; Tetzlaff and Soulsby, 2008). Also the RIM model has provided a framework to infer groundwater chemistry profiles from stream chemistry (Seibert et al., 2009). However, even at the local scale spatial variability in groundwater chemistry overrules temporal variation and requires regular sampling of extensive well networks (Kiewiet et al., 2019). Within meters of each other, groundwater signatures can vary greatly (Penna et al., 2016). Three key parameters for chemical characterization of groundwater in boreal forests are dissolved organic carbon (DOC), pH and ionic strength. DOC concentrations in groundwater is the result of interaction between water and carbon rich materials in the shallow subsurface environment that are associated with paludification (Lavoie et al., 2005). More specifically for near stream areas, the width of the riparian zone is associated with the size of the potential carbon pool and the subsequent DOC concentrations (Ledesma et al., 2015). Apart from its role in food-web structures and carbon transport, DOC also increases the acidity (decrease pH) of soils and surface waters (Buffam et al., 2007). Electrical conductivity (EC) can be used as a proxy for the ionic strength, or total amount of dissolved ions in water (Corwin and Lesch, 2005). Water contact time with minerals and weathering processes are important factors determining EC (Saarenketo, 1998), with increasing EC indicating longer interactions (Hayashi, 2004; Peralta-Tapia et al., 2015).

In the context of spatial variability of riparian groundwater chemistry, it can be expected that DOC, pH and EC differ between DRIP and non-DRIP riparian areas (Fig. 1). DRIPs are associated with high groundwater levels and wet, organic rich soils with vegetation that favors wet conditions, while non-DRIPs have drier top soils and deeper groundwater levels (Kuglerová et al., 2014a). Inherent to their topographic setting, DRIPs drain a large upland area, while non-DRIPs typically drain only a small surrounding area of the riparian zone or they are recharge zones for adjacent DRIPs. Moreover, the water in DRIPs travels a longer distance horizontally; in presumably wet, highly permeable, organic rich soil. Non-DRIP water, on the other hand, is likely to infiltrate vertically through an oxic, organic rich top soil, before being transported a relative short distance horizontally through supposedly more mineral substrate. This implies that the contact time of the water with wet, organic soil and drier, mineral soil is different for both cases, which should lead to contrasting water chemistry.

In this study we characterize groundwater in a paired well network that is specifically designed to incorporate (saturated) riparian areas with large contributing areas (DRIPs) and drier parts of the riparian zone with small contributing areas (non-DRIPs). We hypothesize that groundwater in DRIPs has higher DOC concentrations and lower pH compared to non-DRIPs. The deeper groundwater levels in non-DRIP areas, and longer contact times with mineral soil relative to organic soil, leads us

to expect that EC will be higher in non-DRIP water compared to DRIPs. Furthermore we discuss the implications of using a binary categorization of the riparian zone opposed to continuous, process based approaches.

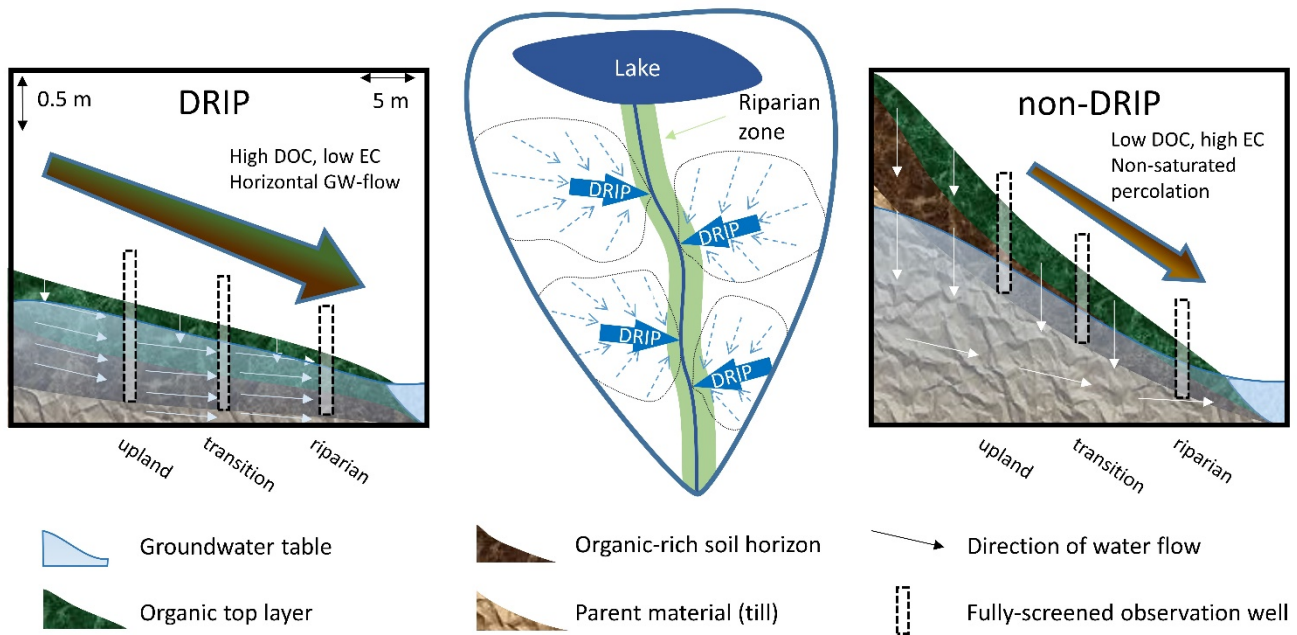



Figure 1 Conceptual illustration of the two types of hypothesized riparian areas along a boreal stream. Discrete Riparian Inflow Points (DRIPs) are focal points in the riparian zone (lightgreen) where pathways converge before reaching the stream (central panel). DRIPs typically have flatter topography and higher groundwater tables compared to non-DRIPs. The outer panels show DRIP and non-DRIP riparian zones. Green layers represent the approximate extent of the organic layer. Brown layers are riparian soils with high organic matter content. Light brown layers represent parent material. Transparent blue overlay represents the groundwater table. Black bars represent well transects of respectively DRIP areas on the left-hand side and non-DRIP areas on the right-hand side. Large arrows suggest relative hydrological contribution with color fill that matches soil layer with which groundwater has interacted most.

2 Material and methods

To test our hypothesis we collected DRIP and non-DRIP groundwater across a riparian gradient during different seasons. Using linear mixed effect models (LMM's) we analyzed the role of DRIPs on biogeochemical composition of riparian groundwater, in relation to spatial and temporal variability. We performed our study in Krycklan, a boreal forested catchment in northern Sweden.

2.1 Study area

The Krycklan catchment is situated near the town of Vindeln, Sweden (64°14′N, 19°46′E, Fig. 2). The bedrock is predominately Svecofennian metasediments and metagreywacke. Quaternary deposits consist mostly of till (51%) and sorted sediments (30%). Land cover is dominated by forest (87%), and there is 9% mire cover. Furthermore there are sporadically thin soils and bedrock, and a small fraction of arable land (2%). The climate is characterized as cold humid temperate type, with almost 6 months of snow cover. The yearly average temperature is 1.8 °C, and annual precipitation is 614 mm, and the annual mean runoff approximates 311 mm (Laudon et al., 2013). The well network is situated along streams referred to as C4, C6, and C8 (Laudon et al., 2013), with a drainage area of respectively 18, 110, and 230 ha. Catchments C4 and C6 have been widely studied in regard of lateral flow and groundwater and surface water interaction and can be referred to in other studies as Kallkälsmyrsbäcken and Stortjärnsbäcken (Laudon et al., 2004b, 2007). At the C6 hydrological stations flows vary from a few liters per second baseflow to 200 l/s peak flows (Ploum et al., 2018). The yearly hydrograph is characterized by sustained baseflow throughout the winter months, followed by spring snowmelt floods in April and May (Fig. S1). In summer and

autumn low flow conditions are common with occasional rain-induced flow events. From November onwards, flow reduces as temperatures fall below 0 °C and baseflow conditions set in.

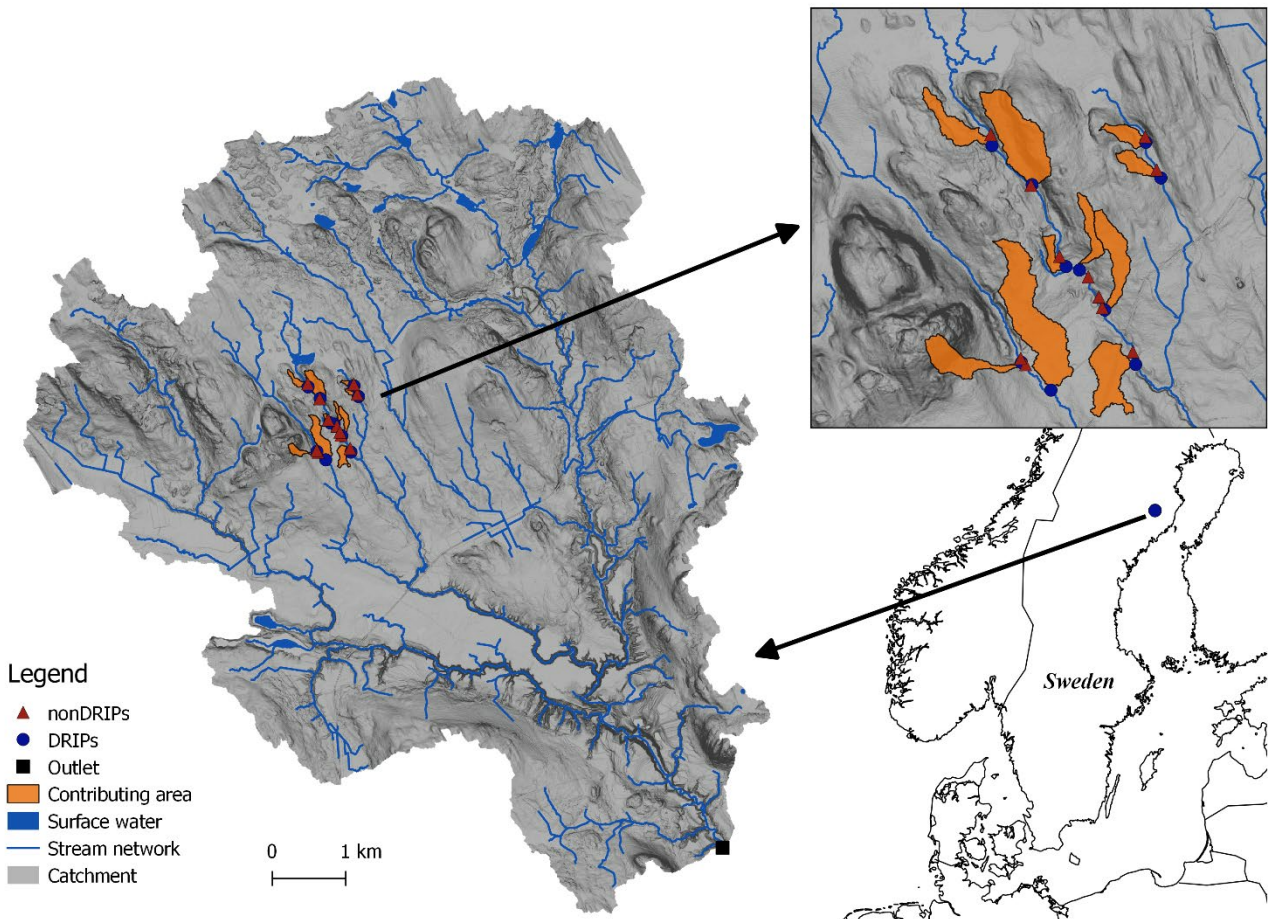



Figure 2 Krycklan catchment in Northern Sweden. The upper right panel shows the particular study area where the well network has been installed. The red triangles and blue dots indicate respectively non-DRIP and DRIP transects, consisting of three wells placed at 20, 10 and <5 meters from the stream. The black square indicates the catchment outlet. In orange the contributing areas are indicated of each well transect. Non-DRIP contributing areas are typically too small to be depicted.

2.2 Site selection and sampling well infrastructure

Discrete Riparian Inflow Points (DRIPs) were selected by considering wet areas, based on a topographic wetness index, and selecting large step changes in catchment area along stream networks using flow accumulation algorithms (Ågren et al., 2014; Beven and Kirkby, 1979; O'Callaghan and Mark, 1984). DRIPs were typically recognized in the field as wet corridors in the forest characterized by their flat topography, wet soil conditions, moss-dominated vegetation, and decrease in tree density (Fig. S2). The DRIPs (n = 10) were selected with contributing upslope area varying from 0.6 to 7.7 ha, with a mean contributing area of 2.7 ha. Non-DRIPs had an upslope contributing area between 4 and 80 m^2 (on average 17 m^2). The DRIPs have been field-validated (Ploum et al., 2018) and surveyed on species richness (Kuglerová et al., 2014a). For some sites chemical and thermal signatures further corroborated the location where riparian water discharged into the stream (Leach et al., 2017).

The setup of this study consists of a well network with a total of 60 fully screened PVC wells (30 mm diameter) arranged in 10 paired transects. Each transect consisted of a riparian well, situated typically between 1 and 5 meter from the stream, a transition well at approximately 10 meters from the stream, and an upland well 20 meters from the stream. Transects followed the local topography, to approximate local hydraulic gradients and flow paths. The non-DRIP transects were installed close (<50 m) to each DRIP transect to ensure similarity in local conditions. All wells were drilled until resistance, or an aquitard layer. Riparian wells had a mean depth of 95 cm (σ = 37 cm), transition wells 99 cm (σ = 42 cm), and upland wells 121 cm (σ = 55 cm). We assumed that the water sampled from the well is a weighted average of the phreatic aquifer, down to the depth

of the well. Given the exponentially decaying hydraulic conductivity with depth, this assumption would imply that, under fully saturated conditions, the majority of the water is therefore from the upper soil layers, referred to as the dominant source layer (Ledesma et al., 2015). Given that context, lateral flow below the well bottom was considered negligible compared to the flow in the vertical domain of our well installations. For a small subset of riparian sampling wells, water levels were available from directly neighboring wells (<2 m apart). Figure S1 shows an exemplar time series of these wells and a hydrograph for 2018. The mean depth to water table for those time series was 9.6 cm (σ = 4.2 cm) for DRIP wells, and 54.5 cm (σ = 17.3 cm) for non-DRIP wells.

2.3 Groundwater sampling and chemical analysis

The well network was sampled using suction cup lysimeters and vacuumed glass bottles (Blackburn et al., 2017). The wells were pumped before installing the suction cups to ensure water from the aquifer was sampled and without any stagnant well water. The bottles were collected after approximately 24 hours and subsampled, filtered and analyzed within 48 hours. In addition, a more intensive sampling campaign was conducted for a series of riparian wells only. These were sampled following a similar protocol, but instead of suction cup lysimeters, a peristaltic pump was used for the collection of water samples.

Water samples were collected during spring, summer and autumn of the hydrological years 2016 (Q=328 mm, P=629 mm) and 2017 (Q=259 mm, P=572 mm). In total 359 samples were analyzed from six sampling campaigns, of which 200 from DRIP wells and 159 from non-DRIP wells. Non-DRIP wells occasionally had too low water level to collect a representative water sample. For analysis of dissolved organic carbon (DOC), a subsample was filtered (0.45 μm) into acid-washed high-density polyethylene bottles (rinsed three times) and kept at 4 °C before laboratory analysis. DOC was measured by acidifying the sample and combustion using a Shimadzu TOC-V$_{PCH}$. The pH and EC were subsampled without headspace into acid-washed high-density polyethylene bottles (rinsed three times) and kept at 4 °C before laboratory analysis. Samples were analyzed using a Mettler Toledo DGi117-water probe for pH and Mettler Toledo InLab741 probe for electrical conductivity.

2.4 Statistical analysis

We used linear mixed-effect models (LMM) to analyze patterns in DOC, pH and EC. The analysis was performed in R using *lmer* models from the R-package *lme4* (Bates and Maechler, 2009; Bates et al., 2014). The LMM's provided a non-parametric approach to explain variability in the response variables by fixed effects (factors that were included in the study design) and random effects. Random effects account for factors which were not part of the study design, but possibly affected variability in DOC, pH and EC. The fixed effects considered in this study were the hydrological pathways (HP - DRIP, non-DRIP), position in the landscape relative to the stream (POS – riparian, transition, upland), season when the samples were taken (TIME – spring, summer, autumn), and the two-way interaction between HP and POS and TIME, respectively. The included random effects were the stream identity and the transect identity along which the wells were situated. In this way we accounted for specific catchment and hillslope properties. The model structure selection was based on the lowest AIC (Akaike's Information Criterion).

We evaluated the model performance using Type II Wald F tests with Kenward-Roger degrees of freedom (since all explanatory variables are factors). F statistics indicate the explained variance as a ratio of unexplained variance. An effect was considered significant if p-values <0.05. We evaluated the assumption of Gaussian distribution of errors by inspecting residuals and quantile distributions. For DOC five outliers, and for pH two outliers were removed from the upper quantile. For EC one in the lowest tail and two in the highest tail of the distribution. For comparing contrasts of levels within explanatory factors (for example DRIP vs. non-DRIP comparisons), we investigated least square means using R-package *lsmeans*, including Tukey adjustment to account for potential differences in sample size (Lenth and others, 2016). Furthermore, the marginal and

conditional coefficient of determination (R^2_{mar} and R^2_{con}) was presented to compare explained variance by the fixed effects, and the variance explained by the fixed and random effects together (R-package *MuMln,* Barton, 2014).

3 Results

3.1 DOC

5 The water collected in wells situated in the DRIPs had a higher mean DOC concentration (33.9 mg/l) compared to non-DRIP wells (19.9 mg/l, Fig. 3). DOC concentrations in DRIPs increased from upland wells (29.2 mg/l) towards the riparian wells (36.3 mg/l), while in non-DRIP riparian wells DOC concentration increased from 16.4 to 20.1 mg/l (DF=19, p=0.03). When we only accounted for gradients between upland and riparian wells (without distinction between DRIP or non-DRIP sites) differences were not as large, but still significant (from 22.8 mg/l to 28.2 mg/l, DF=327, p=0.0001). Although DOC

10 concentrations in the upland groundwater of DRIPs was already high, the overall gain in DOC concentrations from the upland to the riparian wells was most accountable to DRIPs (DF=326, p=0.0003). Average DOC concentrations were contrasting in the upland wells (29.2 mg/l and 16.4 mg/l for DRIP and non-DRIPs, respectively), but were statistically not significant (p=0.1844, Fig. 4 upper left panel). In summer and autumn, DOC concentrations in DRIP groundwater (36.4 and 33.3 mg/l) were twice as high as non-DRIP groundwater (18.0 and 17.7 mg/l, Fig. 5, upper panels). However, during snowmelt in spring,

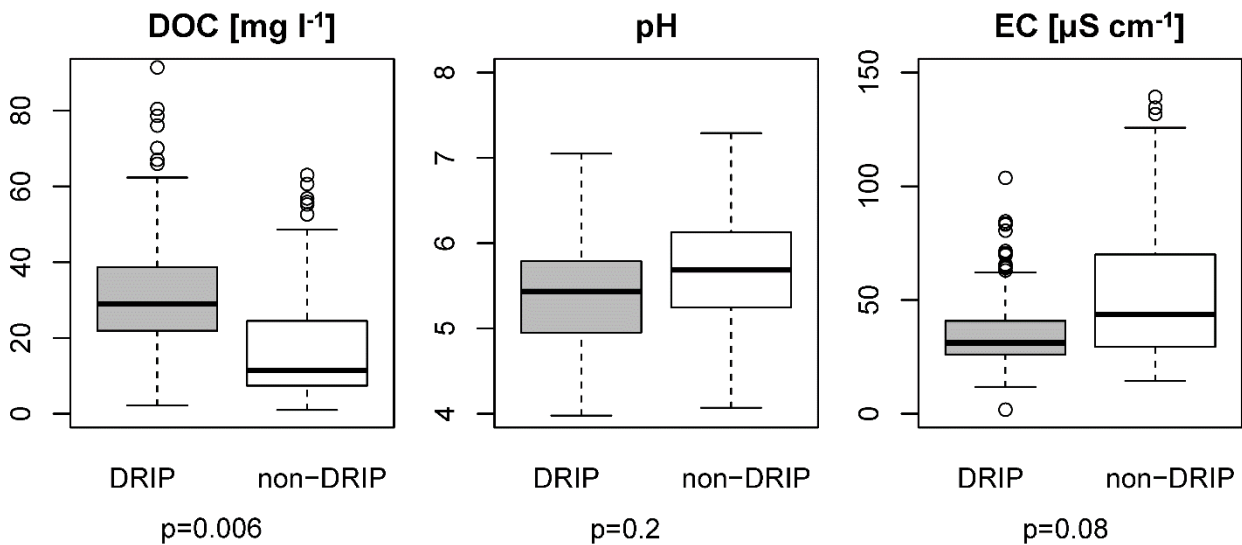
15 this difference reduced. This change was a result of an of average 20% decrease in DOC concentrations in DRIPs (28.5 mg/l) compared to the summer average. In non-DRIP areas there were no significant contrasts, although there was a small increase in spring (21.6 mg/l) compared to summer and autumn (18.0 and 17.7 mg/l, p=0.4986 and p=0.3019). Overall, the fixed effects alone explained 22% of the variance in DOC found in the groundwater well network. With the random effects included the explained variance was 68%.

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Figure 3 Groundwater chemistry of DRIP versus non-DRIP. DRIP boxplots are presented in grey and non-DRIP boxplots in white. Each panel represents one response variable. Whiskers represent the 25th and 75th percentile. P-values were obtained by an F test, p-values <0.05 were considered significant.

3.2 pH

25 Although typically associated with DOC, the pH was not as distinctly different between DRIP and non-DRIP water as DOC (Fig. 3). Overall the fixed effects accounted for 13% of the variance, and 55% including random effects (Table 1). Mean pH levels were 5.38 for DRIPs and 5.66 for non-DRIPs (DF=16, p=0.2). Position in the landscape had more effect on the variability in pH: the upland pH was similar at DRIPs and non-DRIPs and decreased towards the riparian area (5.66 to 5.40, P<0.0001). Although no significant effect was found for interaction between the landscape position and hydrological conditions (Table

1), the least square means analysis showed a pronounced decrease in pH from upland to riparian wells in the DRIP areas (5.57 to 5.19, P<0.0001, Fig. 4 middle panels). The second important explanatory variable was seasonality (TIME in Table 1). The most notable was the increasing pH from summer to autumn (5.37 to 5.70, P<0.0001), both in DRIP and non-DRIP areas (Fig. 5, center panel and center-right panel). In the transition to spring, pH decreased again (pH$_{spring}$=5.48), mostly due to a shift in the DRIPs (p=0.04). Furthermore the variability in pH in non-DRIP water was high compared to DRIP areas, especially during summer (Fig. 5, center plot).

3.3 EC

Mean electrical conductivity from DRIP water was 36.2 µS/cm, which was lower (p=0.08) compared to the mean of non-DRIP water (51.6 µS/cm, Fig. 3). The variance in EC was mostly explained by POS and TIME, and the interaction between HP and POS (Table 1). Overall the conductivity increased from the upland to the riparian wells (39.3 to 48.0 µS/cm) and increased as well from spring to autumn (39.7 to 48.7 µS/cm, Fig. 4 lower panels). The interactions between groundwater conditions and the position relative to the stream were mostly related to two specific contrasts. The variability in EC in non-DRIP groundwater increased from the upland to riparian wells, while in DRIP areas the EC remained stable (Fig. 4, bottom row). Moreover large differences were found between DRIP and non-DRIP in the riparian wells, where the EC in non-DRIP riparian areas was twice as high as the EC in DRIPs (63.6 µS/cm compared to 32.4 µS/cm). In the upland areas, the DRIP and non-DRIP water was similar. Non-DRIP water increased from 40.5 µS/cm to 62.4 µS/cm from the upland wells towards the riparian wells, while DRIPs even decreased in conductivity (38.2 and 32.4 µS/cm for upland and riparian wells). Over the different seasons (TIME), the contrasts between DRIP and non-DRIP chemistry were consistent (Fig. 5, lower panels). The interaction between groundwater and seasonality (TIME) was not found to have an effect on EC. The only specific contrasts for both DRIP and non-DRIP was a 5µS/cm decrease from autumn to spring (P$_{DRIP}$=0.05, P$_{non-DRIP}$=0.0007). Overall, the explained variance of our LMM was 70% for EC, compared to 22% when only accounted for fixed effects (Table 1).
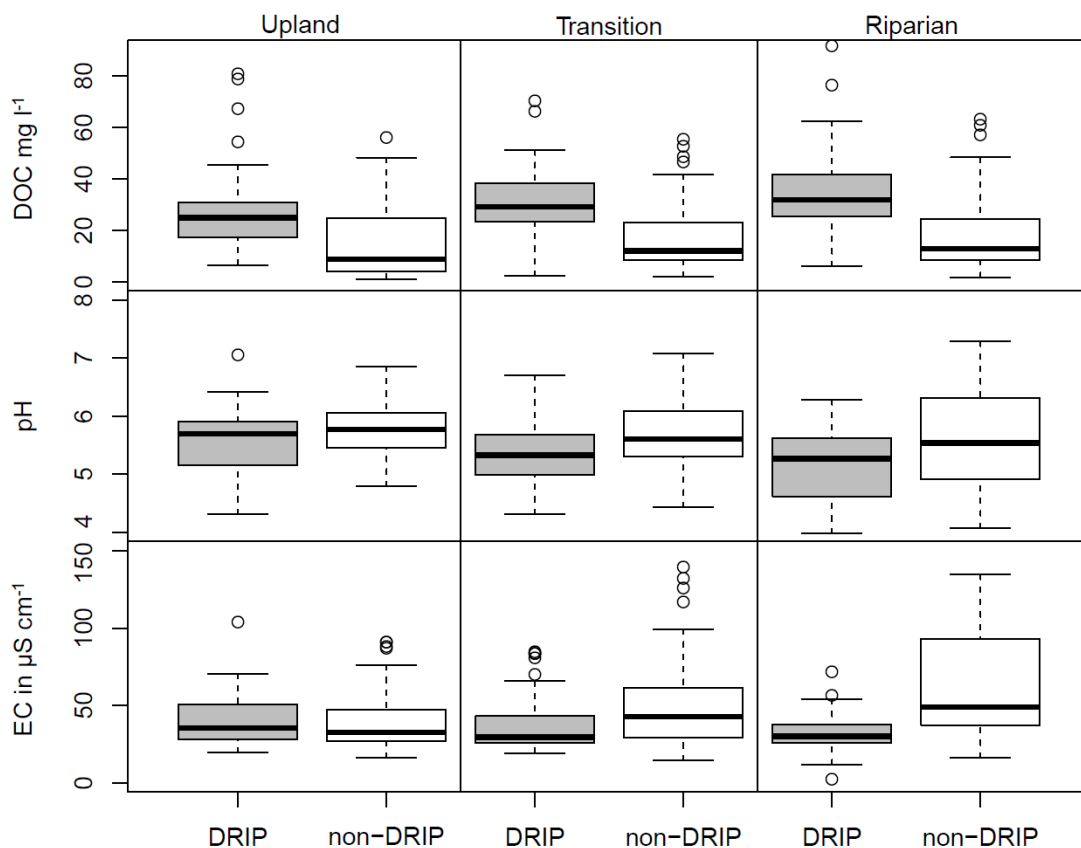
Figure 4 Groundwater chemistry gradients from upland to riparian wells. In each column DOC, pH and EC are presented for a location relative to the stream (Riparian, Transition and Upland). Within each panel DRIP boxplots are presented in grey and non-DRIP boxplots in white.
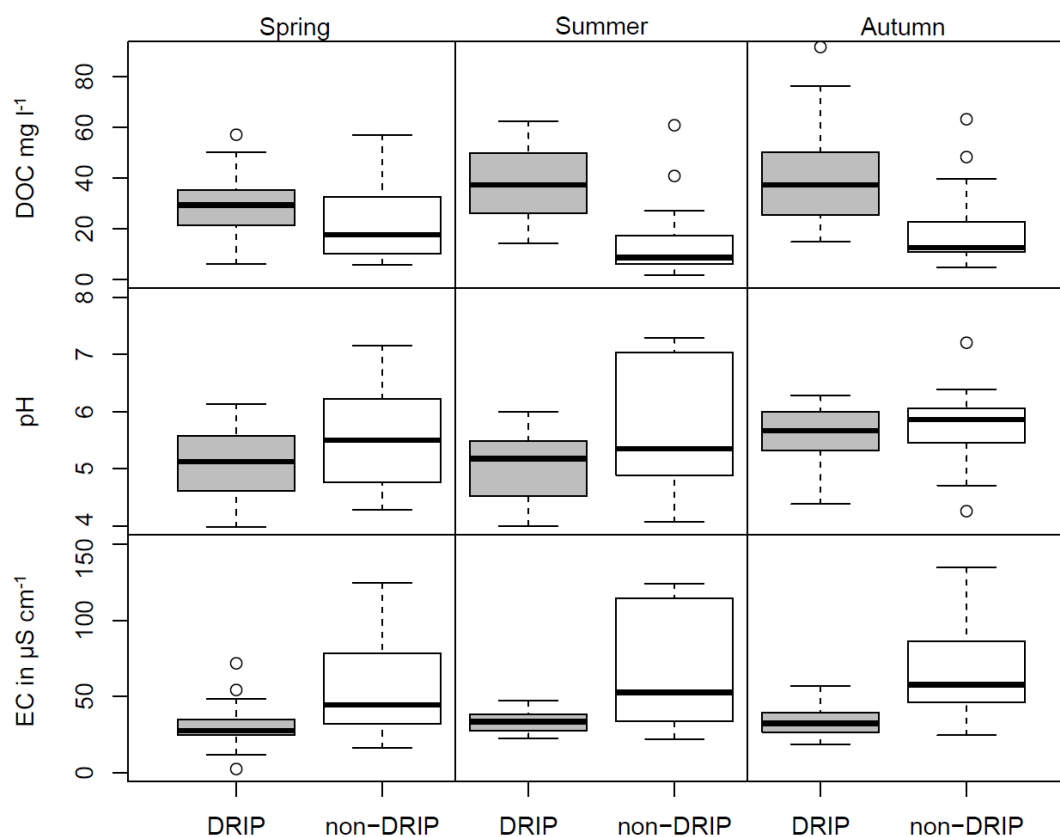
Figure 5 Groundwater chemistry in a seasonal gradient of the riparian wells. In each column DOC, pH and EC are presented for the spring, summer and autumn season. Within each panel DRIP boxplots are presented in grey and non-DRIP boxplots in white.

4 Discussion

5   Our riparian groundwater sampling campaigns demonstrated that on average DOC concentrations in DRIPs were almost twice as high compared to the less hydrologically active riparian areas (non-DRIPs). Groundwater chemistry of DRIPs was more constant from the upland to the riparian zone, and remained relatively stable across seasons compared to non-DRIPs. The groundwater chemistry of non-DRIPs was characterized by 40% higher EC than DRIPs, and increasing variability towards the stream and across seasons. Differences in pH were less distinct, and mostly accountable to seasonal changes. These results

10   confirm our hypothesis that DRIPs have a more DOC-rich groundwater chemistry associated with organic soils, while non-DRIP water can be associated with chemistry originating from mineral soil dominated systems. However, apart from the commonly tested factors, we found that site specific properties play a major role in explaining spatiotemporal variability in the chemistry of groundwater.

15   These findings demonstrated that DRIPs and non-DRIPs appear to be dominated by different processes. The DRIPs already have a distinct DOC-rich groundwater chemistry upland of the near-stream area, high groundwater tables, and typically flat local topographic gradients. They could be considered as cryptic wetlands (Creed et al., 2003), with the exceptional property of linking a large upland area to the riparian zone, and subsequently the stream network. Contrary to that, the non-DRIP transects were characterized by distinct increasing EC, deeper and more fluctuating groundwater tables (Fig. S1), and steeper

20   local topography. These transects resembled the typical riparian hillslopes with vertical chemistry profiles that for example have been studied intensively in this study area (Grabs et al., 2012; Ledesma et al., 2013; Lidman et al., 2017). As such, the large spatial variability in non-DRIP groundwater chemistry supports the idea of dynamic water tables across the riparian zone that drive chemical variability through activation of different soil layers such as the DSL. Our results reflected this through the large temporal variability in non-DRIP groundwater chemistry across seasons. As such riparian groundwater inputs from

non-DRIPs are likely to be most relevant during hydrological events (when groundwater table become increasingly dynamic), while DRIPs provide groundwater inputs both during events and low flow periods.

Our results showed that also without the DRIP/non-DRIP distinction, a significant difference can be found between upland and riparian groundwater in DOC, pH and EC (Table 1, POS). From upland to riparian wells groundwater was enriched in DOC and EC. This demonstrated that existing 2D conceptual models of chemical enrichment across riparian hillslope apply to our well network as well (Ledesma et al., 2018a). However, from a longitudinal point of view along the stream, our distinction of DRIP and non-DRIP transects allowed to further highlight DRIPs as specific areas of interest across the riparian zone-stream interface for groundwater inputs. For seasons (TIME) we also observed significant differences between spring, summer and autumn for pH and EC, and a close to significant difference for DOC (Table 1, TIME). The sampling campaigns represent seasonal snapshots that mostly demonstrate a higher pH and decreased EC in autumn, while summer and spring samplings were, without the distinction of DRIPs and non-DRIPs, similar in pH and EC. However, when we accounted for DRIP and non-DRIP transects more processed-based interpretations can be made. Specifically, we found that during spring flood conditions, the high DOC concentrations in DRIP groundwater decreased 20%, and became less spatially variable. We believe that snowmelt dilution of groundwater is a likely cause for the decreased DOC concentrations during spring, given that the fully screened wells represent groundwater from the entire vertical soil profile, including overland (or over-ice) flow. Furthermore, ice sheet formation in the DRIP areas has been reported previously, which can route water over the ice surface instead of the organic rich subsurface flow paths, such as the DSL (Ploum et al., 2018). These overland-flow findings are similar to dilution effects and soil frost effects reported for wetland dominated streams during spring floods (Laudon et al., 2004a, 2011). In contrast to DRIPs, riparian groundwater in non-DRIP areas increased in DOC and in variability during the snowmelt season (from 17.7 to 21.6 mg/l). This is likely associated with the increase in groundwater level (Fig. S1), and the activation of the dominant source layer in the upper section of the soil (Ledesma et al., 2015). The increased variability could be related to different timing of rising groundwater levels, for example due to local conditions that affect snow melt rates on hillslopes such as shading or sun exposure. As such our sampling campaigns provided a snapshot of the elapse of the snowmelt flood.

With comparison of riparian groundwater chemistry through the DRIP/non-DRIP concept, we have studied two different riparian hydrological connectivity types: DRIPs had hydrological connection with large upslope contributing areas (on average 2.7 ha), and mostly saturated soil conditions (Fig. S1), while non-DRIPs were characterized by draining individual hillslopes (on average 17 m^2) and having lower groundwater levels in the riparian zone (Fig. S1). Earlier work in the study area has demonstrated that the extent of the riparian zone and contributing area play an important role in the available soil carbon pool and the related DOC export from riparian zones to streams (Ledesma et al., 2015). However the latter covers riparian zones with contributing areas that range between 2.5 and 1500 m^2. Between such riparian hillslope contributing areas and initiation of streams (e.g. 10-20 ha), there is a wide range of features that focus water towards the perennial network. Where ephemeral streams are often clear extension of the stream channel, which activate mostly during hydrological events (Ågren et al., 2015), DRIPs have no such stream-like features and should be more associated with the terrestrial landscape than the stream network. Such features have been represented in different landscapes across the world and highlight specific processes such as: groundwater discharge zone, groundwater hotspots, cryptic wetlands, swales, focused seepage, discrete seepage, springs, upwelling zones, preferential discharge, and zero-order basins (Creed et al., 2003; Hayashi and Rosenberry, 2002; Tsuboyama et al., 2000). With the term DRIPs we aimed to fill the gap between riparian hillslopes and (fractal) stream networks as riparian landscape features that have hydrological connection to large upland contributing areas, but lack stream channel formation.

Given the stable DOC concentrations and the large role in stream flow generation (Leach et al., 2017; Ploum et al., 2018), the DRIP concept could potentially be used to scale riparian contributions to headwaters on catchment level (Laudon and Sponseller, 2018). A preliminary analysis showed that 57% of the Krycklan catchment is draining into the stream network through DRIPs, spatially covering only 12% of the riparian zone (preliminary analysis in supplementary material). However, the topography driven approach behind our DRIP concept might miss certain contributions that are not necessarily related to surface topography, especially in areas where phreatic aquifers are not underlain by till deposits, or on scales that surpass the headwater basins (Devito et al., 2005). Previous work has demonstrated that in boreal catchments the input of deeper/older groundwater (with high EC) increases with drainage area, up to a threshold where old and new groundwater input reach a balance (Peralta-Tapia et al., 2015). Future work could be directed towards further chemical analysis of DRIPs and non-DRIPs and their role in groundwater-surface water interactions throughout the catchment. Although the visible effect of DRIPs on streams likely decreases in higher order streams, links between hydrological pathways on groundwater chemistry dynamics have been found to significantly affect the chemistry of a fifth order river (Carlyle and Hill, 2001). Further, flow paths known as watertracks have been shown as important biogeochemical controls on higher order Arctic rivers (Harms and Ludwig, 2016; McNamara et al., 1999).

Spatial characterization of groundwater chemistry has been studied as an integrated signal of the phreatic aquifer (Kiewiet et al., 2019), but also using piezometers or lysimeters at specific depths, to depict vertical chemical profiles (Grabs et al., 2012; Lidman et al., 2017). Our approach was considered to represent a mixture of riparian groundwater that is likely to flow into the stream during various hydrological conditions. Where the aforementioned studies relate vertical water chemistry profiles to water level fluctuations to obtain process-based understanding, our study focused on finding patterns in generalizable factors such as spatial distributions (upland to riparian), different seasons (spring, summer and autumn) and hydrological connectivity. In that way, our study can be contextualized as an approach that potentially allows characterization of control points in the landscape with use of minimal information. The relative contributions and biogeochemical characteristics of DRIPs and non-DRIP riparian zones in the longitudinal dimension, can potentially be combined with models that specify vertical profiles of groundwater chemistry, such as the RIM model (Seibert et al., 2009). As such we can identify within the riparian zone which parts exert a large control on stream water quality and quantity.

Along the stream networks, the delineation of DRIP/non-DRIP areas in the riparian zone can help to implement hydrologically adapted buffers in forest management, ensuring that waterbodies maintain a good water quality (Kuglerová et al., 2014b; Tiwari et al., 2016; Wallace et al., 2018). Traditionally, forest practices considered fixed width buffers even though the riparian function is not homogeneous around all water bodies (Buttle, 2002). Besides the extent of the riparian soils (Ledesma et al., 2018b), species richness within the RZ (Kuglerová et al., 2014a), and the extent of (ephemeral) stream networks (Ågren et al., 2015), our results support that variable widths should be considered in riparian buffer management. We found that DRIP water had already a distinct chemical signature before entering the RZ: 80% of the DOC originated from upland riparian wells. This suggests that the chemical role that is associated with RZ's, extends further away from the stream than the traditional fixed-width buffer management considers.

For identification of control points, improving hydrological models, and sustainable forest management practices, a binary approach with little need of local properties can be a very useful tool. However, to understand the underlying mechanisms and the link to the landscape, hydrology of RZ's should be considered non-binary (Klaus and Jackson, 2018). Our LMM's showed that a large part of the variance is explained by the random effects, which contain information regarding the unique properties of individual transects and to a lesser extent the subcatchments. The large variation in non-DRIPs leads to statistically weak contrasts, but this does not mean non-DRIP RZ's are less important. It demonstrated that an important chemical change also

occurs in riparian non-DRIP areas, but their complexity overpassed the binary simplifications we have made in this study design. To explain the variance that was accounted for using random factors, it could be of interest to further analyze local landscape characteristics, subsurface soil properties and groundwater level dynamics to decipher whether soil, biology or hydrology define biochemical characteristics throughout the RZ.

5 Conclusions

Are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest? Yes, based on our findings there is a strong link between the hydrological pathways in the riparian zone, and the DOC concentrations of riparian groundwater. At the confluence of hydrological pathways in the riparian zone, discrete riparian inflow points (DRIPs), we found groundwater with an organic-rich, relatively stable chemistry, compared to the remaining, drier riparian areas. Importantly, DRIPs seem to be supplying this chemically distinct groundwater independently of time and space. Combining the organic-rich chemical characteristic and dominant hydrological contributions to headwaters, DRIPs fulfill a specific role in explaining longitudinal variability of DOC concentrations along stream reaches. We propose that DRIPs can be *control points* in the boreal riparian forest for the transport of carbon to small streams. To our knowledge, this study is the first to characterize spatial groundwater chemistry that a priori incorporated hydrological pathways in the study design.

However, to fully evaluate the impact of DRIPs on stream water generation and the associated stream chemistry, there is the need to further investigate the hydrological activation, and a broader chemical characterization. To understand the mechanisms and processes that link hydrological pathways and groundwater chemistry in boreal forest, we suggest to move towards non-binary approaches incorporating groundwater fluctuations, soil properties and landscape characteristics.

Data availability

Data is available upon reasonable request through the first author (stefan.ploum@slu.se). Krycklan data is openly available through the Svartberget database: https://franklin.vfp.slu.se/

Author contributions

LK and HL conceptualized the study design and methodology, supervised data analysis, interpretation and writing process. AP conducted the well installation, provided field support, reviewed the written text and was involved in discussions. SP was responsible for collection of data and data analysis, figures, interpretation and writing and revision of the manuscript.

Competing interests

HL is a member of the editorial board of this special issue of Hydrology and Earth System Sciences.

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References

Ågren, A., Lidberg, W., Strömgren, M., Ogilvie, J. and Arp, P.: Evaluating digital terrain indices for soil wetness mapping–a Swedish case study, Hydrology and Earth System Sciences, 18(9), 3623–3634, 2014.

Ågren, A., Lidberg, W. and Ring, E.: Mapping temporal dynamics in a forest stream network—implications for riparian forest management, Forests, 6(9), 2982–3001, 2015.

Barton, K.: Multi-model inference. R package MuMIn version 1.10. 5, 46,, 2014.

Bates, D. and Maechler, M.: lme4: Linear mixed-effects models using S4 classes (R package version 0.999375–31)[Computer software],, 2009.

Bates, D., Mächler, M., Bolker, B. and Walker, S.: Fitting linear mixed-effects models using lme4, arXiv preprint arXiv:1406.5823, 2014.

Bernhardt, E. S., Blaszczak, J. R., Ficken, C. D., Fork, M. L., Kaiser, K. E. and Seybold, E. C.: Control Points in Ecosystems: Moving Beyond the Hot Spot Hot Moment Concept, Ecosystems, 20(4), 665–682, 2017.

Beven, K. J. and Kirkby, M. J.: A physically based, variable contributing area model of basin hydrology/Un modèle à base physique de zone d'appel variable de l'hydrologie du bassin versant, Hydrological Sciences Journal, 24(1), 43–69, 1979.

Bishop, K., Buffam, I., Erlandsson, M., Fölster, J., Laudon, H., Seibert, J. and Temnerud, J.: Aqua Incognita: the unknown headwaters, Hydrological Processes, 22(8), 1239–1242, 2008.

Blackburn, M., Ledesma, J. L., Näsholm, T., Laudon, H. and Sponseller, R. A.: Evaluating hillslope and riparian contributions to dissolved nitrogen (N) export from a boreal forest catchment, Journal of Geophysical Research: Biogeosciences, 122(2), 324–339, 2017.

Briggs, M. A. and Hare, D. K.: Explicit consideration of preferential groundwater discharges as surface water ecosystem control points, Hydrological Processes, 32(15), 2435–2440, 2018.

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

Burgin, A. J. and Groffman, P. M.: Soil O2 controls denitrification rates and N2O yield in a riparian wetland, Journal of Geophysical Research: Biogeosciences, 117(G1), 2012.

Buttle, J.: Rethinking the donut: the case for hydrologically relevant buffer zones, Hydrological Processes, 16(15), 3093–3096, 2002.

Carlyle, G. and Hill, A.: Groundwater phosphate dynamics in a river riparian zone: effects of hydrologic flowpaths, lithology and redox chemistry, Journal of Hydrology, 247(3-4), 151–168, 2001.

Cirmo, C. P. and McDonnell, J. J.: Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review, Journal of Hydrology, 199(1-2), 88–120, 1997.

Corwin, D. and Lesch, S.: Apparent soil electrical conductivity measurements in agriculture, Computers and electronics in agriculture, 46(1-3), 11–43, 2005.

Creed, I., Sanford, S., Beall, F., Molot, L. and Dillon, P.: Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes, Hydrological Processes, 17(18), 3629–3648, 2003.

Davies-Colley, R. J. and Rutherford, J. C.: Some approaches for measuring and modelling riparian shade, Ecological Engineering, 24(5), 525–530, 2005.

Devito, K., Creed, I., Gan, T., Mendoza, C., Petrone, R., Silins, U. and Smerdon, B.: A framework for broad-scale classification of hydrologic response units on the Boreal Plain: is topography the last thing to consider?, Hydrological processes, 19(8), 1705–1714, 2005.

Grabs, T., Bishop, K., Laudon, H., Lyon, S. W. and Seibert, J.: Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports, Biogeosciences, 9(10), 3901–3916, 2012.

Harms, T. K. and Ludwig, S. M.: Retention and removal of nitrogen and phosphorus in saturated soils of arctic hillslopes, Biogeochemistry, 127(2-3), 291–304, 2016.

Hayashi, M.: Temperature-electrical conductivity relation of water for environmental monitoring and geophysical data inversion, Environmental monitoring and assessment, 96(1-3), 119–128, 2004.

Hayashi, M. and Rosenberry, D. O.: Effects of ground water exchange on the hydrology and ecology of surface water, Groundwater, 40(3), 309–316, 2002.

Hotchkiss, E., Hall Jr, R., Sponseller, R., Butman, D., Klaminder, J., Laudon, H., Rosvall, M. and Karlsson, J.: Sources of and processes controlling CO_2 emissions change with the size of streams and rivers, Nature Geoscience, 8(9), 696, 2015.

Hunsaker, C. T. and Levine, D. A.: Hierarchical approaches to the study of water quality in rivers, BioScience, 45(3), 193–203, 1995.

Jencso, K. G., McGlynn, B. L., Gooseff, M. N., Wondzell, S. M., Bencala, K. E. and Marshall, L. A.: Hydrologic connectivity between landscapes and streams: Transferring reach-and plot-scale understanding to the catchment scale, Water Resources Research, 45(4), 2009.

Kiewiet, L., Freyberg, J. von and Meerveld, H. van: Spatiotemporal variability in hydrochemistry of shallow groundwater in a small pre-alpine catchment: the importance of landscape elements, Hydrological Processes, 2019.

Kirchner, J. W.: A double paradox in catchment hydrology and geochemistry, Hydrological processes, 17(4), 871–874, 2003.

Klaus, J. and Jackson, C. R.: Interflow Is Not Binary: A Continuous Shallow Perched Layer Does Not Imply Continuous Connectivity, Water Resources Research, 54(9), 5921–5932, 2018.

Kuglerová, L., Jansson, R., Ågren, A., Laudon, H. and Malm-Renöfält, B.: Groundwater discharge creates hotspots of riparian plant species richness in a boreal forest stream network, Ecology, 95(3), 715–725, 2014a.

Kuglerová, L., Ågren, A., Jansson, R. and Laudon, H.: Towards optimizing riparian buffer zones: Ecological and biogeochemical implications for forest management, Forest Ecology and Management, 334(15), 74–84, 2014b.

Laudon, H. and Sponseller, R. A.: How landscape organization and scale shape catchment hydrology and biogeochemistry: insights from a long-term catchment study, Wiley Interdisciplinary Reviews: Water, 5(2), e1265, 2018.

Laudon, H., Seibert, J., Köhler, S. and Bishop, K.: Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff, Water resources research, 40(3), 2004a.

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

Laudon, H., Sjöblom, V., Buffam, I., Seibert, J. and Mörth, M.: The role of catchment scale and landscape characteristics for runoff generation of boreal streams, Journal of Hydrology, 344(3-4), 198–209, 2007.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M. and Köhler, S.: Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling, Ecosystems, 14(6), 880–893, 2011.

Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M. and Bishop, K.: The Krycklan Catchment Study—a flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape, Water Resources Research, 49(10), 7154–7158, 2013.

5 Lavoie, M., Paré, D., Fenton, N., Groot, A. and Taylor, K.: Paludification and management of forested peatlands in Canada: a literature review, Environmental reviews, 13(2), 21–50, 2005.

Leach, J., Lidberg, W., Kuglerová, L., Peralta-Tapia, A., Ågren, A. and Laudon, H.: Evaluating topography-based predictions of shallow lateral groundwater discharge zones for a boreal lake-stream system, Water Resources Research, 53(7), 5420–5437, 2017.

Ledesma, J., Grabs, T., Futter, M., Bishop, K. H., Laudon, H. and Köhler, S.: Riparian zone control on base cation concentration in boreal streams, Biogeosciences, 10(6), 3849–3868, 2013.

10 Ledesma, J., Kothawala, D. N., Bastviken, P., Maehder, S., Grabs, T. and Futter, M.: Stream dissolved organic matter composition reflects the riparian zone, not upslope soils in boreal forest headwaters, Water Resources Research, 54(6), 3896–3912, 2018a.

Ledesma, J. L., Grabs, T., Bishop, K. H., Schiff, S. L. and Köhler, S. J.: Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments, Global change biology, 21(8), 2963–2979, 2015.

Ledesma, J. L., Futter, M. N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R. A., Laudon, H., Bishop, K. H. and Köhler, S. J.: Towards
15 an improved conceptualization of riparian zones in boreal forest headwaters, Ecosystems, 21(2), 297–315, 2018b.

Lenth, R. V. and others: Least-squares means: the R package lsmeans, Journal of statistical software, 69(1), 1–33, 2016.

Lidman, F., Boily, Å., Laudon, H. and Köhler, S. J.: From soil water to surface water–how the riparian zone controls element transport from a boreal forest to a stream, Biogeosciences, 14(12), 3001, 2017.

Lupon, A., Denfeld, B. A., Laudon, H., Leach, J., Karlsson, J. and Sponseller, R. A.: Groundwater inflows control patterns and sources of
20 greenhouse gas emissions from streams, Limnology and Oceanography, 2019.

McGlynn, B. L. and McDonnell, J. J.: Quantifying the relative contributions of riparian and hillslope zones to catchment runoff, Water Resources Research, 39(11), 2003.

McNamara, J. P., Kane, D. L. and Hinzman, L. D.: An analysis of an arctic channel network using a digital elevation model, Geomorphology, 29(3-4), 339–353, 1999.

25 O'Callaghan, J. F. and Mark, D. M.: The extraction of drainage networks from digital elevation data, Computer vision, graphics, and image processing, 28(3), 323–344, 1984.

Penna, D., Van Meerveld, H., Zuecco, G., Dalla Fontana, G. and Borga, M.: Hydrological response of an Alpine catchment to rainfall and snowmelt events, Journal of hydrology, 537, 382–397, 2016.

Peralta-Tapia, A., Sponseller, R. A., Ågren, A., Tetzlaff, D., Soulsby, C. and Laudon, H.: Scale-dependent groundwater contributions
30 influence patterns of winter baseflow stream chemistry in boreal catchments, Journal of Geophysical Research: Biogeosciences, 120(5), 847–858, 2015.

Ploum, S. W., Leach, J. A., Kuglerová, L. and Laudon, H.: Thermal detection of discrete riparian inflow points (DRIPs) during contrasting hydrological events, Hydrological Processes, 32(19), 3049–3050, 2018.

Rocher-Ros, G., Sponseller, R. A., Lidberg, W., Mörth, C.-M. and Giesler, R.: Landscape process domains drive patterns of CO2 evasion
35 from river networks, Limnology and Oceanography Letters, 2019.

Saarenketo, T.: Electrical properties of water in clay and silty soils, Journal of applied geophysics, 40(1-3), 73–88, 1998.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M. and Bishop, K.: Linking soil-and stream-water chemistry based on a Riparian Flow-Concentration Integration Model, Hydrology and earth system sciences, 13(12), 2287–2297, 2009.

Smith, D. G.: Effect of vegetation on lateral migration of anastomosed channels of a glacier meltwater river, Geological Society of America
40 Bulletin, 87(6), 857–860, 1976.

Tetzlaff, D. and Soulsby, C.: Sources of baseflow in larger catchments–Using tracers to develop a holistic understanding of runoff generation, Journal of Hydrology, 359(3-4), 287–302, 2008.

Tiwari, T., Lundström, J., Kuglerová, L., Laudon, H., Öhman, K. and Ågren, A.: Cost of riparian buffer zones: A comparison of hydrologically adapted site-specific riparian buffers with traditional fixed widths, Water Resources Research, 52(2), 1056–1069, 2016.

45 Tsuboyama, Y., Sidle, R. C., Noguchi, S., Murakami, S. and Shimizu, T.: A zero-order basin—Its contribution to catchment hydrology and internal hydrological processes, Hydrological Processes, 14(3), 387–401, 2000.

Vidon, P. G.: Not all riparian zones are wetlands: Understanding the limitation of the "wetland bias" problem, Hydrological Processes, 31(11), 2125–2127, 2017.

Wallace, C., McCarty, G., Lee, S., Brooks, R., Veith, T., Kleinman, P. and Sadeghi, A.: Evaluating Concentrated Flowpaths in Riparian Forest Buffer Contributing Areas Using LiDAR Imagery and Topographic Metrics, Remote Sensing, 10(4), 614, 2018.

Tables

Table 1 Summary of statistics from LMM models for DOC, pH and EC. The three columns show the response variables DOC, pH, and EC. The upper two rows show the marginal and conditional coefficient of determination (R^2_{mar} and R^2_{con}), which explain variance by the fixed effects, and the variance by the fixed and random effects together. For each explanatory variable and the interaction with HP, the p-value and F-statistic is presented. HP differentiates between DRIP and non-DRIPs. POS represents the three positions in along transects being: riparian, transition and upland. TIME represents the three different seasons when sampling has taken place: spring, summer and autumn. Significant codes: p< 0.001 '***', 0.001<p<0.01 '**', 0.01<p<0.05 '*', 0.05<p<0.1 '.', p>0.1 '-'. Explanatory variables with a 'variable1:variable2' represent the interaction between both variables.

		DOC	pH	EC
R^2_{mar}		0.22	0.13	0.21
R^2_{con}		0.68	0.55	0.70
HP	p-value	0.012 (*)	0.20 (-)	0.052 (.)
	F	8.47	1.99	4.36
POS	p-value	<0.0001 (***)	0.0001 (***)	<0.001 (***)
	F	10.02	9.24	7.08
TIME	p-value	0.054 (.)	<0.0001 (***)	<0.0001 (***)
	F	2.95	13.48	11.31
HP:POS	p-value	0.18 (-)	0.11 (-)	<0.001 (***)
	F	1.70	2.24	32.11
HP:TIME	p-value	<0.0001 (***)	0.75 (-)	0.49 (-)
	F	12.07	0.288	0.72