A parsimonious model of longitudinal stream DOC patterns based on groundwater inputs and in-stream uptake

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Abstract

The supply of terrestrial dissolved organic carbon (DOC) to aquatic ecosystems affects local in-stream processes and downstream transport of DOC in the fluvial network. However, we have an incomplete understanding on how terrestrial DOC

15   inputs alter longitudinal variations of DOC concentration along headwater stream reaches because groundwater discharge, groundwater DOC concentration and in-stream DOC uptake vary at relatively short spatial and temporal scales. In the riparian zone, the convergence of subsurface flow paths can facilitate the inflow of terrestrial DOC from large upslope contributing areas to narrow sections of the stream. We refer to these areas of flow path convergence as discrete riparian inflow points (DRIPs). In this study, we ask how longitudinal patterns of stream DOC concentrations are affected by DRIPs, as they are

20   major inputs of terrestrial DOC and important locations for in-stream processes. We used a mixing model to simulate stream DOC concentrations along a 1.5 km headwater reach for fifteen sampling campaigns with flow conditions ranging from droughts to floods. Four sets of model scenarios were used to compare different representations of hydrology (distributed inputs of DRIPs vs diffuse groundwater inflow), and in-stream processes (passive transport vs in-stream biological uptake). Results showed that under medium (10-50 l/s) and high flow conditions (>50 l/s), accounting for lateral groundwater inputs

25   from DRIPs improved simulations of stream DOC concentrations along the reach. Moreover, in-stream biological uptake improved simulations across low to medium flow conditions (< 50 l/s). Only during an experimental drought, longitudinal patterns of stream DOC concentration were simulated best using diffuse groundwater inflow and passive transport scenarios. These results show that the role of hydrology and in-stream processes on modulating downstream DOC exports varies over time. Importantly, we demonstrate that accounting for preferential groundwater inputs to the stream is needed to capture

30   longitudinal dynamics in mobilization and in-stream uptake of terrestrial DOC. The dominant role of DRIPs in these transport and reaction mechanisms suggests that consideration of DRIPs can improve stream biogeochemistry frameworks and help inform management of near-stream areas that exert a large influence on stream conditions.

1 Introduction

35 Running waters play a critical role in the global carbon (C) cycle because they transport dissolved organic carbon (DOC) from lands to oceans (Cole et al., 2007). Accounting for stream DOC fluxes within stream networks can be valuable for understanding net in-stream C retention (Alexander et al., 2007; Bernal et al., 2018) and catchment-integrated evasion of C (Wallin et al., 2013), as well as for assessing and managing the brownification of large water bodies (Kritzberg et al., 2020). Across fluvial networks, headwater and high-order river segments have different controls of C dynamics. In headwaters,

40 terrestrial source-transport mechanisms are considered dominant drivers of DOC dynamics (Creed et al., 2015). The organization of flow paths to riparian zones (RZ) (Jencso et al., 2010; McGlynn and McDonnell, 2003; Ploum et al., 2020), riparian wetness regimes (Vidon, 2017), and local differences in soil organic carbon stocks (Grabs et al., 2012) are major controls of the spatiotemporal variability of terrestrial DOC fluxes to streams. Further, recent studies have shown that headwaters can have a reactive role as well, which can reduce downstream supply of DOC (Bernal et al., 2018; Hotchkiss et

45 al., 2015). Mineralization by biota is a major removal mechanism of terrestrial DOC, in addition to abiotic processes such as adsorption, flocculation, and photooxidation (Mineau et al., 2016). Since the upstream supply influences downstream DOC dynamics, the entire stream network relies on terrestrial DOC sources and fluxes from RZ to headwaters (Raymond et al., 2016). Therefore, it is important to understand where and when RZs hydrologically connect to headwaters, and what effect this connection has on headwaters stream biogeochemistry (Casas-Ruiz et al., 2017).

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To integrate the supply of terrestrial DOC fluxes and removal in aquatic ecosystems, we need to combine source-transport hydrochemical and in-stream C spiraling frameworks (Li et al., 2020). While there are hydrochemical frameworks that integrate spatial heterogeneity of terrestrial DOC fluxes to streams (Seibert et al., 2009), they are mostly suitable during high flow conditions, when stream DOC dynamics are dominated by source-transport mechanisms, and in-stream uptake processes

55 are less significant (Raymond et al., 2016). By contrast, in-stream processes are mostly measured during low flows and within reaches with no lateral inputs (Mineau et al., 2016), and therefore, little is known about the role of in-stream biota on controlling DOC fluxes during storms or snow melt periods (Talbot et al., 2018; Wollheim et al., 2018). Moreover, the few quantitative biogeochemical frameworks that consider both source-transport and in-stream processing often rely on a sparsely distributed gauging stations, which do not fully capture the spatiotemporal variability of DOC dynamics within the fluvial network (Futter

60 et al., 2007). A major influence on local stream DOC dynamics that is not captured by gauging stations is the spatial distribution of groundwater discharge (Briggs and Hare, 2018). Discrete riparian inflow points (DRIPs) convey substantial fluxes of DOC from large upslope contributing areas to narrow sections of the stream (Ploum et al., 2020). Subsequently the labile DOC that DRIPs convey to headwater streams leads to in-stream uptake directly downstream of DRIPs (Lupon et al., 2019). Depending on physical stream conditions and local microbial communities (Berggren et al., 2009; Kothawala et al., 2015; Wollheim et

65 al., 2015), this means that DRIPs are important conveyors of terrestrial DOC to streams, but also potential hotspots of in-stream DOC uptake.

To represent local evasion of C from streams to the atmosphere in C budgets, it is important to consider landscape features such as DRIPs (Rocher-Ros et al., 2019). To identify and characterize the groundwater supply from DRIPs to streams, there

70 is a growing body of research that combines field-based methods with digital elevation models, and remote sensing approaches (Antonelli et al., 2020; Barclay et al., 2020; Briggs et al., 2019; Leach et al., 2017; Lidberg et al., 2019; Rosenberry et al., 2016; Selker et al., 2006). However, to quantify the supply of terrestrial DOC from DRIPs to stream networks and to consider subsequent in-stream uptake, it is important to characterize the spatial variability in groundwater chemistry as well. This remains an ongoing challenge because groundwater chemistry is highly variable in space and time (Kiewiet et al., 2019), and

75 groundwater dynamics often need to be extrapolated from a relative small number of observations (Rinderer et al., 2019). As such, the way groundwater and streams are currently monitored does not facilitate a systematic consideration of source-

transport mechanisms and in-stream reactions that are associated with discrete inputs of groundwater, such as DRIPs. To represent DRIPs and their associated effects on stream DOC dynamics, it is important to understand what happens with stream DOC concentrations between monitoring stations, and to understand what the influence is of DRIPs on longitudinal stream

80   DOC dynamics.

In this study, we integrate source-transport mechanisms and in-stream uptake in a model framework, by considering DRIPs as the primary driver of both hydrological and biogeochemical processes that influence patterns of stream DOC concentrations. We used a mixing model to simulate stream DOC concentrations along a 1.5 km headwater reach, for fifteen sampling

85   campaigns with flow conditions ranging from droughts to floods. With this modelling approach, our objective was to disentangle the control of terrestrial DOC inputs and in-stream DOC uptake on longitudinal stream DOC concentrations during different flow conditions. In different model scenarios, we accounted for two types of transport mechanisms: 1) assuming uniform, diffuse inflow of groundwater along the reach and 2) by assuming groundwater inflow relative to upslope contributing area (UCA). These two assumptions were than combined either with the assumption that the stream is a passive pipe, or with

90   the assumption that in-stream DOC uptake takes place directly downstream of DRIPs.

2 Methods

2.1 Study area

We conducted our study in the Krycklan catchment in northern Sweden (64°14′ N, 19°46′ E), along a 1.5 km stream segment located between the gauging stations C5 and C6 (Fig. 1) (Laudon et al., 2013). The gauging station C5 is the outlet of lake

95   Stortjärn (4.2 ha), with a catchment area of 65 ha. The gauging station C6 is situated 1.5 km downstream, and has a catchment area of 110 ha. The catchment consists of pine-dominated forest, mostly underlain by post-glacial till soil (72%). Iron podzols and thin soils can be found in the upland areas, and in the RZ the shallow subsurface (<1.2 meter) is dominated by peat.

For the period 1981 – 2010, the average temperature was 1.8 °C and the average annual precipitation in Krycklan was 614

100   mm, of which 35-50% fell as snow (Laudon and Ottosson Löfvenius, 2016; Laudon et al., 2013). Recently, it has been reported that winter and fall temperatures are increasing, and that snow cover is decreasing (Laudon et al., 2021). On average, approximately 50% of the annual precipitation translates to streamflow. The hydrological regime at gauging stations C5 and C6 is dominated by the annual snowmelt peak, occurring around May (100-200 l/s), but at C5 peak flows are dampened by the lake (Leach and Laudon, 2019). In summer and autumn, low flows dominate (5-10 l/s), but are alternated with medium to

105   high flows (25-75 l/s) as a response to rain events. During the winter and early spring, the stream is snow and ice covered with flows around 1-2 l/s. At C5, streamflow is mostly driven by lake level variations as a response to water contributed from the surrounding mire complex. As a result, peak flow events are dampened and recession limbs decrease slowly (Fig. S1). The downstream effect of the lake is a dominant aspect of the discharge and chemistry at C6 (Leach and Laudon, 2019). At C6, discharge can respond much faster to hydrological events compared to C5 and is characterized by steep rising limbs (Ploum

110   et al., 2018). This hydrological response is typically a result of rapid increases of shallow groundwater tables in the RZ, enabling periods of flow through highly conducting organic soil layers in the upper decimetres of the soil profile (Ledesma et al., 2015). The lateral inputs from the RZ are dominated by discrete riparian inflow points (DRIPs), which route 60% of the upslope contributing areas to 5% of the stream length (Leach et al., 2017). At DRIPs, flow paths from the upland converge in the RZ, which leads to near-surface groundwater levels and organic-rich groundwater chemistry (Ploum et al., 2020).

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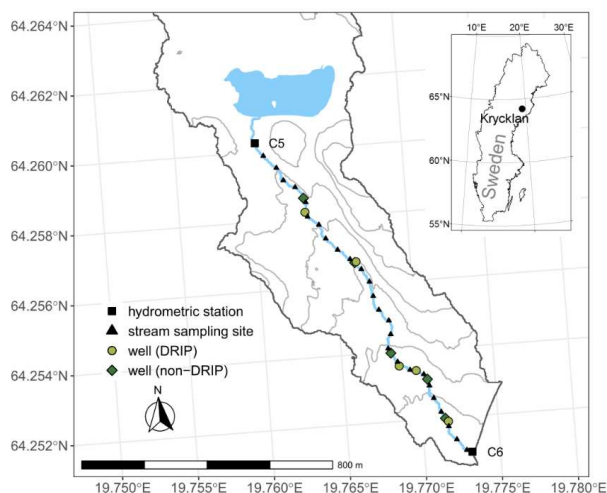


Figure 1 The Stortjärnsbacken subcatchment in Krycklan, Sweden. The stream segment starts at the outlet of lake Stortjärn (gauging station C5), and ends at the downstream gauging station C6. Stream sampling sites at approximately 50 meter increments are indicated with triangles. Light green circles (DRIPs) and dark green diamonds (non-DRIPs) represent groundwater wells along the reach. At DRIPs, flow paths converge in the riparian zone.

2.2 Field measurements and laboratory analysis

Field measurements were collected between May 2017 and May 2019. In total, we conducted 15 sampling campaigns with different streamflow conditions, which ranged from drought conditions to peak flows (Fig. S1). Ten sampling campaigns were centred around the snowmelt periods of 2017-2019, and five around a lake damming experiment in August 2017. In this experiment, the upstream lake was blocked, and after a period of artificial drought a series of controlled flows were released using a pump (Gómez-Gener et al., 2020).

For each sampling campaign, stream water was collected along the stream segment at approximately 50 meter intervals over 1200 meters, dividing the stream into 25 reaches (Lupon et al., 2019). Riparian groundwater was sampled from a paired well network setup, which included pairs of DRIP and non-DRIP wells (Ploum et al., 2020). The fully screened, PVC wells (30 mm diameter) were positioned 1-5 m from the stream edge, and had a depth of approximately 1 m. Five of the stream reaches were directly associated with a DRIP groundwater well, and five directly with a non-DRIP well. Two additional DRIPs were identified after installation of GW wells, and are therefore without a well and groundwater samples (Fig. 2, dashed vertical lines). At one stream reach, two DRIPs are located (Fig. 2, marked with 513).

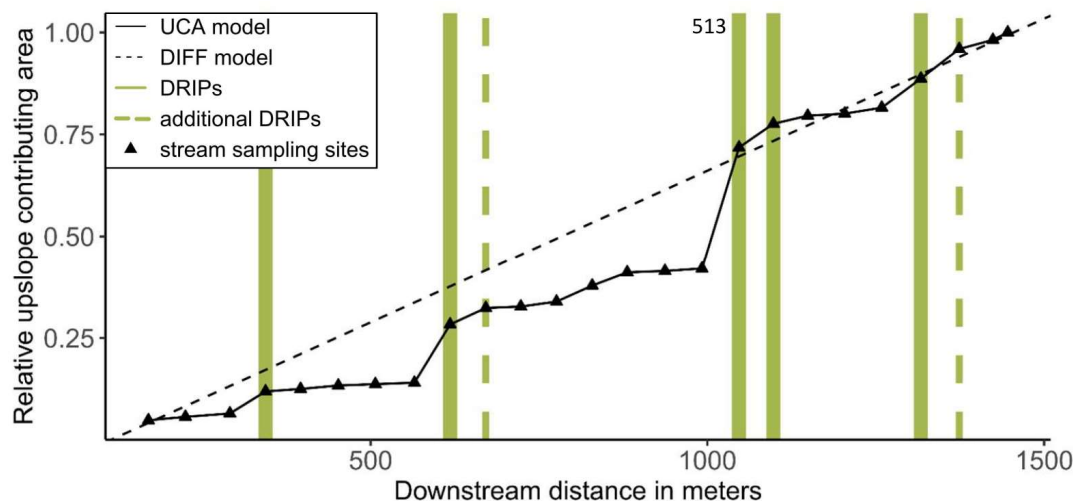
Stream water was collected from the talweg with acid-washed high-density polyethylene bottles. Groundwater wells were sampled using suction cup lysimeters and vacuumed glass bottles, or by using a peristaltic pump to fill acid-washed high-density polyethylene bottles. The wells were pre-pumped to ensure we did not sample stagnant water. Stream water was collected using grab samples. Bottles for both stream water and groundwater were rinsed three times before filling with minimal headspace. Within 24 hours, all samples were filtered (0.45 μm) and kept refrigerated at 4 °C before analysis. DOC analysis consisted of acidification of the sample, followed by combustion using a Shimadzu TOC-V$_{CPH}$. The analysis was repeated at least three times per sample resulting in a DOC concentration in mg/l and a percent standard deviation.

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Figure 2 Relative upslope contributing area along the stream reach. The solid line is the relative gain in upslope contributing area between each of the stream sampling sites (triangles), which referred to as UCA model. The dashed line represents the DIFF model, which assumes uniform, diffuse inflow of groundwater along the entire reach. Green vertical bars indicate locations of discrete riparian inflow points equipped by GW wells (DRIPs; solid) and additional DRIP sites without GW wells (dashed). In-stream
150 **dissolved organic carbon (DOC) uptake was considered only in those reaches comprising DRIPs (i.e. after the vertical bars).**

2.3 Model framework and data input

We used a mixing model that considered the stream DOC concentration at location i to be a result of upstream DOC flux and the net lateral riparian groundwater flux that is gained between upstream location i-1 and i. In addition, we considered that
155 riparian DOC inputs were subjected to in-stream uptake.

$$DOC_{stream,i} = \frac{(DOC_{stream,i-1}*Q_{i-1}) + DOC_{gw,i}*(Q_i - Q_{i-1}) - uptake_i}{Q_i} \qquad (1)$$

where $DOC_{stream,i}$ and $DOC_{stream,i-1}$ are the stream DOC concentration at location i and i-1, respectively; Q_i and Q_{i-1} are
160 the streamflows at locations i and i-1, respectively; $DOC_{gw,i}$ is the groundwater DOC concentration at location i, and $uptake_i$ is the in-stream DOC uptake associated with lateral groundwater labile DOC inputs (see below). We used this equation in combination with different assumptions for the terms that represent streamflow and in-stream uptake.

2.3.1 Riparian groundwater DOC concentrations

Out of the 25 stream reaches, there were ten reaches where DOC_{gw} was directly obtained from DRIP and non-DRIP wells.
165 From the remaining 15 reaches, 13 were classified as non-DRIP zones and were represented by the chemistry of the nearest non-DRIP wells. When DOC_{gw} in non-DRIP wells were not available, their DOC_{gw} was weighted based on the mean of all other non-DRIP wells. The remaining 2 stream reaches were classified as DRIPs because these stream reaches had comparable UCA to DRIPs: both reaches exceeded the 75th percentile of the gained upslope contributing area (UCA) relative to catchment area, similar to DRIP reaches. In these two cases, DOC_{gw} was considered as the mean of all DRIP wells (Fig. 2, dashed vertical
170 bars). Lastly, the DOC_{gw} at the stream location indicated with 513 in Figure 2 had two DRIPs flowing into the stream at the same location. Here DOC_{gw} was a weighted average based on the DOC_{gw} of both DRIP wells. For the averaging, the UCA of the two DRIP wells relative to the total gain in UCA at that location was used. On 2018-05-11, DOC_{gw} of both wells was not available, and therefore we considered the mean of the other DRIP wells.

2.3.1 Streamflow and lateral groundwater inputs

Streamflow at each location (Q_i) was considered in two ways. Both approaches assume that all net gain in streamflow between the two hydrological stations C5 and C6 is a result of shallow lateral groundwater input from the RZ. One scenario assumed that the local gains in streamflow were driven by diffuse groundwater inflow (hereafter referred as "DIFF", Fig. 2), where the net gain in streamflow is distributed according to gained stream distance:

$$Q_{diff,i} = (Q_{C6} - Q_{C5}) * \frac{(L_i - L_{i-1})}{L_{total}} \qquad (2)$$

where Q_{C5} and Q_{C6} is the streamflow at the gauging stations C5 and C6, respectively (both in l/s). L_{total} is the total length of the C5-C6 stream segment (1200 m), L_i is distance between C5 and the sampling location i, and L_{i-1} the distance of the upslope stream sampling location.

The other scenario (hereafter referred as "UCA", Fig. 2) was based on Leach et al. (2017), in which lateral groundwater inputs were distributed proportional to the gain in upslope contributing area at each riparian reach:

$$Q_{uca,i} = (Q_{C6} - Q_{C5}) * \frac{UCA_i}{(A_{C6} - A_{C5})} \qquad (3)$$

where UCA_i is the upslope contributing area that is gained along the reach (between locations i and $i-1$), which was used to distribute the net gained streamflow ($Q_{C6} - Q_{C5}$) proportional to the total gain in catchment area between the lake and the downstream outlet ($A_{C6} - A_{C5}$). This approach emphasized the hydrological contributions of DRIPs, because of their large contributing areas relative to the rest of the RZ.

2.3.2 In-stream DOC processing

We considered two different scenarios regarding in-stream DOC processing. One scenario considered that the stream was acting as a passive pipe for DOC (i.e. no in-stream DOC uptake), while the other scenario considered that stream biota rapidly take up the DOC originating from lateral groundwater inputs. We did not consider the scenario that DOC coming from upstream locations were taken up along the stream, as previous studies in Krycklan have suggested that this rarely occurs (Tiwari et al., 2014).

At each location (i), in-stream DOC uptake of lateral groundwater DOC inputs ($uptake_i$, in mg C/s) was estimated as follows:

$$uptake_i = DOC_{gw,i} * Vf/60 * width_i * length_i \qquad (4)$$

where $DOC_{gw,i}$ is the DOC concentration of riparian groundwater (in mg/l), Vf the DOC uptake velocity (in mm/min) associated with riparian carbon, and $width_i$ and $length_i$ are the mean channel width and the reaction path length of each reach (both in m). Based on previous work at this particular study segment, we assumed that in-stream DOC uptake mostly occurred immediately downstream of DRIPs (Lupon et al., 2019). We accounted for this by setting the $length$ of all reaches to zero, except for those where a DRIP was located (Fig. 2). At these reaches, $length_i$ was the distance between DRIPs and the location i, instead of the total length between $i-1$ and i. This prevented overestimations of reaction times and path lengths

over which in-stream uptake took place. For in-stream DOC uptake from riparian groundwater, we used a Vf = 0.6±0.06 mm/min. This value is the median ambient DOC Vf obtained from a literature review and has been shown to realistically

215 simulate in-stream DOC uptake at whole river networks (Mineau et al. 2016). Because Vf depends on temperature, streamflow, DOC composition, and microbial assemblages, we tested values for Vf ranging between 0.25 and 1.11 mm/min yielded. These values yielded similar model results for the simulations that considered in-stream DOC uptake (Fig. S2).

2.4 Model scenarios, uncertainties and performance criteria

In total, our model approach resulted in four scenarios per sampling campaign (Table 1). For each sampling date, the model

220 scenarios were informed with the same DOC_{gw} concentrations, but assumed different representations of catchment hydrology and in-stream DOC processing. "DIFF_NOBIO" assumes diffuse groundwater inputs and passive transport of DOC in the stream. "DIFF_BIO" also assumes diffuse groundwater inputs, but accounts for in-stream DOC uptake downstream from DRIPs. The "UCA_NOBIO" model assumes that groundwater inputs are distributed proportional to their UCA and no in-stream DOC uptake, which means that DRIPs contribute a relatively large component of the net gained stream water compared

225 to non-DRIP stream sections. The "UCA_BIO" model assumes groundwater inputs proportional to UCA as well, and accounts for in-stream DOC uptake downstream from DRIPs.

Table 1 Overview of model assumptions. First column indicates model name. Second column indicates whether the streamflow is assumed as uniform diffuse rate along the reach, or distributed based on upslope contributing area. The third column indicates
230 whether in-stream uptake of DOC by biota is included.

MODEL SCENARIO	HYDROLOGY	BIOLOGY
DIFF_NOBIO	Diffuse	No uptake
DIFF_BIO	Diffuse	Uptake
UCA_NOBIO	Upslope contributing area	No uptake
UCA_BIO	Upslope contributing area	Uptake

To account for uncertainties in our streamflow observations, water sample analysis and model assumptions, we used a stochastic approach to evaluate our model simulations. This means that we compared the range of uncertainty in our simulations to the range of uncertainty in the observations. For each scenario we executed a 100 model runs, with each run

235 using a randomized sample for every observation and every computation. We presented the simulated $DOC_{stream,i}$ using an uncertainty band that represented 66% of the randomized model runs (mean +/- one standard deviation). The randomizations for each sample were based on normal distributions considering 10% uncertainty of streamflow observations and DOC uptake velocity, and the percentage standard deviation from the laboratory analysis (for most samples this was <2%). For each run, the model generates a single ("deterministic") value for $DOC_{stream,i}$. This means that for the next downstream location the

240 gained uncertainty (from the streamflow, DOC uptake velocity and laboratory analysis) is incorporated as a single value of $DOC_{stream,i-1}$. As such, DRIPs can have large influence on the uncertainty band and sampling days with relative large gains in streamflow from groundwater inputs can have increasing uncertainty bands further downstream. In the case that upstream from location i the uncertainty band in DOC_{stream} was large, but the uncertainty of the lateral input at location i was small, the uncertainty band can become narrower.

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We evaluated the simulations using a number of goodness of fit metrics, computed using the "hydroGOF" R-package (Zambrano-Bigiarini, 2020). We computed the root mean squared error (RMSE), percent bias (PBIAS), Nash-Sutcliffe efficiency (NSE), and coefficient of determination (R^2) for each sampling. RMSE aggregates the magnitude of errors in mg/l. We considered a 2 mg/l magnitude of error acceptable. PBIAS shows systematic errors in the simulations as a percent deviating

250   from the observations, where positive values indicate overestimation and negative values underestimation. We considered a
5% bias acceptable. NSE ranges from -∞ to 1, and shows how the variance of the simulation corresponds to the variance in
observations. R^2 compares variances as well, but the simulated and observed variance is considered a cloud of points, which
does not account for the ability of to simulate patterns in the observations. For both NSE and R^2, we considered that values >
0.5 were indicating that the model was capturing the general direction and variance of stream DOC concentrations. For R^2,
255   these assumption was only true if the relation between observed and simulated stream DOC concentrations was positive.

3 Results

During the study period, the net gain in streamflow along the segment ranged between 8% and 90%, with an average of 37%
(Fig. S1). Stream DOC concentration ranged between 15 to 32 mg/l and generally decreased along the C5-C6 stream segment
(11 out of 15 sampling campaigns) (Fig. 3). The variability in stream DOC concentration along the segment and across different
260   flow conditions was reasonably well captured by all models because, although the models rarely captured the entire
longitudinal pattern, the order of magnitude of the simulations was within the range of the observations, and the general
direction of the simulated values corresponded with the observations. For the majority of the simulations, RMSE were in the
order of 2 mg/l and PBIAS was within a range of -5% to 5% (Table 2). Further, for 10 out of 15 sampling campaigns, at least
one model had an R^2 greater than 0.5 (Table 2). However, only in four sampling campaigns, the NSE of at least one model
265   was greater than 0.5 (Table 2, Fig. 3F, K-M).

3.1 Snowmelt 2017

The sampling campaigns of spring 2017 captured an early snowmelt peak, and the receding limb of a rain-on-snow event (Fig
3A-E). At the onset of the snowmelt peak, stream DOC concentration ranged between 25 and 30 mg/l and showed a marked
longitudinal pattern (Fig. 3A-B). In the first sampling campaign, the two scenarios assuming diffusive groundwater inputs
270   captured the decreasing trend of stream DOC concentration in the first 700 m, but underestimated the concentrations at the
downstream section of the stream segment (Fig. 3A). In the second sampling campaign, none of the models correctly captured
the longitudinal patterns of stream DOC concentrations (NSE<0), as all them simulated uniform concentrations around 27
mg/l (Fig. 3B). Around the time of the rain-on-snow event, stream DOC concentrations were more uniform along the section
than during the two previous sampling days, ranging between 15 and 20 mg/l (Fig. 3C-D). The headwater lake contributed the
275   majority of the stream water during these sampling campaigns (Fig S1). During sampling campaign C, between the snowmelt
and rain-on-snow event, the UCA_NOBIO scenario yielded the lowest RMSE and PBIAS, and highest R^2 (Fig. 3C). For all
scenarios, NSE < 0. The second rain-on-snow sampling campaign had similar flow conditions as C, but none of the scenarios
resulted in an accurate simulation (Fig. 3D, Table 2). During the post-snowmelt low flow on 2017-06-02 (Fig. 3E), step changes
in stream DOC concentrations that coincided with DRIPs were well captured by the two scenarios that consider in-stream
280   uptake (NSE=0.81 and NSE=0.5 for the "DIFF_BIO" and "UCA_BIO" models, respectively). For those scenarios, the RMSE
and PBIAS were also acceptable. By contrast, the scenarios without in-stream uptake ("DIFF_NOBIO" and "UCA_NOBIO")
did not meet our criteria, except for R^2.

3.2 Experimental drought 2017

The sampling campaigns in the summer of 2017 (Fig. 3F-J) consisted of a rain event, an experimental drought, a controlled
285   lake water flood pulse and post-flood base flow conditions. The absolute gain in streamflow was small during these sampling
campaigns (0-5 l/s), but the relative gain varied between 9% and 90% (Fig S1). During the rain event and the drought, stream
DOC concentration increased along the segment (between 17 and 28 mg/l) and distinct step changes in DOC concentrations
occurred at the locations where DRIPs flow into the stream (Fig. 3F-H). For the rain event, none of the models accurately

simulated the observed patterns (Fig. 3F). For the first drought sampling campaign, the model "DIFF_NOBIO" most accurately

290 simulated the longitudinal variability in stream DOC concentration (NSE=0.48, Table 2), while the two models that accounted for in-stream DOC uptake ("DIFF_BIO" and "UCA_BIO") underestimated stream DOC concentrations and were partially out of bounds (Fig. 3G). "UCA_NOBIO" overestimated stream DOC concentrations along the entire stream section (Table 2). The second drought sampling campaign showed similar model results, but the pattern produced by scenario "DIFF_NOBIO" was less successful (Fig. 3H). The following flood pulse and post-flood base flow conditions resulted in uniform stream DOC

295 concentrations along the stream segment. Subsequently, all models had low RMSE and PBIAS, but NSE indicated that patterns were not well reproduced (Fig. 3I-J, Table 2).

3.3 Snowmelt 2018 and 2019

In the spring of 2018 and 2019, mostly snowmelt peak flow conditions were captured (Fig S1), which were characterized by flows exceeding 100 l/s and diurnal snowmelt patterns. In all sampling campaigns, stream DOC concentrations generally

300 decreased along the stream segment, yet there were step changes indicating either dilution or enrichment of DOC at the DRIP locations (Fig. 3K-O). Our modelling results show that, for the 2018 spring flood, pattern simulations met all our criteria for at least one scenario (Fig 3K-M, Table 2). The scenario that better fit the data were the "UCA_NOBIO", the "DIFF_BIO" and the "UCA_BIO", for the first, second and third sampling campaigns, respectively (Fig 3K-M, Table 2). During the 2019 spring peak flow, both "UCA" scenarios overestimated stream DOC concentrations at two DRIPs, while the "DIFF" scenarios more

305 closely represented the observations (Fig. S1 and Fig. 3N). Further, none of the models performed well (NSE and R^2 <0.5; Table 2). In the receding limb of the snowmelt peak flow, none of the models were able to capture the increments in stream DOC concentration between DRIPs (Fig. 3O).
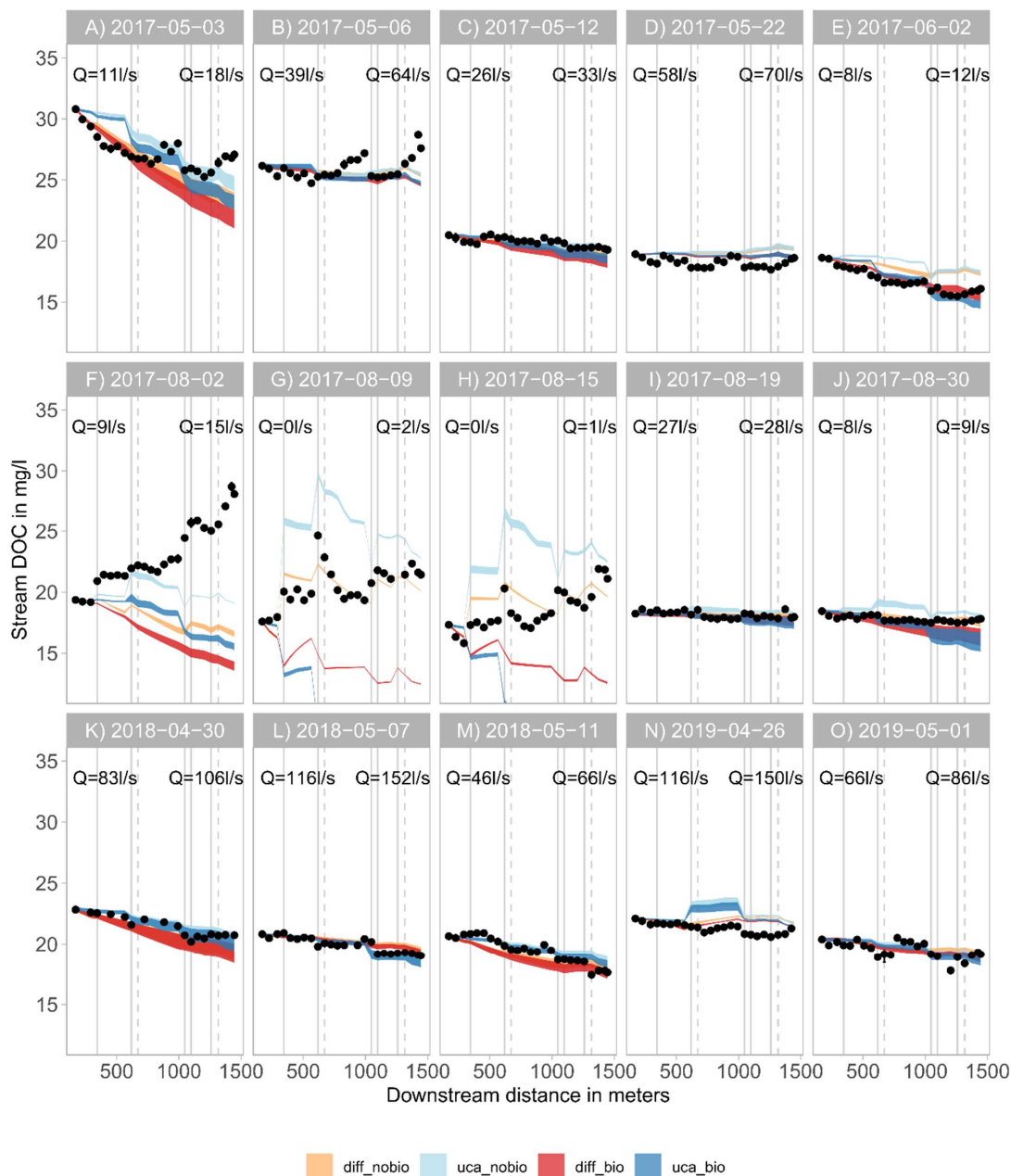
Figure 3 Longitudinal patterns of stream dissolved organic carbon (DOC) concentrations along the C5-C6 stream segment. Each panel, indicated by label and date, shows one sampling campaign. The black dots are the observed stream DOC concentrations. The coloured bands show the simulations of the four models. The vertical grey lines show the locations of DRIPs with wells (solid) and DRIPs without wells (dashed). The streamflow (Q) at gauging stations C5 and C6 are shown for each sampling campaign.

315 **Table 2 Model performance by sampling campaign. Each box represents a sampling campaign, indicated with A-O. The letters correspond to the panels in Figure 3. For each model, the goodness of fit metrics RMSE, PBIAS, NSE and R² are presented. The bold numbers indicate that the value was considered acceptable based on our criteria in section 2.4.**

	DATE	MODEL	RMSE [MG/L]	PBIAS [%]	NSE	R²		DATE	MODEL	RMSE [MG/L]	PBIAS [%]	NSE	R²
A	17-05-03	DIFF_NOBIO	1.89	**-3.6**	-0.90	**0.60**	**I**	17-08-19	DIFF_NOBIO	**0.3**	**0.5**	-0.06	0.07
		DIFF_BIO	2.73	-6.8	-3.27	0.59			DIFF_BIO	**0.25**	**0.3**	0.11	0.26
		UCA_NOBIO	1.66	**2.8**	-0.47	0.51			UCA_NOBIO	**0.4**	**1.2**	-1.1	0.14
		UCA_BIO	1.97	**-1.0**	-1.30	0.50			UCA_BIO	**0.29**	**0.6**	-0.03	0.24
B	17-05-06	DIFF_NOBIO	1.09	**-0.1**	-0.31	0.12	**J**	17-08-30	DIFF_NOBIO	**0.3**	**0.9**	0.03	**0.57**
		DIFF_BIO	1.29	**-2.2**	-1.06	0.19			DIFF_BIO	1.0	**-4.4**	-12.37	0.44
		UCA_NOBIO	1.04	**-0.1**	-0.30	0.09			UCA_NOBIO	0.9	**4.6**	-8.42	0.01
		UCA_BIO	1.38	**-2.4**	-1.24	0.25			UCA_BIO	**0.35**	**1.1**	-0.91	0.22
C	17-05-12	DIFF_NOBIO	**0.61**	**-2.4**	-0.99	**0.50**	**K**	18-04-30	DIFF_NOBIO	1.26	-5.3	-1.31	**0.84**
		DIFF_BIO	**0.88**	-3.4	-4.68	0.45			DIFF_BIO	1.18	-4.8	-1.05	**0.87**
		UCA_NOBIO	**0.56**	**-1.7**	-0.81	**0.53**			UCA_NOBIO	**0.36**	**0.1**	**0.83**	**0.90**
		UCA_BIO	**0.94**	**-3.6**	-4.28	**0.52**			UCA_BIO	**0.63**	**-2.1**	0.44	**0.86**
D	17-05-22	DIFF_NOBIO	1.09	5.3	-6.6	0.10	**L**	18-05-07	DIFF_NOBIO	**0.38**	**0.9**	0.62	**0.73**
		DIFF_BIO	**0.71**	3.3	-2.42	0.04			DIFF_BIO	**0.34**	**0.9**	0.69	**0.78**
		UCA_NOBIO	1.07	5.2	-6.05	0.13			UCA_NOBIO	0.82	**-2.6**	-0.68	**0.83**
		UCA_BIO	**0.68**	3.2	-2.58	0.05			UCA_BIO	0.81	**-2.4**	-0.77	**0.82**
E	17-06-02	DIFF_NOBIO	1.26	6.7	-0.72	**0.77**	**M**	18-05-11	DIFF_NOBIO	0.68	**-2.2**	0.63	**0.79**
		DIFF_BIO	**0.41**	**0.6**	**0.81**	**0.86**			DIFF_BIO	0.92	-4	0.27	**0.80**
		UCA_NOBIO	1.62	8.9	-1.93	**0.63**			UCA_NOBIO	0.71	**2.1**	0.59	**0.90**
		UCA_BIO	**0.65**	**0.2**	**0.50**	**0.84**			UCA_BIO	**0.4**	**0.4**	0.85	**0.93**
F	17-08-02	DIFF_NOBIO	6.28	-22.6	-4.77	0.70	**N**	19-04-26	DIFF_NOBIO	**0.87**	**3**	-3.36	0.21
		DIFF_BIO	7.96	-28.7	-8.16	0.84			DIFF_BIO	**0.68**	**2.3**	-1.46	0.01
		UCA_NOBIO	4.24	-13.5	-1.69	0.09			UCA_NOBIO	1.79	6.7	-15.97	0.01
		UCA_BIO	6.52	-22.2	-5.29	0.89			UCA_BIO	1.52	5.8	-12.32	0
G	17-08-09	DIFF_NOBIO	1.16	**-1.3**	0.48	**0.54**	**O**	19-05-01	DIFF_NOBIO	**0.65**	**0.4**	0.2	0.23
		DIFF_BIO	6.91	-30.9	-16.57	0.40			DIFF_BIO	**0.67**	**-0.2**	0.18	0.27
		UCA_NOBIO	5.06	20.8	-8.87	0.37			UCA_NOBIO	**0.65**	**-0.7**	0.19	0.42
		UCA_BIO	11.34	-50	-44.99	0.57			UCA_BIO	**0.71**	**-0.8**	-0.13	0.38
H	17-08-15	DIFF_NOBIO	1.57	**4.4**	0.01	0.30							

DIFF_BIO	5.1	-23.1	-9.01	0.52
UCA_NOBIO	4.78	22.4	-7.99	0.12
UCA_BIO	8.66	-39.5	-28.02	0.63

4 Discussion

Our observations showed that longitudinal stream DOC concentrations between the two gauging stations varied spatially

320 during different flow conditions. While during some sampling campaigns stream DOC concentration was uniform along the stream segment (around 20 mg/l), at other occasions it varied between 15 and 30 mg/l. Especially at DRIPs, we observed step changes in stream DOC concentrations, indicating that DRIPs can both decrease and increase stream DOC concentrations. We considered that these changes can be attributed to dilution and enrichment of DOC, as well as to in-stream removal of DOC. To understand what controlled patterns of stream DOC concentrations at the various flow conditions, we simulated stream

325 DOC concentrations based on terrestrial DOC fluxes and local in-stream DOC uptake. We compared four different model scenarios with the observed stream DOC profiles. Our results showed that including DRIPs in a stream-based mixing model for DOC helps to explain longitudinal patterns through both terrestrial source-transport mechanisms as well as in-stream uptake of DOC.

330 Our modelling exercise demonstrated that accounting for spatial variability in lateral groundwater inputs can improve simulations of stream DOC dynamics that occur along the stream segment. Most step changes in DOC coincided with DRIP locations, which suggests that supply of DOC was an important influence on stream DOC concentrations. The different patterns simulated by model scenarios DIFF_NOBIO and UCA_NOBIO shows that acknowledging spatial variability in hydrology can improve stream DOC simulations, or at least indicate where step changes occur. For example during the snowmelt event

335 of 2018 the model scenario UCA_NOBIO was able to represent step changes in stream DOC concentrations that coincide with the location of DRIPs (Fig. 3K and Table 2). This corroborates that spatial variability in groundwater hydrology related to landscape organization has a major influence stream DOC patterns (Covino et al., 2021; Dupas et al., 2021; Rocher-Ros et al., 2019). As such, model frameworks that integrate the spatial variability in hydrology from hillslopes to stream reaches and catchments can help represent variability in hydrological connectivity between gauging stations (Jencso et al., 2009; Seibert

340 et al., 2009). However, the other sampling campaigns show that for most of the flow conditions, the hydrology is only one of the components that explains stream DOC patterns. As such our findings suggests it is equally important to represent of spatial variability in C sources in relation to landscape organization, as well as the associated biogeochemical dynamics (Grabs et al., 2012; Hale and Godsey, 2019; Wollheim et al., 2018).

345 We showed that accounting for in-stream DOC uptake improved predictions of longitudinal stream DOC concentrations during medium flow conditions (from 10 to 50 l/s). Especially, the example in June 2017 (Fig 3E) shows how step changes are accurately reproduced by the "UCA_BIO" scenario. However, during extremely high and low flows, in-stream DOC uptake did not contribute to longitudinal stream DOC concentrations. These results concur with previous studies recently performed in headwaters (Lupon et al., 2019; Seybold and McGlynn, 2018), and suggest that aquatic biological activity becomes enhanced

350 at the transition between low and high flows due to increases in labile DOC supply from terrestrial systems. However, our results also support the idea that, beyond a certain flow threshold (> 100 l/s), the benefits of increased substrate supply become overwhelmed by low water residence times and physical disturbance (Raymond et al. 2016). Interestingly, we observed that the influence of in-stream processes on water chemistry was minimal during low flows. A possible explanation for the observed behaviour is that, during the experimental drought, stream reaches were longitudinally disconnected from each other and

355   therefore, the role of in-stream processes to affect downstream reaches was limited (Gómez-Gener et al., 2020). Overall, our
       results indicate that the pipe vs reactor behaviour of boreal headwater streams is closely tied to changes in lateral inputs of
       DOC from RZ.

       Our model framework represented the source of lateral DOC inputs based on groundwater samples from a riparian well
360   network that compared DRIP and non-DRIP groundwater chemistry (Ploum et al., 2020). This allowed to distinguish between
       the spatial variability in riparian groundwater chemistry associated with different soil wetness regimes (Vidon, 2017). For
       example during snowmelt conditions, when occasionally DRIP water can be routed over ice (Ploum et al., 2018), local
       decreases in DOC concentrations in stream DOC concentrations were captured by the model. Also during the experimental
       drought, the representation of spatial variability in groundwater was more important that hydrology or in-stream uptake: during
365   the experimental droughts, the scenario that approximated the stream DOC patterns the most was the "DIFF_NOBIO". This
       result suggests that, under conditions as these, stream DOC patterns might not be directly related to the quantity of groundwater
       inputs, but rather to the thermal and chemical conditions that groundwater discharge creates at the local level (Briggs and Hare,
       2018). However, we also see limitations of our groundwater sampling approach. For example, our groundwater sampling
       campaigns were not able to represent temporal DOC dynamics associated with variability in groundwater travel times
370   (Heidbüchel et al., 2020), event scale variability in riparian DOC mobilization (Werner et al., 2019), or the activation of DOC
       from different soil layers (Ledesma et al., 2018).

       Apart from the limitations of our groundwater sampling campaigns, we identified other limitations in the hydrological
       components and the in-stream uptake components of the model as well. The sampling campaign of a rain event on 2017-08-
375   02 (Fig. 3F) is a clear example of mismatch between our simulations and the observations: while stream DOC concentrations
       increased along the reach, our model scenarios simulated a decreasing pattern. The observed step changes in stream DOC
       concentrations at the DRIPs is in agreement with the consistently high DOC loads that are characteristic for DRIP groundwater
       (Ploum et al., 2020). Also, during the rising limb of the snowmelt event (Fig. 3B), discrepancies were found between our
       simulations and the observed patterns: our model scenarios produced a uniform DOC pattern, while the observations showed
380   increasing DOC concentrations along the reach which abruptly decreased at DRIPs. This observed pattern can be explained
       by activation of organic top soils at non-DRIP reaches by rising groundwater levels (Ledesma et al., 2018) and by overland or
       over-ice flow at DRIPs (Ploum et al., 2018). These examples and the observed patterns that can be explained by our previous
       work, suggests that the model framework and the data input have some limitations representing the dynamics of streamflow
       generation along the stream segment. It is likely that there is discrepancy between our spatial distribution of gained streamflow
385   based on UCA and the effective runoff to streams during different flow conditions (Ambroise, 2004; Klaus and Jackson, 2018).
       Especially, during the spring snowmelt, our model scenarios do not capture the complexity of flow paths and the timing of
       lateral inputs that are associated with snowmelt hydrology (Laudon et al., 2004; Lyon et al., 2010). Besides the source-transport
       mechanisms on hillslope scale, other catchment characteristics affected the performance of the model as well. For example,
       during some high flow conditions (Fig. 3K-M, Fig S1) the lateral groundwater inputs were relatively small compared to the
390   streamflow contributions of the upstream lake (Leach and Laudon, 2019). In these cases, the observed DOC pattern was fairly
       uniform, which made it less challenging for the different scenarios to meet our performance criteria. Also, for event-scale
       dynamics during rain or snowmelt events, the lake was potentially an important influence on stream conditions along this
       segment: while the lateral groundwater inputs respond quickly to rain or snowmelt, the lake response can be delayed (Leach
       and Laudon, 2019).

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       For the in-stream uptake component of our model, we did not take into account processes that produce (i.e. resuspension) or
       remove (i.e., photodegradation, adsorption) DOC from the water column. Further, in-stream DOC uptake was assumed to

occur only downstream of DRIPs and at a uniform rate across flow conditions. Previous studies have shown that uptake rates can vary over time as a function of temperature, DOC composition, and microbial assemblages (Berggren et al., 2009; Mineau

400   et al., 2016). While the use of other values for *Vf* resulted in similar model output (Fig. S2), we cannot discard the idea that *Vf* varied among DRIPs and/or over time due to changes in groundwater DOC composition and temperature. Regardless, our model framework demonstrated that UCA can be useful to identify "reactive" reaches by considering DRIPs as major locations of biological activity. Similarly, others have demonstrated that spatial patterns in DOC concentrations along headwaters are associated with biological activity and stream water permanence driven by terrestrial flow path organization (Lupon et al.,

405   2019, Hale and Godsey, 2019).

For future studies, we have identified two directions that can be useful to improve our simulations of stream DOC dynamics along boreal headwaters. For the representation of the spatial heterogeneity in riparian hydrochemistry, the hydrological representation of lateral groundwater inputs through the distinction of DRIP and non-DRIP riparian zones can be further

410   developed. For this matter, integrative hydrochemical frameworks that represent fluxes from various soil layers would be useful to include, especially at non-DRIPs because here groundwater levels are more dynamic compared to DRIPs (Seibert et al., 2009). Furthermore, it can be of interest to downscale the number riparian groundwater chemistry samples to understand what minimum set of groundwater samples is required to represent the spatial heterogeneity in sources of lateral DOC inputs from RZs to streams. A preliminary analysis indicated that the most optimal strategy to reduce model uncertainty was to

415   monitor DRIPs individually, while averaging DOC concentrations at non-DRIPs (Ploum, 2021). However, given that non-DRIP groundwater chemistry changes with groundwater table fluctuations (Ledesma et al., 2015; Ploum et al., 2020), it is likely that optimizing groundwater sampling campaigns requires careful consideration of the antecedent groundwater conditions.

5 Conclusions

420   The objective of this study was to understand the influence of discrete riparian inflow points (DRIPs) on longitudinal patterns of stream DOC concentrations along a headwater reach. More specifically, our aim was to integrate source-transport mechanisms and in-stream uptake in a model framework, by considering DRIPs as the primary driver of both hydrological and biogeochemical processes that influence patterns of stream DOC concentrations. The purpose of this modelling exercise was to disentangle the role of terrestrial DOC inputs and in-stream uptake during different flow conditions. We found that source-

425   transport mechanisms as well as the in-stream uptake associated with DRIPs had occasionally a large influence on longitudinal DOC patterns. The different model scenarios showed that depending on flow conditions, the dominant influence of lateral groundwater inputs and in-stream uptake on stream DOC patterns shifted. As such, the identification and characterization of groundwater chemistry of DRIPs can be used to represent major lateral groundwater inputs to stream channels, and to highlight reactive reaches within stream networks. This study contributes to the greater goal of integrating hydrological and

430   biogeochemical models (Li et al., 2020), explicit consideration of groundwater discharges in quantitative frameworks (Briggs and Hare, 2018), and the spatial assessment of removal mechanisms of DOC in stream networks (Mineau et al., 2016).

Data availability

The presented data in this study can be requested through the first author. Krycklan data is openly available through the

435   Svartberget database: https://franklin.vfp.slu.se/

Author contributions

SP was responsible for study concept, data collection and analysis, model framework, figure compilation, result interpretation, and writing. AL contributed to study concept, data collection, model framework, result interpretation and writing. JL and HL contributed to model framework, result interpretation and writing. LK designed GW well infrastructure and contributed to
440   result interpretation and writing process.

Competing interests

The authors declare that the research was conducted without commercial or financial support that could be construed as potential conflict of interest.

Acknowledgements

445   This study was funded by Oscar and Lili Lamm Foundation and Svenska Forskningsrådet Formas. The Krycklan catchment is also supported by SITES (VR), SKB, KAW and the Kempe Foundation. AL was supported by the program Beatriu de Pinós, funded by the Government of Catalonia and the Horizon 2020 research and innovation program (BP-2018-00082). We acknowledge Andrés Peralta-Tapia for well installations, and the staff at Svartberget research station and Laura Coulson for assisting with sample collection. We thank Kelly Hondula for support with RStudio troubleshooting during analysis and figure
450   compilation.

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