Dear Editor,

Thank you for considering this revised manuscript. We provide here a summary of the major changes in form a bullet-point list.

- We have specified the title, research question and overall emphasis towards DOC in riparian groundwater, instead of the earlier used "spatial variability in groundwater".
- We have revised the methods section such that it contains more hydrogeological background and information about the well infrastructure. We added in the supplementary materials an example of groundwater level data to demonstrate how DRIP and non-DRIP differ from each other.
- We have clarified the definition of DRIPs in the introduction, methods and discussion, and elaborated on the differences to the rest of the riparian zone, and ephemeral streams.
- We rewrote the discussion and removed the speculations about implications for stream chemistry. Instead we have focused on contextualizing our findings to other work related to riparian groundwater.

In the section below we answer the review comments one by one in red, and provide the manuscript with tracked changes

Page numbers and lines refer to the revised manuscript without tracked changes.

General comment

This is a concise paper that compares groundwater chemistry in sub-catchments of the Kryckland observatory and asks questions about chemical variability in relation to hydrological pathway. The paper is written in a clear and concise way with not much to complain about in the introduction and results. The paper clearly shows and describes the variability of groundwater chemistry in relation to its hydro- logical activity. This is a very relevant result that is worth being published in HESS.

Answer: Thank you for evaluating the manuscript and the constructive commentary. Below we will present responses in red to each point that is addressed.

However, I have some point of criticism that should be addressed: Groundwater was sampled with fully screened wells which means that there is an unknown integration of water quality over depth potentially changing between sampling campaigns. The authors should carefully discuss the pros and cons of this approach.

Answer: We agree with Referee #1. We extended section 2.2, for example:

P5, L20: "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)."

and added a paragraph in section 4 (Discussion P10, L39, see below).

Later on in the text there seems to be a not-outspoken assumption of vertical homogeneity of groundwater quality and a high weight on lateral heterogeneity. This needs to be made more clear and concise as this new DRIP-concept seems to stand against the former RIM- (Seibert et al. 2009) and DSL-concepts (Ledesma et al. 2015) that were derived from the same study site.

Answer: We agree that further elaboration was needed, in combination with the previous comment, regarding the vertical heterogeneity in the groundwater quality and the associated RIM and DSL concepts. Our study could be considered complimentary to the existing literature, rather than opposing. To clarify this we changed the introduction, for example:

P2, L21: "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)."

P3, L16: "Also the RIM model has provided a framework to infer groundwater chemistry profiles from stream chemistry (Seibert et al., 2009)."

In the discussion we have added a section starting P10, L31, in which we address the following on L39:

"In that way, our study can be contextualized as an approach that potentially allows characterization of control points in the landscape with use 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. "

The authors used linear mixed-effect models (LMM) to analyze spatiotemporal patterns of groundwater chemistry. There should be some effort in the text to justify the choice of this method and also on the choice of predictors. One could argue that the authors did not look hard enough to include other predictors (e.g. local TWI) but instead chose a method which can handle random effects from unaccounted factors.

Answer: The use of LMM was justified by the setup of the groundwater well network. Given that this is, to our knowledge, the first groundwater chemistry database that has been designed and compiled a priori based on three factors (hydrological pathways, distance to stream and season), we deem those factors as our only true testable factors. Since the study sites were selected partly based on TWI, TWI and DRIP vs. non-DRIP are inherently correlated. Given the large improvement of the model by the inclusion of random factors which are describing spatial dependency of the samples, we discussed that there is a large part of spatial variability in groundwater chemistry left to be explained by factors that are not included by our study. We deliberately attempted to explain groundwater chemistry in a simple manner with generic and a priory set predictors, and explaining variability by unique properties of the study sites would impair any upscaling of our findings.

Finally, I have a major concern with the discussion section that is rather an implication section centered on the question what the varying groundwater quality would mean for stream chemistry. However, this was not part of the study design. So the discussion should rather be focused around the question, why the measured groundwater quality was different in different parts of the riparian zone.

Answer: We agree that the discussion was rather speculative and conceptual. We have rewritten the discussion section (P9 to P11), with the aim to have a balanced interpretation of our findings with other groundwater-based studies, and reduced speculations regarding implications for streams.

What came into my mind here: Aren't DRIPs just an extension of the fractal stream network into the catchment. DRIPs are along topographic depressions funneling water flow in the same way as the stream network. The major difference is that they are not (permanent) pathways of surface flow but rather pathways of shallow subsurface flow. Maybe I missed that connection in earlier studies that were cited here. I however very much like the idea to refine the view on riparian zone by that type of concepts focused around major flowpaths.

Answer: We agree that in a sense DRIPs could be considered a part of the stream network especially during a high flow conditions. However, it is in our eyes essential to consider not only the hydrological definition but also the biogeochemical definition. And for the latter, the most important property of DRIPs is the highly organic substrate, and the generally high water tables. This is something that is not typical for stream channels and therefore we would argue that they are a unique landscape feature.

In essence I support this manuscript but ask for a substantial revision of the discussion section and a better justification of field and statistical methods.

Answer: Thank you for the constructive comments.

Specific comments Abstract:

L13: This sentence is potentially misleading. What is meant by chemical variability in the riparian boreal forest? The linkage of riparian groundwater as described beforehand forest is not clear.

Answer: The sentence was:

"Given the important chemical function of the riparian zone, we therefore ask the question: are hydrological pathways and chemical variability linked in the riparian boreal forest?"

We changed this section and now the related sentence is formulated (P1, L18):

"We therefore ask the question: are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest?"

L20: The pairing of hydrological connection and groundwater condition cannot be understood here. Can you find a more telling factor name?

Answer: We changed the factor name to HP, hydrological pathways (P6, L24).

L20: The water provided by DRIPS – is that surface water discharging from the DRIP or groundwater within the DRIP?

Answer: Combined with the short comment we realized our definition of DRIPs was not clear and raised confusion. DRIPs are discharging groundwater from the shallow subsurface. During events the watertable can rise above the surface and have a surface water like appearance. As such they are not surface waters, or part of the stream channel. We have included a picture in the supplementary materials to clarify what DRIPs look like in the landscape (Fig. S2).

L23: "chemically more stable" may be misleading. Do you mean spatially and/or temporally homogeneous?

Answer: We have adopted the suggestion.

Introduction

P2L1: While I in general like such comparisons the idea of headwaters as "capillaries" was not immediately clear to me.

Answer: We rephrased the sentence to:

"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."

P3L10-13: These two sentences need some references.

Answer: These sentences were changed to:

"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). "

Methods

Fig. 2: The catchment delineation is somewhat distracting. I suggest to limit the catchment boundaries to the catchment with studied DRIPs/ nonDRIPs. What determines the catchment outlet? A gauging station? Maybe show them to make clear that this was not completely arbitrarily chosen.

Answer: We have updated the figure. The gauging station at the outlet was indicated and catchment boundaries removed.

P5L6: TWI units are not [ha] – what do you mean by "topographic wetness index (2 ha threshold)"?

Answer: This section was changed to:

P5,L7: "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). 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."

P6L1: Can you specify the wells in terms of diameter and material? What is the meaning of a groundwater sample taken in a fully screened well? Do you expect this to be a representative sample from all depths or rather a sample from the most conductive depth? In the latter case the depths where most water is coming from may change over time with changing groundwater levels. I would like to see a critical evaluation of your sampling design and drawbacks (assets?) of the chosen methods! The methods chapter is likely not the right place.

Answer: We have changed section 2.2 to include more details about the well installations P5L15-P6L3. In combination with the earlier suggestion to change the discussion, we included a section covering different approaches (P10L31).

Results

P7L4: I don't understand why you jump in directly with that statement in the second sentence already.

Answer: We have restructured the paragraph (P7L3).

P7L26: Did you expect more distinct differences? Keep in mind that the pH is a logarithm of concentrations and small changes can mean a lot compared to DOC and EC.

Answer: In earlier work the soil pH in DRIPs were found to be distinctly higher as non-DRIPs, which was expected to be reflected in the groundwater pH (Kuglerová et al., 2014). We were aware of the pH scales sensitivity but expected perhaps more distinct differences given the field-based observations of DRIP and non-DRIP riparian areas.

P8L16: When you talk about seasonality you mean factor TIME, right? It would be helpful to stick to those factor names and provide it in brackets if other words such as seasonality are used.

Answer: We have added TIME in brackets where we used seasonality or other terms that refer to the TIME factor in section 3.

Fig. 4: I suggest that you indicate if the mean is significantly differing in individual panels. That would improve readability here. Same is true for Fig. 3 and 5

Answer: The box plots show medians and p-values would be computed by means. Although we do provide a p-value for the Figure 3 box plots, this is a general statistic that does not do justice to the complexity of the dataset. Figures 3-5 are mostly aiming to show the elapse in variability over space and time, rather than proving significant differences at the individual plot or season level.

Discussion

The discussion makes strong links of groundwater spatial variability to stream chemistry temporal variability. But this is not what was shown in the results. I miss a discussion of why groundwater quality was as it was measured and presented above. All the discussion is rather focusing on implications.

Answer: We have rewritten the discussion section and reduced the speculations regarding stream implications (P9-P11).

P9L23 to P10L3: I have problems following the argumentation here. Why does the contrasting chemistry of DRIPS and non-DRIPS explains why pre-event water is quickly mobilizes? Do we really need DRIPS and non-DRIPS to explain temporal variability of stream chemistry within an event? That is also covered by vertical chemical heterogeneity (taking Seibert's RIM for instance).

Answer: We argued that the vertical chemical heterogeneity is still valid, but that in a horizontal plane the hydrological conditions (or storage state) of the riparian zone are dominating the way this vertical chemical heterogeneity is translated to lateral contributions to streams. For DRIPs the mobilization can be extremely fast since there is no unsaturated zone to store more water. In contrast, non-DRIPs are presumably delayed in response due to the vertical infiltration and rise of groundwater tables before a contribution to the stream is initiated. In combination with previous comments we have included more explicitly the DSL and RIM concepts in the discussion.

P10L26: The generalization (that totally make sense) of your findings to the larger scale of the Kryckland catchment is a selling point. I suggest to base the statement made here on DRIPS in catchments on a sound and reproducible analysis and not on a personal communication.

Answer: The statement was based on a reproducible analysis which we provided in the supporting material.

I have reviewed the draft manuscript: 'Are hydrological pathways and variability in groundwater chemistry linked in the riparian boreal forest?' submitted by Ploum et al for possible publication in HESS. I like the general premise of this study, eg that preferential flowpaths from hillslopes through riparian zones need to be better considered when characterizing the baseflow controls on stream chemistry and dissolved organic carbon availability (DOC). Too many riparian studies are based around 'uniformed' or random piezometer transect designs, and without the hydrological flow context, the groundwater chemistry data are difficult to interpret. I do think this material is appropriate for HESS, though the paper could benefit from a change in emphasis and additional heat tracing data that it seems the authors may have already collected.

Answer: Thank you for reviewing the manuscript and providing constructive suggestions to improve the manuscript.

Currently, the primary question addressed by the study is posed as: 'Are hydrological pathways and variability in groundwater chemistry linked in the riparian boreal forest?' There have been many studies to document strong variance in groundwater chemistry as controlled by varied advective flowpaths, too numerous to list here. The current study by Ploum and all is unique from many of these as the preferential flowpaths in question source varied dissolved constituents to headwater streams. I suggest the authors refocus the main question to something like: 'Do DRIP's represent preferential conduits of DOC-rich groundwater to headwater streams in a boreal forest?' Or something at least more specific to this study than 'variability in groundwater chemistry'. It seems that the most compelling data presented in this study show the 'DRIPs' in this boreal headwater system are enriched in DOC, which presumably results in higher flux of DOC to the channel via preferential shallow groundwater discharge compared to more diffuse flow through till (though hydrological fluxes are not actually measured or inferred here). Further, the authors document interesting temporal trends in DOC and SpC, the latter being much less meaningful without additional chemical characterization.

Answer: We have changed the title and research question to "Are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest?"

In general, I feel the LMM statistical analysis was appropriate for assessing DRIP/non DRIP well DOC, pH, and EC. The results between these binary classifications are interesting, though for all the effort on well installation and sample collection some basic hydrological data seem missing. Where lateral gradients measured between wells and the stream? Were any hydraulic conductivity tests performed? Do we have any idea of groundwater flow rate/flux to the stream from DRIP vs non-DRIP zones? This is a flowpath-based study but the reader is left without any real flow-based hydrogeological information. The addition of some basic quantitative hydrogeological data, and perhaps some additional measured parameters such as dissolved oxygen, could have nicely increased the impact of this study.

Answer: We had no comprehensive groundwater flux data to quantify flow from DRIPs and non-DRIPs. A few hydraulic conductivity tests were performed under summer low flow conditions in 4 DRIP wells, but we did not deem this representative to use in the study. Instead we have provided more hydrological background information in section 2.2 (P5L15) and Figure S1.

In addition to that, previous work has shown that continuous saturated conditions occur in the DRIPs and that topographic gradients are low (Kuglerová et al., 2014). Also DEM based flow accumulation

model and in-stream measurements indicate that DRIPs provide disproportionally large water contributions, but they remain difficult to quantify and their detectability varies throughout various events (Leach et al., 2017; Lupon et al., 2019; Ploum et al., 2018).

Without any evaluation of piezometer water age (eg dissolved gas-, isotope-based) the discussion of old vs new water contributions is highly speculative and should be scaled back. I really like the concept you put forth of DRIPs as drivers of younger water fractions in streams where low permeability soils dominate (eg tills), though it is difficult to support this using EC as the primary parameter. Despite these criticisms I do think this work could make an important addition to HESS after some revision considering the major comments below and that of the other reviewers.

Answer: We agree that our young-old water discussion was speculative and this part of the discussion is replaced by comparisons to existing riparian groundwater concepts.

The statement is made toward the end of the Introduction: 'However, in order to determine whether DRIPs matter for stream biogeochemistry, chemical characterization of the discharging groundwater is needed.' Yes, but this is only half of the equation, the other being the flux of groundwater to the stream which was not evaluated here in any way. It seems at least some data specific to groundwater discharge was collected in these streams and presented by Ploum et al 2018. Where many of the DRIPs instrumented here with piezometers identified in the stream as preferential discharge points using heat tracing? If so that data could be briefly included here with an additional figure, and go a long way to convincing the reader that the wet topographic low points mapped here as DRIPs are actual preferential flowpaths from the hillslope to the stream. Without any such thermal or hydrological gradient/permeability data it is difficult to accept with confidence that the DRIPs mapped here are actual preferential flow zones, compared to the surrounding soils. To be clear I think that the hydrogeologic interpretation of DRIPs made by the authors is likely generally correct, particularly after reading/watching Ploum et al 2018, but the current paper would benefit greatly from some groundwater flow-based data.

Answer: We agree with referee #2 that anomalies in groundwater chemistry without hydrological fluxes have limited meaning for streams. However for this study we argue that there is already sufficient support to assume that the studied DRIPs have important implications for stream chemistry, which would be undetectable if hydrological fluxes were no different than non-DRIP riparian zones. The earlier work on our DRIP sites showed that the DRIPs provide the majority of the lateral fluxes to the stream using thermal and isotope stream signatures (Leach et al., 2017). Although this study also demonstrated that the fluxes are difficult to match with contributing areas of the DRIPs, biogeochemically the DRIPs alter streams such that observable differences have been reported in gas fluxes as a result of stream processes (Lupon et al., 2019). This leads us to believe that, although we currently have no reported hydrological fluxes of all the studied DRIPs, they can be considered as the dominant lateral hydrological fluxes to the stream. We have added exemplar groundwater level data in Fig S1.

I list several more major comments below (I realize some are a bit redundant with this narrative) followed by some more minor text suggestions:

1. A main conclusion of this work is stated as: 'We concluded that hydrological pathways and spatial variability in groundwater are linked, and that DRIPs are important control points in the boreal landscape.' Can you build on this statement in the abstract to be more specific to your study? Near stream shallow chemical variability has long been linked to flowpaths. Perhaps comment more specifically in the abstract regarding the spatial variability you observed to set your work apart from previous studies. The Results section discusses some temporal patterns, but I do not see this data reflected in any of the figures or tables. You could develop a figure specific to the interesting temporal patterns, this information is shown somewhat in Table 1 'TIME' variable analysis but could be shown more explicitly. Also, I think the fact that your research indicates DRIPs our important DOC pathways to the boreal stream corridor is quite important.

Answer: We have specified our research question towards DOC, as that is the major component of our analysis and our interpretations. The temporal patterns referred to the differences between seasons, which we added as a discussion section starting P9L14.

2. Under your definition, are DRIPs only driven by surface topography and wetness? There are numerous instances of preferential discharge of groundwater and interflow through the riparian zone through highly permeable sediments that are not correlated with surface topography, and in glacial sediments often occur at local topographic high points (sand and gravel deposits transecting the riparian zone). I agree that local topographic depressions often lead to saturated conditions in the riparian zone, but that is not the same thing as strong hydrologic connectivity to the stream channel, which depends on the combination of lateral gradient and sediment permeability. Previous work by this group (Ploum et al 2018) used heat tracing methodology to locate/confirm preferential discharge of riparian water to the stream channel, which makes sense. However the current work does not seem to tie the definition of DRIP to actual observed high-discharge points, which I think is unfortunate. Not all saturated depressions will be points of preferential discharge to the channel, which strongly depends on soil permeability. Further, according to your statement: 'water in DRIPs travels a longer distance horizontally; in presumably wet, highly permeable, organic rich soil." It seems your definition of DRIP is relatively narrow, and based around forested headwaters similar to where your study has been conducted. I think it would be quite helpful for you to more specifically define 'DRIP' early in the manuscript (in the Introduction), and acknowledge that this definition applies to only a subset of preferential riparian groundwater discharge zones in headwater systems. Your broad definition of DRIP in section 2.2 (eg 'groundwater discharge zone, groundwater hotspots, cryptic wetlands, swales, focused seepage, discrete seepage, springs, upwelling zones, preferential discharge, ephemeral streams and zero-order streams') does not seem to apply to the functional definition you apply here for shallow lateral flow above the mineral soil horizon, so please be clear on what definition you are using for this study.

Answer: We have removed the DRIP definition section and refer to DRIPs from the introduction P3L5 onwards. In section 2.2 we have added data that clarifies that the difference in contributing area is a major property of DRIPs that makes is distinctly different from other saturated riparian areas that may not have large contributing areas (P5L7). We have also clarified in the discussion (P9L1) that DRIPs can be seen as a landscape feature that is distinctly different from riparian hillslopes that have been studied in this study area, and that DRIPs do not fit in the definition of ephemeral streams or other features in the existing literature that refer to specific processes.

3. It is not clear to me how DRIPs are defined for 'upland' areas. . . do you use the same definition based on topographic depression and wetness index that you use for the riparian zone DRIP areas?

Answer: Yes, the upland wells in the DRIP transects were predicted based on the same criteria as riparian DRIP wells. The exact location of upland wells of DRIPs were then determined in the field starting from the riparian well following the surface topography in order to approximate the most likely hydrological flow paths.

4. Abstract L10 and elsewhere: it is somewhat of a misnomer that all riparian flowpaths lead to biogeochemical alteration of discharging water chemistry. Low-carbon mineral soils and highly preferential flowpaths such as peat pipes and other macropores can yield little alteration in hillslope and deeper groundwater discharge. In fact your findings indicate that DRIPs lead to less net reaction then more diffuse groundwater discharge through the riparian zone: 'Moreover, DRIPs were chemically more stable from the upland area to the stream'. You might check out this commentary for some relevant discussion : (https://onlinelibrary.wiley.com/doi/10.1002/hyp.11153)

Answer: We agree that the generalization was too broad and we changed this to (P1,L10):

"Here wet, carbon-rich soils can change water 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."

In addition we have emphasized that the function of the riparian zone changes with wetness state on P2L16:

"Moreover, wetness state changes the chemical function of the RZ (Vidon, 2017)."

5. It would seem fully screened wells down to apprx 1.5 m depth would integrate shallow 'DRIP' water and deeper mineral soil water, how did you account for this?

Answer: The wells were drilled until resistance or until a first aquitard was encountered. Given the exponentially decaying hydraulic conductivity profile, we can assume that the majority of the water is DRIP (or non-DRIP) water. We have addressed this on P5L2:

"Given that context, lateral flow below the well bottom was considered negligible compared to the flow in the vertical domain of our well installations."

I think your statements in the Discussion section regarding 'old' and 'young' water are a bit to speculative, as this is essentially only based on EC data, a parameter influenced by a number of flowpath process. It does not seem like any age dating/isotope analysis was performed, so how confident can you be regarding relative water ages/residence times?

Answer: We agree that our young/old water discussion is speculative, and we have replaced this part of the discussion.

Also, you mention the piezometers were installed until they reached a hard layer. Did this depth vary systematically from DRIP to non-DRIP locations? If so you could include that data, as depth to rock/confining layer can also be a strong control on shallow groundwater flowpath chemistry.

Answer: We have included well depth information on P5L19:

"All wells were drilled until resistance, or an aquitard layer. Riparian wells had a mean depth of 95 cm, transition wells 99 cm, and upland wells 121 cm."

Fig 1: Although we might expect local shallow percolation in non-DRIP near stream zones, groundwater flow is likely dominated by the lateral component toward the stream (in gaining stream reaches), though the discharge magnitude may be reduced compared to preferential discharge points. I suggest you alter the 'vertical groundwater flow' language in the 3rd panel of this Figure, the vertical flow you refer to may instead by non saturated percolation toward the water table, where groundwater flow is pre- dominantly horizontal.

Answer: We agree that non-saturated percolation is a more appropriate term for this process and we changed the figure accordingly

Have you measured any vertical head gradients at the wells, and lateral gradients between wells, to support these conceptual diagrams?

Answer: We have provided exemplar groundwater level data in Figure S1. Unfortunately we have no lateral gradients to further support our conceptual diagram.

Fig 3- The caption could be simplified, you do not need to define DRIPs in the caption as this is done in the text

Answer: We changed the caption

Minor points:

Pg 2:

L2 repeat of the word 'landscape', please look for replacement

Answer: We corrected this

L3 I am not sure what you mean by 'newly introduced water', can you be more specific?

Answer: This sentence changed to (P2L4): "Lateral groundwater inputs account for a large part of the streamflow of small streams, magnifying groundwater controls on stream CO2 emissions (Hotchkiss et al., 2015)."

L19 do you have a reference example to associate with: 'Traditionally, streamflow generation has often been assumed to be driven by spatially diffuse groundwater exchange often released at a constant rate.'?

Answer: This sentence and the following sentence changed to (P2L20):

"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)."

Pg 4

L20: could cite here the hydrographs shown in Ploum et al 2018

Answer: We added the reference

L24: you would not consider the fall period to be 'baseflow' dominated as well or is this just a winter condition in your watershed system?

Answer: We considered baseflow as the flow conditions in winter given the snow dominated region we performed our study. In autumn low flow conditions can occur but not as long and consistent as during winter due to regular rain events. In winter snow and soil frost inhibit flow in the shallow subsurface and 'true' baseflow conditions occur.

Pg 7

L13: replace 'double as high'

Answer: We have changed this to 'twice as high'

Variability in landscapes is a challenge for understanding how landscapes influence water chemistry in space and time. By developing a sampling design based on a hypothesis about how water is flowing through the riparian zone, this study has provided new insights into the hydrobiogeochemical structures that shape the connection between landscapes and waters. This has practical implications for the design of buffer strips that are widely used in water management. As such this paper can be a valuable contribution to the literature. I think its value would be enhanced if a few points in the paper got further attention.

Answer: Thank you for providing this short comment, we will incorporate the points in our revised manuscript.

One concerns the distinction drawn between DRIPs and the confluences of ephemeral streams on page 5, lines 19-21. The text here was not clear. I think the authors are trying to say that such confluences are not included in their definition of DRIPS since DRIPS do not have clear channels. It would be good if this could be clarified.

Answer: We replaced this section and included a paragraph in the discussion to clarify the context of DRIPs in relation to ephemeral streams and other features that have been studied. Figure S2 was added to demonstrate how a DRIP looks like in the landscape. We agree that emphemeral stream and DRIPs differ from each other by the presence of a clear channel in the case of emphemeral streams, while this is not the case for DRIPs. In practice it can occur that DRIPs have a small channel-like appearance within the very last meter when it merges with the stream, for example when there is bank height difference.

A second point I suggest that the authors address concerns the discussion of relative contributions from DRIPs and Non-DRIPS to stream chemistry under different flow conditions (page 10, lines 29-34). This part of the discussion talks about the contrasting chemistries coming from DRIPS and non-DRIPS. But the effect of chemical differences in the source waters on stream chemistry depends on the proportion of water coming from the different source waters. Is there some assumption underlying this part of the discussion about how much water comes from DRIPs relative to non-DRIPS during high and low flow conditions? Clarification of that would help make the points in this part of the discussion more persuasive.

Answer: We have rewritten the discussion, and reduced the implications for streamflow. However we have added an example of the spring flood (P914) to demonstrate that rising groundwater levels in non-DRIP riparian zone results in higher DOC concentrations. However we have not further elaborated on the implications for stream chemistry here to remain the focus on groundwater related topics. As pointed out, the change in water sources of the stream during events, likely means that non-DRIPs play a larger role than during low flow conditions where groundwater levels are lower. We have added Figure S1 to demonstrate this. We have reported earlier that detectability of DRIPs changes throughout events and seasons (Ploum et al., 2018), which also suggests that DRIP/non-DRIP contributions vary over time.

Furthermore, if the DRIPS do not include the confluences of intermittent streams with the perennial stream channel, it would be important to mention what these ephemeral streams are doing to contribute to the high-flow stream chemistry being talked about in the discussion.

Answer: We agree that intermittent streams should be included when evaluating high-flow stream chemistry. A clean channel-like feature might respond faster to hydrological inputs compared to

DRIPs. That being said, relative to non-DRIP riparian hillslopes, the responsiveness of shallow subsurface runoff generation of DRIPs possibly falls in the same order of magnitude as intermittent streams. Similar to the comment above, we have reduced the speculations about stream implications. On P10L8 we highlight that ephemeral streams and DRIPs are two different features that both focus water towards perennial networks.

One final question, the concept of a "DRIP initiation threshold" is mentioned on page10 line 35, but a definition of what this means is not given. Please explain the term.

Answer: We have changed this section and elaborated on the selection process by providing the ranges of contributing areas. P5L9:

"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 m2 (on average 17 m2)."

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

5 Stefan W. Ploum¹, Hjalmar Laudon¹, Andrés Peralta-Tapia², Lenka Kuglerová¹

¹Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, 901 86 Umeå, Sweden ²Department of Ecology and Environmental Sciences, Umeå University, 901 87 Umeå, Sweden

Correspondence to: Stefan W. Ploum (stefan.ploum@slu.se)

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Abstract.

The riparian zone, or near-stream area, plays a fundamental role for the biogeochemistry of headwaters. Here <u>wet, groundwater</u> <u>carbon-rich soils can undergoes-change water chemistrychemical transformation</u> before it enters the stream. <u>In the boreal</u> forest, the riparian zone plays an especially important role in the export of dissolved organic carbon (DOC) to streams.

- 15 However, the riparian zone is not uniform and spatial variability of <u>riparian</u> 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). <u>Given the important chemical function of the riparian zone, we therefore ask the question: are hydrological pathways and chemical variability linked in the riparian boreal forest? To answer this question, we <u>Combining the chemical function of the riparian zone and the convergence of hydrological pathways, we hypothesize that</u></u>
- 20 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 hydrological connection/groundwater conditionDRIP/non-DRIP. Our results showed that DRIPs provided DOC rich water (34 mg/l) with relatively low EC (36 µS/cm). The so-called 'non-DRIP' riparian water had on</p>
- 30 average 40% lower DOC concentrations (20 mg/l) and 45% higher EC (52 µS/cm). Moreover, DRIPs were chemically more stable from the upland area to the stream (20 25 meter) and more constant throughout different seasonsspatially and temporally homogeneous. In contraryst, non-DRIP water transformed distinctly in the last 25 meters to the stream, and chemical variability was also changed acrosslarger between the seasons. We concluded that hydrological pathways and spatial variability in riparian groundwater DOC concentrations are linked, and that, and that DRIPs can be seen asare important control points in the boreal
- 35 landscape. <u>Characterizing DRIPs in headwater catchments can be useful fThis finding is important for upscaling of stream carbon inputs in boreal stream ecosystems, and for implementing delineating of hydrologically adapted adaptation buffers into for riparian forest management practices. However, for understanding underlying processes and mechanisms, we propose to investigate spatial variability of groundwater chemistry in a non-binary context, focusing on how groundwater chemistry relate to a gradient of hydrological fluctuations, soil properties and landscape characteristics.</u>
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1 Introduction

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Headwater <u>streams</u> can be seen as the capillaries of the landscape: <u>although small in appearance</u>, <u>collectively they make up</u> the majority of a stream network.⁺ The rich variety in hydrology, biology and chemistry of headwaters is tightly connected to processes in the surrounding landscape their catchments (Bishop et al., 2008; Hunsaker and Levine, 1995)(Bishop et al., 2008; Hunsaker and Levine, 1995). Newly introduced terrestrial Lateral groundwater inputs accounts for a large part of the streamflow of small streams, magnifying groundwater controls on stream processes <u>CO</u>₂ emissions (Hotchkiss et al., 2015)(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)(Hayashi and Rosenberry, 2002). This near-

stream area, or so called riparian zone (RZ), holds important functions such as chemical transformation of hillslope water

- 10 (Cirmo and McDonnell, 1997)(Cirmo and McDonnell, 1997), thermal regulation (Davies-Colley and Rutherford, 2005)(Davies Colley and Rutherford, 2005) and erosion control (Smith, 1976)(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)(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
- 15 water dominates streamflow generation, instead of event-based water contributions from hillslopes (McGlynn and McDonnell, 2003)(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., 2018; Lidman et al., 2017)(Ledesma et al., 2018; Lidman et al., 2017). However, RZ's are not just 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., 2017)
- 20 <u>2014b)(Buttle, 2002; Kuglerová et al., 2014b). Moreover, wetness state changes the chemical function of the RZ (Vidon, 2017).</u> It is therefore important to further investigate which parts of the riparian zone matter most for <u>element transport</u>, stream flow generation and associated water chemistrybiogeochemical processes.
- Saturated areas of the riparian zone provide the majority of stream water (Penna et al., 2016). Traditionally, sIn hydrological models streamflow generation has often treamflow generation has often been assumed conceptualized as a to be driven by spatially diffuse groundwater exchange often released at a constant rate. Although this assumption is convenient for hydrological modelling effortsprocess, in practice the occurrence of which limits the ability to spatially express points of focused groundwater discharges of groundwater is more rule than exception (Briggs and Hare, 2018) Some models, such as the RIM model and DSL concept, have considered the vertical heterogeneity in riparian groundwater
- 30 <u>fluxes to boreal streams (Ledesma et al., 2015; Seibert et al., 2009). Also But also longitudinally along streams reaches from a chemical perspective, it is necessary to account for hydrological and biogeospatial chemical dynamics heterogeneity within the RZ. For example, permanently saturated riparian areas have been identified as main stream flow generators (Penna et al., 2016), and For example, wet riparian areas have been associated with denitrification, and as well as retention and transformation of (labile) OM, compared to drier, oxic, riparian soils (Blackburn et al., 2017; Burgin and Groffman, 2012; Seibert et al., 2017; Burgin and Groffman, 2012;</u>
- 35 <u>Ledesma et al., 2018</u>(Blackburn et al., 2017; Burgin and Groffman, 2012; Ledesma et al., 2018). In terms of vegetation, groundwater discharge zones are hotspots for diversity (Kuglerová et al., 2014a)(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
- 40 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). Taken all togetherCombining 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)(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)(Briggs and Hare, 2018).

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For the hydrological characterization of riparian inputs, <u>Tvarious approaches can be used across scaleshe occurrence of</u> saturated areas in the RZ is linked to preferential hydrological pathways that route upland water towards streams. Although subsurface pathways do not entirely follow surface topography (<u>Devito et al., 2005</u>)(<u>Devito et al., 2005</u>), it has been demonstrated that topographic depressions are a good indicator for accumulation areas of water, ponding, shallow groundwater

- 10 tables and concentrated flow paths in the near-stream area (Ågren et al., 2014; Jencso et al., 2009; Wallace et al., 2018)(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. (Leach et al., 2017). 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). However, Tthese so called discrete Discrete riparian Riparian inflow Inflow points
- 15 Points (DRIPs, Fig. S2), provide consistent 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)(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. AA recent study demonstrated temporal dynamics has showed increases in in increasing
- 20 greenhouse gas concentrations evasion from the stream reach in close downstream proximity of DRIPs, yet the magnitude of these increases varied temporally (Lupon et al., 2019)(Lupon et al., 2019). Also in Arctic systems has the presence of riparian wet areas partially explains explained stream CO₂ evasion (Rocher-Ros et al., 2019)(Rocher Ros et al., 2019). These latter findings 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 stream concentration of the discharging encoded.
- 25 characterization of the discharging groundwater is needed.

Characterizing groundwater chemistry is an especially challenging task. Previously this challenge has been by-passed by assuming that groundwater is a well-mixed source of water (Kirchner, 2003)(Kirchner, 2003), or by inferring groundwater chemistry from base flow chemistry of streams (Peralta-Tapia et al., 2015)(Peralta-Tapia et al., 2015).- Also the RIM model

- 30 <u>has provided a framework to infer groundwater chemistry profiles from stream chemistry (Seibert et al., 2009).</u> 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)(Kiewiet et al., 2019)</u>. Within meters of each other, groundwater signatures can vary greatly (Penna et al., 2016)(Penna et al., 2016). Three key parameters for chemical characterization of groundwater in <u>boreal forests</u> are dissolved organic carbon (DOC), pH and ionic strength. DOC concentrations in groundwater is the result of
- 35 interaction between water and carbon rich materials in the shallow subsurface environment that are associated with paludification (Lavoie et al., 2005)(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)(Buffam et al., 2007). Electrical conductivity (EC) can be used as a proxy for the ionic strength,
- 40 or total amount of dissolved ions in water (Corwin and Lesch, 2005)(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).

Therefore, water that has long residence time with mineral soils typically has elevated EC levels.

In the context of spatial variability of riparian groundwater <u>chemistry</u>, 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

- 5 <u>al., 2014a)(Kuglerová et al., 2014a)</u>. 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 <u>vertically</u> 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
- 10 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) saturated riparian areas with large contributing areas riparian areas (DRIPs) and drier parts of the riparian zone drier parts of the riparian zone drier parts of the riparian zone drier parts of the riparian 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
- 15 mineral soil relative to organic soil, leads us to expect that EC will be higher in non-DRIP water compared to DRIPs.



Figure 1 Conceptual model of hydrological pathways in riparian boreal forest. Discrete Riparian Inflow Points (DRIPs) are focal points in the riparian zone (lightgreen) where pathways confluence before reaching the stream (central panel). 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.

- 10 Figure 1 Conceptual model of hydrological pathways in riparian boreal forest. Discrete Riparian Inflow Points (DRIPs) are focal points in the riparian zone where pathways confluence before reaching the stream (central panel). Groundwater flow towards DRIP and non-DRIP RZ (arrows in left and right panel) is conceptualized as predominantly horizontal and vertical, respectively. 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 or mineral horizons. Transparent blue overlay represents the groundwater table. Black bars
- 15 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.

5 in northern Sweden

2.1 Study area

The Krycklan catchment is situated near<u>the town of</u> 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 <u>bed</u>rock, 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)(Laudon et al., 2013). The streams along which the-well network is situated are in the Svartberget research forestalong streams, referred to as C4, C6, and C8 (Laudon et al., 2013)(Laudon et al., 2013), with a drainage area of respectively 18, 110, and 230 ha. Catchments C4 and C6 have been widely

15 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)(Laudon et al., 2004, 2007). 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

20 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. <u>The black square indicates the catchment outlet. In orange the contributing areas</u> are indicated of each well transect. Non-DRIP contributing areas are typically too small to be depicted.

2.2 Site selection and sampling well infrastructureDRIP definition

- Saturated riparian areas have been defined in the landscape based on a topographic wetness index (2 ha threshold) and flow
 accumulation algorithms (Ågren et al., 2014; Beven and Kirkby, 1979; O'Callaghan and Mark, 1984). Discrete Riparian Inflow
 Points (DRIPs) were The 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). 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 m² (on average
- 10 <u>17 m²</u>). The DRIPs have been field-validated and surveyed on species richness (Kuglerová et al., 2014a)(Kuglerová et al., 2014a). For some sites chemical and thermal signatures further corroborated the location were riparian water discharged into the stream (Leach et al., 2017)(Leach et al., 2017).

These areas are referred to as discrete riparian inflow points, or DRIPs (Ploum et al., 2018).

We use the term DRIPs for a collection of phenomena that have been described in literature using a variety of terms 15 for the confluence of terrestrial water before it is incorporate in the stream network. Some of these existing terms are: groundwater discharge zone, groundwater hotspots, cryptic wetlands, swales, focused seepage, discrete seepage, springs, upwelling zones, preferential-discharge, ephemeral-streams and zero-order streams (Creed-et-al., 2003; Hayashi and Rosenberry, 2002; Tsuboyama et al., 2000). The existing terms often inherently refer to specific water sources (e.g. groundwater), specific morphology (e.g. stream) or process (e.g. upwelling), while in practice these 20 confluences represent a spectrum of how hillslope water reaches surface water. Seeps, groundwater discharge, springs or similar terms are associated with relatively deep groundwater, however the water provided by DRIPs is not always groundwater, but can also be overland runoff consisting of rain or snowmelt water. In our case also the terminology referring to channels with temporary flow (ephemeral or intermittent streams, zero order channels) would not justify areas where we encounter inflow without a defined channel or flow path. With the DRIP term we indicate a confluence 25 point in the riparian zone that provides a stream with terrestrial water, possibly provided by different sources of water over time.

2.3 Groundwater sampling and chemical analysis

The setup of this study consists of a well network with a total of 60 <u>fully screened PVC</u> fully screened 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

- 30 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. which was in all cases within 1.5 meter from the soil surface Riparian wells had a mean depth of 95 cm, transition wells 99 cm, and upland wells 121 cm... We assumed that the water sampled from the well is a weighted average of</p>
- 35 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 Each transect consisted of a riparian well, situated
- 40 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. (<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 for DRIP wells, and 54.5 cm for non-DRIP wells during the year of 2018.</p>

2.3 Groundwater sampling and chemical analysis

Data collection involved six groundwater sampling campaigns. Water samples were collected during spring, summer and autumn of the 2016 and 2017 hydrological years. The well network was sampled using suction cup lysimeters and vacuumed glass bottles (Blackburn et al., 2017)(Blackburn et al., 2017). The wells were pumped before installing the suction cups to

- 5 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 <u>following a similar protocol</u>, but instead of suction cup lysimeters, using a peristaltic pump was used for the collection of water samples.
- 10 <u>Data-collection-involved six-groundwater sampling campaigns.</u> Water samples were collected during spring, summer and autumn of the 2016 and 2017 hydrological years. In total 359 samples were analyzed from the 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 acidwashed high-density polyethylene bottles (rinsed three times) and kept at 4 °C before laboratory analysis. DOC was measured
- 15 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

- 20 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)(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 groundwater
- 25 condition<u>the hydrological pathways</u> (GWHP 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 GWHP 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).
- 30 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
- 35 (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)(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*)(<u>Barton, 2014</u>)(Barton, 2014).

3 Results

3.1 DOC

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 upland wells towards the riparian wells from 29.2 mg/l to

- 5 (36.3 mg/l), while in non-DRIP riparian wells DOC concentration increased from 16.4 to 20.1 were much lower (20.1 mg/l₅ (DF=19, p=0.03).₅ gaining only 3.7 mg/l from the upland to riparian wells. 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). <u>Therefore</u>Although DOC concentrations in the upland groundwater of DRIPs was already high, the overall gain in riparian-DOC concentrations from the upland to the riparian wells
- 10 was most accountable to DRIPs (29.2 mg/l to 36.3 mg/l, 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, this difference reduced. This change was a result of an average 20% decrease in DOC concentrations in DRIPs (28.5 mg/l)
- 15 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%.
- The position gradient had higher explanatory power (Table 1), but differences were much smaller compared to the differences
 between DRIPs and non DRIPs (from 22.8 mg/l to 28.2 mg/l, DF=327, p=0.0001). In the upland wells there was no statistical difference in DOC concentrations between DRIP and non-DRIPs (p=0.1844, Fig. 4 upper left panel), even though mean DOC concentrations are contrasting (29.2 mg/l and 16.4 mg/l for DRIP and non DRIPs, respectively). DOC concentrations in DRIPs increased towards the riparian wells (36.3 mg/l), while in non-DRIP riparian wells DOC concentration were much lower (20.1 mg/l, DF=19, p=0.03), gaining only 3.7 mg/l from the upland to riparian wells. Therefore the overall gain in riparian DOC
- 25 concentrations was most accountable to DRIPs (29.2 mg/l to 36.3 mg/l, DF=326, p=0.0003). In terms of seasonality, there was a weak yet significant effect on DOC concentrations when considering all the wells together (Table 1, TIME, p=0.054). However, just as the position gradient, there was also an interaction between GW and TIME explaining variability in DOC concentrations. In summer and autumn DRIPs had double as high DOC concentrations (36.4 and 33.3 mg/l), compared to non-DRIP areas (18.0 and 17.7 mg/l, Fig. 5, upper panels). However, during snowmelt in spring, this difference disappeared. This
- 30 change was a result of an average 20% decrease in DOC concentrations in DRIPs (28.5 mg/l) compared to the summer average. In non-DRIP areas there were no such 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%.



Figure 3 Groundwater chemistry of DRIP versus non-DRIP. DRIP boxplots are presented in grey and non-DRIP boxplots in white. Each boxplot panel represents one response variable. The water chemistry of the entire well network is separated based on the riparian hydrological condition. DRIPs are wet riparian areas with a large contributing area (left-hand side, in grey). Non-DRIPs are drier riparian areas with mostly local hillslope contributions (right hand side). Whiskers represent the 25th and 75th percentile.

3.2 pH

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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). Instead, 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 the summer to autumn (5.37 to 5.70, P<0.0001), both in DRIP and

15 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

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Mean electrical conductivity from DRIP water was $36.2 \,\mu$ S/cm, which was lower (p=0.08) compared to the mean of non-DRIP water (51.6 μ S/cm, Fig. 3). The variance in EC was mostly explained by POS and TIME, and the interaction between GWHP 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 μ S/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

- 25 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 μ S/cm compared to 32.4 μ S/cm). In the upland areas, the DRIP and non-DRIP water was similar. Non-DRIP water increased from 40.5 μ S/cm to 62.4 μ S/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 30

non-DRIP was a 5 μ S/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

Our riparian groundwater sampling campaigns demonstrated that on average Our results showed that riparian groundwater is highly variable in its chemical composition throughout space and time. DOC concentrations in DRIPs were almost twice as high compared to the less hydrologically active active riparian areas (non-DRIPs). Groundwater chemistry of DRIPs was more

- 5 constant from the upland to the riparian zone, and moreover concentrations remained stable across seasons. The groundwater chemistry of non-DRIPs was characterized by 40% higher electrical conductivity than DRIPs, and increasing variability towards the stream and higher temporal variability across seasons. Differences in pH were less distinct, and mostly accountable to seasonal changes. Our results showed that riparian groundwater is highly variable in its chemical composition throughout space and time. However, we found that parts of this variability cannot only be assigned to commonly used factors, the distance
- 10 to the stream and seasonality, but also to hydrological pathways (DRIP vs. Non DRIP). DOC concentrations in DRIPs were twice as high compared to the less hydrologically active riparian areas (non-DRIPs). The groundwater chemistry of non-DRIPs was characterized by high electrical conductivity, and increasing variability towards the stream and higher temporal variability. Differences in pH were less distinct, and mostly accountable to seasonal changes. These results confirm our hypothesis that DRIPs have a more organic <u>DOC-rich</u> groundwater chemistry, while non-DRIP water can be associated with more mineral
- 15 chemistry. <u>However, apart from the commonly tested factors</u>, we found that site specific properties remain to play a major role in explaining spatiotemporal variability in groundwater chemistry.

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 is a likely cause for the decreased DOC concentrations during spring.

- 20 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
- 25 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.Furthermore, DRIPs had a more constant and stable biogeochemical character compared to non DRIP riparian area across space and time.
- 30 With comparison of riparian groundwater chemistry through the DRIP/non-DRIP concept, we have studied two extreme 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 m²) and having lower groundwater levels in the riparian zone (Fig. S1). Earlier work in the study area has demonstrated that the extend of the riparian zone and contributing area play an important role in the available soil carbon pool
- 35 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 m². 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 as a part of the terrestrial landscape than the stream
- 40 <u>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</u>

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 a large upland contributing areas, but lack stream channel formation.

- 5 <u>Some of these existing terms are: groundwater discharge zone, groundwater hotspots, cryptic wetlands, swales, focused</u> seepage, discrete seepage, springs, upwelling zones, preferential discharge, ephemeral streams and zero-order streams (Creed et al., 2003; Hayashi and Rosenberry, 2002; Tsuboyama et al., 2000). The existing terms often inherently refer to specific water sources (e.g. groundwater), specific morphology (e.g. stream) or process (e.g. upwelling), while in practice these confluences represent a spectrum of how hillslope water reaches surface water. Seeps, groundwater discharge, springs or
- 10 <u>similar terms are associated with relatively deep groundwater, however the water provided by DRIPs is not always</u> groundwater, but can also be overland runoff consisting of rain or snowmelt water. In our case also the terminology referring to channels with temporary flow (ephemeral or intermittent streams, zero order channels) would not justify areas where we encounter inflow without a defined channel or flow path. With the DRIP term we indicate a confluence point in the riparian zone that provides a stream with terrestrial water, possibly provided by different sources of water over time.</u>
- 15

The link between groundwater chemistry, mobilization of (old) groundwater and stream chemistry has puzzled hydrologists, especially when it comes to chemical variability during hydrological events (Kirchner, 2003). The transmissivity feedback mechanism of till soils has been pointed out as a possible resolution of the double paradox for boreal headwaters in the Krycklan catchment (Bishop et al., 2004; Laudon et al., 2004a). On hillslope scale, the dominant source layer (DSL), a highly conductive layer just under the soil surface, plays an important role as rising groundwater rapidly mobilizes 'old water' in the unsaturated zone, and spatially connects various sources of soil water (Ledesma et al., 2015). Across the RZ of headwaters, earlier work has already pointed out that spatial groundwater variability is linked to groundwater conditions and the composition of riparian soils (Grabs et al., 2012). It has also been demonstrated that wet riparian areas similar to DRIPs dictate stream DOC dynamics (Creed et al., 2003; Werner et al., 2019). The contrasting chemistry of DRIPs and non DRIPs presented here further supports the link between hydrological pathways and variability of groundwater chemistry, and possibly explains why pre event water is so quickly mobilized. On event basis, the stream chemistry that is monitored at a single downstream point is an integration of different hydrological responses of DRIPs (Leach et al., 2017; Ploum et al., 2018), and the activation of non DRIP hillslopes. This possibly explains why we encounter chemical variability of old water in the stream, as different

- pre-event water from DRIP and non-DRIPs discharges into the stream. Interestingly, we found that during spring flood conditions, the high DOC in DRIP groundwater decreased and became less spatially variable. In contrast, non DRIP water increased in DOC and in variability during this season. In the case of the DRIP groundwater, we believe that snowmelt dilution is a likely cause for the decreased DOC concentrations during spring. 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
- 35 wetland dominated streams during spring floods (Laudon et al., 2004a, 2011). The non-DRIP areas are typically drier, only drain local hillslopes, and have lower groundwater levels during drier periods (summer). During the spring, groundwater levels rise and water flows through shallow organic soil layers. If DRIP and non-DRIP riparian zones become more similar, why is there no stabilizing and decreasing pattern in DOC in forested streams during spring flood (Laudon et al., 2011)? Given that water transported during high flow events is predominantly old, pre-event soil water, an increased EC could have been expected
- 40 as the old water has relatively longer contact time with the soil prior to mobilization. However, we found no increase in EC during spring, which could lead back to the second part of the double paradox: most of the time non DRIPs have low water tables, but in spring, the organic rich DSL is spatially connected, mobilizing old water that has unlikely been in contact with the mineral subsurface. Although our findings might not be able to provide any resolutions, showing the differences between

DRIP and non DRIP here suggest that there is a further distinction in hydrological functioning within boreal forests, similar to the governing hydrological theories differentiating between forest and wetland dominated catchments (Laudon et al., 2011). The further analysis of event and pre-event water of DRIP/ non-DRIP contributions could shed light on open questions around stream chemistry and runoff generation in boreal headwaters.

5

The difference in chemistry observed between DRIP and non DRIP areas within these headwater streams also promotes a new conceptual model of boreal system 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 hydrology and biogeochemistry on catchment level (Laudon and Sponseller, 2018)(Laudon and Sponseller, 2018). A

- 10 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 (supplementary materialW. Lidberg, personal communication). 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
- 15 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)(Peralta Tapia et al., 2015). The presence of DRIPs in headwaters can play an important role in the balance of old and young water further downstream. Since DRIPs provide low EC water, which presumably is young, and non DRIPs convey older water, stream reaches with shortage or lack of DRIPs would introduce a larger proportion of older water. On the contrary, DRIP dominated headwater catchments likely are dominated by young groundwater. The
- 20 chemical contrasts of 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. -potentially changes the development of chemical patterns across scales observed by Peralta Tapia et al (2015). Moreover, the presence of DRIPs possibly disrupts the mixing process of old and young water in stream networks, making it a longer process to reach chemical stability. Of course, the presence of DRIPs (and their initiation threshold) is tightly coupled with geological setting, as predominantly post glacial till areas promote
- 25 shallow, horizontally dominated groundwater flow. In addition, <u>Although</u> their <u>visible effecteentrol of DRIPs</u> on streams <u>likely</u> <u>decreases</u> of <u>in</u> higher order is likely coupled to the degree of chemical contrast and their hydrological activity. Pstreams, reviously, links between hydrological pathways on groundwater chemistry dynamics have been found to significantly affect the chemistry of a fifth order river (<u>Carlyle and Hill, 2001</u>)(<u>Carlyle and Hill, 2001</u>). Further, flow paths known as watertracks have been shown as important biogeochemical controls on higher order Arctic rivers (<u>Harms and Ludwig, 2016;</u>
- 30 McNamara et al., 1999)(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;

- 35 Lidman et al., 2017). Our approach was considered to represent a mixture of riparian groundwater that is likely to be incorporated in 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
- 40 of control points in the landscape with use 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 remain maintain a theigoodr water quality (Kuglerová et al.,

- 5 2014b; Tiwari et al., 2016; Wallace et al., 2018)(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)(Buttle, 2002). For example the extent of Besides the extend of the riparian soils vary, which showed to be of major influence on terrestrial carbon exports to streams (Ledesma et al., 2018)(Ledesma et al., 2018), Also species richness within the RZ is reliant on many local factors (Kuglerová et al., 2014a)(Kuglerová et al., 2014a)., and the
- 10 Furthermore, the temporal expansion<u>extend</u> and shrinkage of (ephemeral) stream networks and the subsequent contributing riparian area are generally not homogenous (Ågren et al., 2015)(Ågren et al., 2015).₂-O_our results support that also in terms of groundwater chemistry, variable widths should be considered in <u>riparian</u> 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-
- 15 width buffer management considers. Recent advances based on machine learning offer novel tools to implement hydrologically adapted buffer management on regional level (Lidberg et al., 2019).

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)(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 lead 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, of which the but their complexity overpassed the binary

- 25 simplifications we have made in this study design. There is not a clearly defined threshold when a wet riparian area can be considered as a control point for stream dynamics. Not only in terms of hydrological flow paths, but also in the wetness state (which likely dietates a large part of the chemical characteristics). Moving from a topography-driven binary approach towards process based analysis can contribute to understanding the mechanisms behind the contrasting biogeochemical characteristics of the RZ. Here we have shown this for two extremes in terms of hydrological pathways. To explain the variance that was
- 30 accounted for using random factors, it could be of interest to further analyzeNext steps can, for example, include local landscape characteristics, subsurface soil properties and groundwater level dynamics to further decipher whether soil, biology or hydrology define the biochemical characteristics throughout the RZ._ This means that local subsurface conditions across soil horizons and landscape features such as slope, land cover and/or aspect might be able to explain a significant part of the processes that generated spatiotemporal variability in groundwater.

35 5 Conclusions

Are DOC concentrations in riparian groundwater linked to hydrological pathways in the boreal forest? re-hydrological pathways and variability in groundwater chemistry linked in the riparian boreal forest? Yes, based on our findings there is a strong link between the hydrological connection pathways in the riparian zone of the riparian zone, and the groundwater chemistryDOC concentrations of riparian groundwater sampled in different seasons. At the confluence of Hhydrological

40 pathways confluence in the riparian zone, at Discrete Riparian Inflow Points (DRIPs), where we found groundwater with an organic-rich, stable groundwater chemistry, compared compared toto the remaining, remaining, drier riparian zone areas.

Combining the<u>ir organic-rich</u> chemical characteristic and <u>dominant</u> hydrological <u>importance forcontributions to</u> headwaters, we propose that DRIPs are *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 the hydrological pathways in the riparian zone in the study design.

However, to fully evaluate their impact 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.

5 Data availability

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

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.

Acknowledgements

15 This study was funded by Oscar and Lili Lamm Foundation and Svenska Forskningsrådet Formas., but the The Krycklan catchment is also supported by SITES (VR), SKB, KAW and the Kempe Foundation. We acknowledge Anna Lupon and the staff at Svartberget research station for field support. We thank Jason Leach and Ilja van Meerveld for contributing to the discussions and hydrological interpretations.

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Tables

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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 GWHP, the p-value and F-statistic is presented. GWHP 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 '**', <math>0.01 , <math>0.05 '.', <math>p > 0.1 '-'. Explanatory variables with a 'variable1:variable2' represent the interaction between both variables.

		DOC	рН	EC
R ² mar		0.22	0.13	0.21
R ² con		0.68	0.55	0.70
GW<u>HP</u>	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
GWHP:POS	p-value	0.18 (-)	0.11 (-)	<0.001 (***)
	F	1.70	2.24	32.11
<mark>₩<u>₩</u>₽:TIME</mark>	p-value	<0.0001 (***)	0.75 (-)	0.49 (-)
	F	12.07	0.288	0.72

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Supplementary Materials:



Figure S1 Water tables in the riparian zone in 2018. In the second panel specific discharge from the riparian forest.



Figure 2 Photograph of a DRIP in July 2017 by Stefan Ploum

Preliminary analysis of DRIPs across the Krycklan catchment:

- 5 For the preliminary analysis of DRIP coverage across the Krycklan catchment the following approach was followed: The stream network was defined by a 10 ha flow initiation threshold using a 2 meter DEM. Then a DRIP network was defined using a 2 ha initiation threshold. Each point where the 2 ha stream network was incorporated in the 10 ha network, was considered as a DRIP site. The area of the catchment was 62 km. The contributing area of the DRIPs was 35.34 km, which is 57 % of the catchment area. The total length of the stream network was 162.5 km. We considered the total length of both sides
- 10 of the stream as the riparian zone, which was 325 km. The total length of stream banks where DRIPs flow into the stream network was 20.75 km, when assuming a width of 25 meters for each DRIP (n=830). The total area of DRIPs was 12.8% of the total length of stream banks of the 10 ha stream network.