

A parsimonious model of Groundwater flow paths drive longitudinal patterns of stream DOC patterns based on groundwater inputs and concentrations in-stream uptake boreal landscapes

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Abstract

15 ~~The supply of terrestrial Preferential groundwater flow paths can influence dissolved organic carbon (DOC) to aquatic ecosystems affects local in-stream processes concentrations and downstream transport of DOC exports in the fluvial network. However, we have an incomplete understanding on how terrestrial DOC 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 they facilitate the inflow of terrestrial DOC from large upslope contributing areas to narrow discrete sections of the stream. We refer to these areas of flow path convergence, referred as discrete riparian inflow points (DRIPs). However, the mechanisms by which DRIPs influence longitudinal patterns of stream DOC concentrations is still poorly understood. In this study, we ask how DRIPs affect longitudinal patterns of stream DOC concentrations are affected by DRIPs under different hydrologic conditions, as they are can simultaneously act as major input sources of terrestrial DOC and important locations for in-stream processes. We used a mixing model To answer this question, we tested four model structures that account for different representations of hydrology (distributed inputs of DRIPs vs diffuse groundwater inflow) and in-stream processes (no DOC uptake vs in-stream DOC uptake downstream DRIPs) to simulate stream DOC concentrations along a 1.5 km headwater reach for fifteen 14 sampling campaigns with flow conditions ranging from droughts to floods. Four sets of Despite the magnitude and longitudinal patterns of stream DOC concentration varying across campaigns, at least one 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 structure was able to capture longitudinal trends during each campaign. Specifically, our results showed that under medium (10-50 l/s) and during the snow melt period or high flow conditions (>50 l/s), accounting for lateral distributed inputs of DRIPs improved simulations of stream DOC concentration along the reach, because groundwater inputs from DRIPs improved simulations of stream DOC concentrations along the reach. diluted the DOC in transport. Moreover, accounting for in-stream biological DOC uptake immediately downstream of DRIPs 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. during five sampling campaigns that were performed during late-spring and summer, indicating that these locations served as a resource of DOC for aquatic biota. These results show that the role of hydrology and in-stream processes DRIPs on~~

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40 modulating downstream-DOC concentrations, cycling, and exports varies over time. Importantly and depends strongly on
catchment hydrology. Further, we demonstrate that accounting for preferential groundwater inputs to the stream is needed to
capture 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
45 help inform management of near-stream areas that exert a large influence on stream riparian areas under current and future
climatic conditions.

1 Introduction

Running waters Streams and rivers play a critical role in the global carbon (C) cycle because they transport, store and process large amounts of dissolved organic carbon (DOC) from lands to oceans (Cole et al., 2007; Ciais et al., 2013). Accounting for spatial patterns of stream DOC fluxes concentrations within stream networks can be valuable is vital for understanding net in-stream C retention along rivers (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 and coastal ecosystems (Kritzberg et al., 2020). Across fluvial networks, headwater and high-order river segments have different controls of C dynamics. In headwaters, 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 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).

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 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 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 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 is a growing body of research that combines field-based methods with digital elevation models, and remote sensing approaches (Antonelli et al., 2020; Barelay 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 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 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 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 then combined either with the assumption that the stream is a passive pipe, or with the assumption that in-stream DOC uptake takes place directly downstream of DRIPs.

Yet the main drivers controlling spatial variations in DOC concentrations remain unclear, partly because processes occurring at various scales interact in complex ways to influence the concentration and export of DOC to downstream aquatic ecosystems (Laudon and Sponseller 2018).

In boreal regions, landscape features such as wetlands, headwater lakes and riparian zones are major controls of the spatial variability in stream DOC concentrations (Frost et al. 2006; Laudon et al. 2011; Lottig et al., 2013; Kothawala et al., 2015). In peat-rich riparian soils, typical for boreal forest catchments, the combination of wet soil conditions and organic matter accumulation can increase DOC concentrations over short distances (Grabs et al. 2012). The organization of groundwater flow paths can also regulate spatial patterns of stream DOC concentration by conveying substantial fluxes of water from large upslope contributing areas through wet corridors to discrete sections of the stream, referred to as discrete riparian inflow points (DRIPs) (Jencso et al., 2010; McGlynn and McDonnell, 2003; Ploum et al., 2019). DRIPs have been shown to have greater groundwater concentrations of DOC (Ploum et al., 2020; Demars et al., 2020), associated with converging flow paths from large contributing areas, sustained water saturated conditions, moss-dominated vegetation and organic matter accumulation (Ploum et al. 2021). The high connectivity to adjacent streams delivers terrestrial DOC that can be adsorbed, photodegraded or mineralized by aquatic microbial communities (Berggren et al., 2009; Mineau et al., 2016). This processing happens quickly and over relatively short distances (Demars, 2019), thereby generating hot spots of in-stream uptake immediately downstream DRIPs (Lupon et al., 2022). To integrate the role of DRIPs as both suppliers of terrestrial DOC and promoters of DOC uptake in aquatic ecosystems, we need to combine source-transport hydrochemical and in-stream C cycling frameworks (Li et al., 2020). While there are hydrological frameworks that account for flow path convergence (Jencso et al., 2009; Seibert et al., 2009), these features are often not explicitly considered in biogeochemical studies and monitoring strategies (Briggs and Hare, 2018). As a result, the extent to which DRIPs can affect stream DOC concentrations, cycling, and overall C exports at different spatial scales remains largely unknown.

The relative contribution of DRIPs on shaping downstream DOC concentrations and processing likely depends on catchment hydrology. During base flow conditions and small rain events, DRIPs are major contributors of water to stream flow (Leach et al. 2017; Ploum et al., 2019); and hence, they could drive spatial variation in stream DOC concentrations by acting as sources of DOC along streams, as observed for C gases (Lupon et al. 2019; Rocher-Ros et al. 2019). In contrast, the relevance of these flow paths as primary drivers of stream DOC concentrations might be less important during extreme hydrological events (i.e. droughts and floods), when the DRIP-stream hydrological connectivity is low or overwhelmed by either upstream fluxes or diffuse lateral inflows (Leach et al., 2017; Gómez-Gener et al., 2020). Further, catchment hydrology also affects the potential for aquatic biota to act upon the DOC in transport (pulse-shunt concept; Raymond et al. 2016). Large residence times during low and medium flows can promote in-stream DOC mineralization (Casas-Ruiz et al., 2017), while rapid water velocities might overwhelm in-stream DOC uptake during high flows (Bernal et al., 2019). Since the hydrology of many boreal landscapes is rapidly changing due to global change, (Laudon et al., 202; Gómez-Gener et al., 2021), it is important to understand where and when DRIPs hydrologically connect to headwaters, as well as their broader effects on stream C cycling and overall catchment C exports under current and future climatic scenarios.

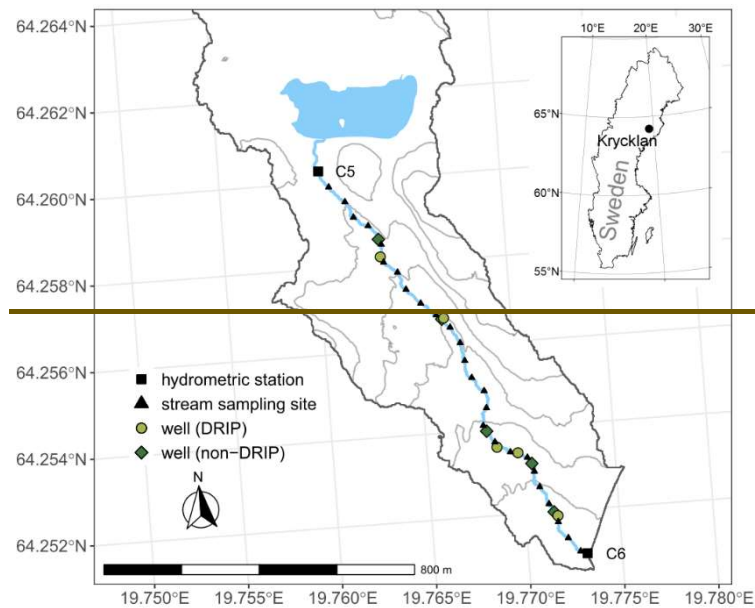
In this study, we assessed the relevance of DRIPs as primary drivers of spatial patterns of stream DOC concentrations along boreal headwater streams. Specifically, we aimed to disentangle the role of DRIPs as terrestrial DOC suppliers vs. hot spots for in-stream DOC uptake during different flow conditions. To do so, we tested four different models to simulate stream DOC concentrations along a 1.5 km headwater reach, for 14 campaigns with flow conditions ranging from droughts to floods. Models accounted for two types of transport mechanisms: 1) assuming uniform, diffuse inflow of groundwater along the reach and 2) assuming the existence of DRIPs by weighting groundwater inflow relative to their upslope contributing area (UCA). These two assumptions were combined either with the assumption that stream biota do not take up the supplied DOC, or with the assumption that in-stream DOC uptake takes place directly downstream of DRIPs (Table 1).

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 reach located between the gauging stations C5 and C6 (Fig. 1) (Laudon et al., 2013). The gauging station C5 is the outlet of lake Stortjärn (4.2 ha), with a catchment area of 65 ha. The gauging station C6 is situated 1.5 km downstream of C5, and has a catchment area of 110 ha. The catchment contributing to the C5-C6 reach 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, while the shallow subsurface soils of the riparian zone (< 1.2-meter-deep) are dominated by peat. Furthermore, wet corridors occur that extend from upland areas to riparian zones, characterized by flat topography, moss-dominated vegetation and decreased tree-density (Ploum et al. 2021). We refer to their connection to streams as discrete riparian inflow points (DRIPs). Soil wetness mapping and flow accumulation maps based on 2x2 Digital Elevation Models demonstrated that the wet corridors occur at 1-10 ha contributing areas (Ågren et al. 2014). To identify DRIPs along the C5-C6 reach, the gain in flow accumulation was aggregated in stream segments of 50 meters. Seven segments fell within the 1-10 ha range, of which five were considered as DRIPs based on previous field-validation consisting of vegetation surveys and thermal and isotopic tracing (Kuglerová et al. 2010, Leach et al. 2017). The five DRIPs are located along the streams reach and collectively account for >60% of the lateral groundwater inflows along the reach, while the remaining lateral inflow is diffused (Leach et al., 2017). No tributaries are present along the stream reach and deep groundwater inflows are minimal in this catchment (Tiwari et al. 2017).

For the period 1981 – 2010, the average temperature was 1.8 °C and the average annual precipitation in Krycklan was 614 mm, of which 35-50% fell as snow (Laudon and Ottosson Lövvenius, 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.~~ On average, approximately 50% of the annual precipitation translates to streamflow. The hydrological regime at ~~gauging stations the C5 and C6 reach~~ 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)~~ alternate with medium to 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<3 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 (Leach and Laudon 2019; 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 (1.5 km downstream), streamflow responds~~ much faster to hydrological events compared to C5 and is characterized by steep rising limbs (Fig 2, Ploum 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).~~



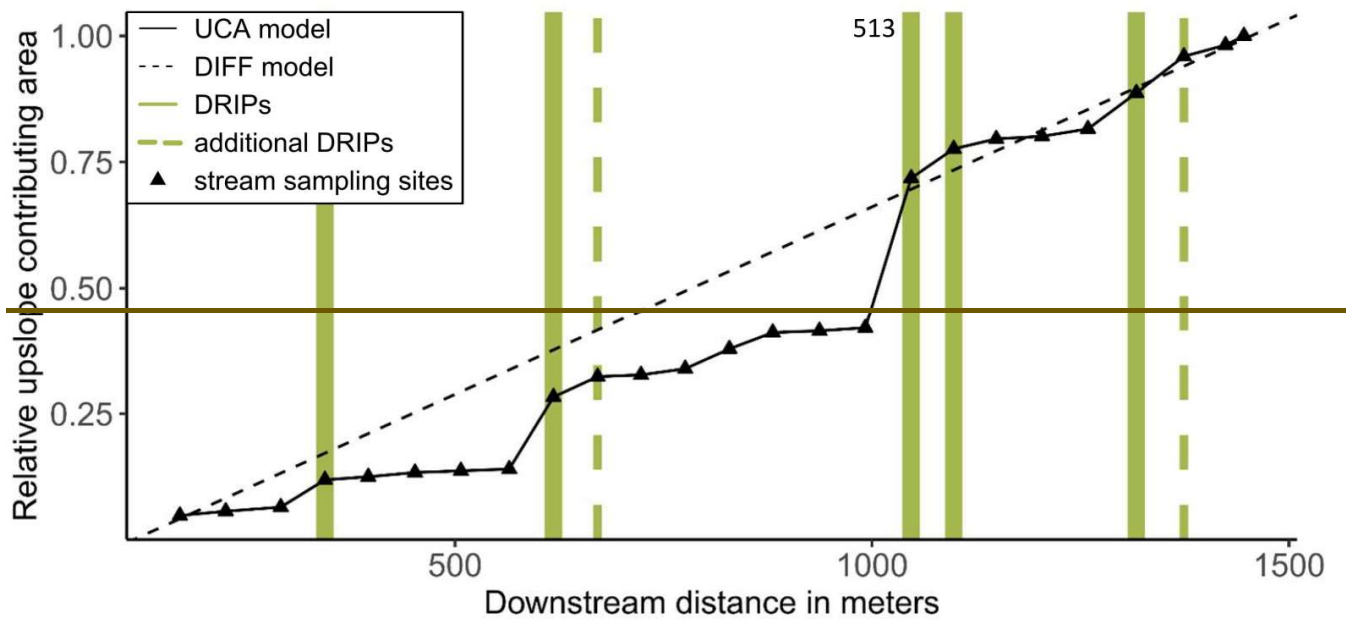
~~Figure 1 The Stortjärnsbacken subcatchment in Krycklan, Sweden. The stream segment starts at the outlet of lake Stortjärn (gauging station C5), and ends at the downstream gauging station C6. Stream sampling sites at approximately 50 meter increments are indicated with triangles. Light green circles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

2.2 FieldStudy design, field measurements and laboratory analysis

Field measurements were collected between May 2017 and May 2019. In total, we conducted ~~15~~14 sampling campaigns with different streamflow conditions, which ranged from drought ~~conditions~~ to peak flows conditions (Fig. S1). ~~Ten~~2). Nine sampling campaigns were centred around the snowmelt periods of 2017-2019, and five around a lake damming experiment in Augustsummer 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). During the course of the artificial drought, the strength of DRIP-stream hydrological connections declined, generating a patchy distribution of lateral DOC inputs similar to those occurring under natural droughts (Gómez-Gener et al., 2020). For each sampling campaign, stream water was collected along the stream reach at approximately 50 meter intervals over 1200 meters, dividing the stream reach into 25 sections (Lupon et al., 2019). Riparian~~Five of the 25 sections had a DRIP discharging into it, while the other 20 sections were fed by small diffuse groundwater ~~was~~inputs (Fig. 1, Fig. 3). For 10 of those sections, we sampled riparian groundwater inputs from a ~~paired~~-well network setup, which included five pairs of DRIP and non-DRIP wells located 1-5 m from the stream edge (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~~). Therefore, we sampled the phreatic groundwater of all DRIPs, but not all the diffuse groundwater inputs discharging into 15 reaches. The PVC wells (30 mm diameter) had a mean depth of 95 cm ($\sigma = 37$ cm) below the soil surface and were fully screened every 5 cm.

Stream water was collected from the ~~talweg~~thalweg with acid-washed high-density polyethylene bottles. Groundwater~~PVC~~ wells were sampled using suction cup lysimeters and ~~vacuumed~~evacuated 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) MCE syringe filters, Millipore® and kept refrigerated at 4 °C ~~before~~until analysis. (< 7 days after filtering). DOC analysis consisted of acidification of the sample for removing inorganic carbon, followed by combustion using a Shimadzu TOC-V_{CPH}. (analytical error: 2%; Laudon et al. 2011). The analysis was repeated at least three times per sample resulting in a DOC concentration in mg/l and a percent standard deviation.



225 **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 dissolved organic carbon (DOC) uptake was considered only in those reaches comprising DRIPs (i.e. after the vertical bars).**

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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 riparian DOC inputs were subjected to in-stream uptake.

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

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where $DOC_{stream,i}$ and $DOC_{stream,i-1}$ are the stream DOC concentration measured at location i and $i-1$, respectively; Q_i and Q_{i-1} are the estimated streamflows at locations i and $i-1$, respectively, and the difference ($Q_i - Q_{i-1}$) represents the net groundwater inflow for that stream section; $DOC_{gw,i}$ is the estimated groundwater DOC concentration at between location $i-1$ and 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

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Out of the 25 stream reaches, there were ten reaches where DOC_{gw} was directly obtained from DRIP and non-DRIP wells. 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 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 We modified the abovementioned model (eq. 1) to represent different assumptions of catchment hydrology (diffuse vs. distributed groundwater inputs) and in-stream DOC processing (no uptake vs. in-stream uptake downstream DRIPs), resulting in four different models (Table 1). The model “Diff” assumed diffuse groundwater inputs and no in-stream DOC uptake. The model “Diff-Bio” also assumed diffuse groundwater inputs, but accounted for in-stream DOC uptake downstream from DRIPs. The model “UCA” assumed that groundwater inputs were distributed proportional to their UCA and no in-stream DOC uptake. Finally, the model “UCA-Bio” assumed groundwater inputs proportional to UCA and accounted for in-stream DOC uptake downstream from DRIPs. Below, we outline the equations used for estimating riparian groundwater DOC concentrations, groundwater inputs and in-stream uptake.

2.3.1 Estimates of riparian groundwater DOC concentrations

For each date, we used direct measurements of groundwater DOC concentrations from wells to estimate DOC_{gw} for 10 sections (i.e. 5 sections with DRIPs and 5 sections without DRIPs). For the remaining 15 sections, we assumed that DOC_{gw} equaled the average of the non-DRIP wells. For all instances where we did not have direct measurements of DOC_{gw} and used estimates based on the means of the non-DRIP observations, we also computed the standard deviation of the mean as a measure of uncertainty in the mixing model framework.

2.3.2 Estimates of streamflow and lateral groundwater inputs

Streamflow at each location (Q_i) was ~~considered~~ represented in the model 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~~ riparian zone. One scenario assumed that the local gains in streamflow were driven by diffuse groundwater inflow (hereafter referred as “~~DIFF~~Diff”, Fig. 23), where the net gain in streamflow is distributed ~~according to gained stream distance~~ evenly along the C5-C6 reach:

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

where Q_{C5} and Q_{C6} ~~is the~~ are 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. 23) 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~~ stream section (s):

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

where UCA_i is the upslope contributing area that is gained along the reach (stream section (i.e. 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 riparian zone.

2.3.2 ~~In~~ Estimates of in-stream DOC processing uptake

We considered two different scenarios regarding in-stream DOC processing uptake. One scenario model considered that the stream was acting as a passive pipe for all terrestrial DOC inputs were transported to downstream ecosystems (i.e., pulse-shunt concept; no in-stream DOC uptake), while the other scenario model considered that stream biota rapidly take up the DOC originating coming from lateral groundwater inputs. (i.e., hot spot concept). We did not consider the scenario that DOC coming from the upstream locations were lake was taken up along the stream, as previous studies in the Krycklan catchment have suggested that this DOC is highly recalcitrant and rarely occurs used by stream biota (Tiwari et al., 2014; Kothawala et al., 2015).

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

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

305 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 sections to zero, except for those where a DRIP was located (Fig. 23). At these reaches sections, $length_i$ 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 $Vf = 0.6 \pm 0.06$ mm/min. This value is the median ambient DOC Vf obtained from a literature review and has been shown to realistically 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 315 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~~ uncertainty and performance criteria

In total, our model approach resulted in four scenarios per sampling campaign (Table 1). For each sampling date, the model scenarios were informed with the same DOC_{gw} concentrations, but assumed different representations of catchment hydrology

320 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 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 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

330 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 using a randomized sample for every observation and every computation. We presented the simulated $DOC_{stream,t}$ using an uncertainty band that represented 66% of the randomized model runs (mean \pm 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 $DOC_{stream,t}$. This means that for the next downstream location the gained uncertainty (from the streamflow, DOC uptake velocity and laboratory analysis) is incorporated as a single value of $DOC_{stream,t-1}$. 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.

345 For each model, we accounted for uncertainty in modelled stream DOC concentrations (Eq. 1) by accounting for errors in streamflow observations, water sample analysis, DOC_{gw} estimates, and DOC uptake velocity. We assumed normally distributed errors for Q_{c5} and Q_{c6} ($\pm 10\%$, based on repeat streamflow gauging; Karlson et al. 2016), DOC_{gw} (either $\pm 2\%$ for sites with measurements based on laboratory analytical precision or ± 1 standard deviation of the mean for sections that rely on estimates), and V_f ($\pm 10\%$, based on Mineau et al. 2016). For each date, each model was run 10000 times using random values selected from these parameter distributions. Error estimates in $DOC_{stream,i}$ were tracked downstream since the values become $DOC_{stream,i-1}$ in the computation for the next stream reach.

We evaluated the ~~simulation~~simulation of each run using a ~~number of two~~ 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 from the observations, where positive values indicate overestimation and negative values underestimation. We considered a 5% bias acceptable. NSE ranges from $-\infty$ 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 , these assumption was only true if the relation between observed and simulated stream DOC concentrations was positive.~~First, we computed the percent bias (PBias, in %), which measures the average tendency of the simulated values to be larger (PBias $> 0\%$) or smaller (PBias $< 0\%$) than their observed ones. We considered that a model successfully simulated the magnitude of stream DOC concentrations if the median value of all runs was within -5% and $+5\%$ bias. Second, we calculated the Spearman correlation (R), which shows if the longitudinal patterns of simulated DOC concentrations mimicked the observed ones. In this case, we considered that a model was capturing the general direction of stream DOC concentrations if the median R of all runs was higher than 0.70.

3 Results

370 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
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
375 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
was greater than 0.5 (Table 2, Fig. 3F, K-M).

3.1 Snowmelt 2017

380 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
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
385 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
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
390 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
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")
395 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
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
400 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
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
405 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

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).

410 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 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 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).

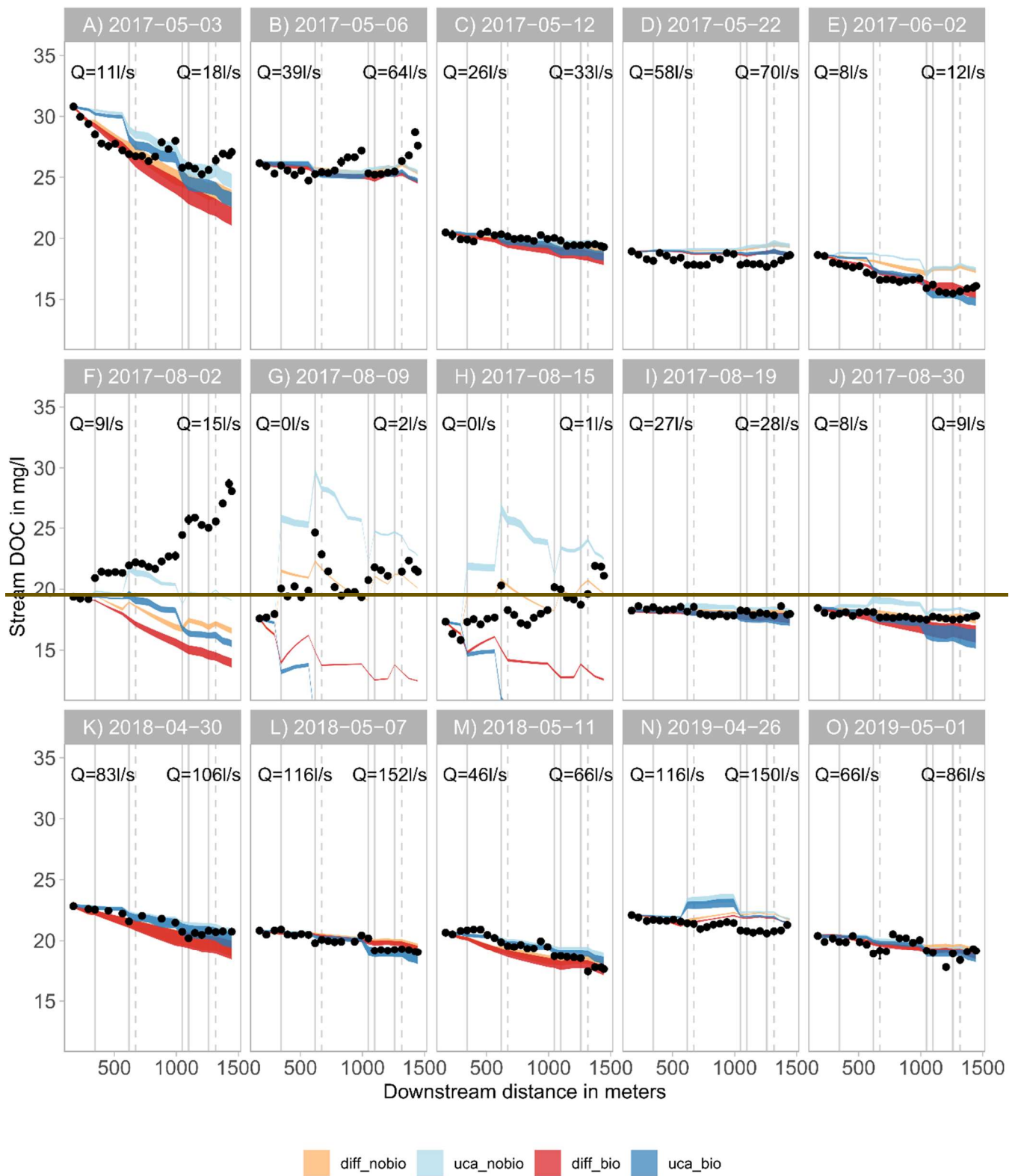


Figure 3 Longitudinal patterns of stream dissolved organic carbon (DOC) concentrations along the C5-C6 stream segment. Each panel, indicated by label and date, shows one sampling campaign. The black dots are the observed stream DOC concentrations. The coloured bands show the simulations of the four models. 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.

425

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	PBIA	NSE	R ²	DATE	MODEL	RMSE	PBIA	NSE	R ²	
			{MG/L †	S {%	{%				{MG/L †	S {%	{%		
A	17-05-03	DIFF_NOBI Θ	1.89	-3.6	-0.90	0.60	I	17-08-19	DIFF_NOBI Θ	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_NOBI Θ	1.66	2.8	-0.47	0.51			UCA_NOBI Θ	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_NOBI Θ	1.09	-0.1	-0.31	0.12	J	17-08-30	DIFF_NOBI Θ	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_NOBI Θ	1.04	-0.1	-0.30	0.09			UCA_NOBI Θ	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_NOBI Θ	0.61	-2.4	-0.99	0.50	K	18-04-30	DIFF_NOBI Θ	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_NOBI Θ	0.56	-1.7	-0.81	0.53			UCA_NOBI Θ	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_NOBI Θ	1.09	5.3	-6.6	0.10	L	18-05-07	DIFF_NOBI Θ	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_NOBI Θ	1.07	5.2	-6.05	0.13			UCA_NOBI Θ	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_NOBI Θ	1.26	6.7	-0.72	0.77	M	18-05-11	DIFF_NOBI Θ	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_NOBI Θ	1.62	8.9	-1.93	0.63			UCA_NOBI Θ	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_NOBI Θ	6.28	-22.6	-4.77	0.7 0	N	19-04-26	DIFF_NOBI Θ	0.87	3	-3.36	0.2 1
		DIFF_BIO	7.96	-28.7	-8.16	0.8 4			DIFF_BIO	0.68	2.3	-1.46	0.0 1
		UCA_NOBI Θ	4.24	-13.5	-1.69	0.0 9			UCA_NOBI Θ	1.79	6.7	-15.97	-0.0 1
		UCA_BIO	6.52	-22.2	-5.29	0.8 9			UCA_BIO	1.52	5.8	-12.32	-0 0
G	17-08-09	DIFF_NOBI Θ	1.16	-1.3	0.48	0.5 4	Θ	19-05-01	DIFF_NOBI Θ	0.65	0.4	0.2	0.2 3
		DIFF_BIO	6.91	-30.9	-16.57	0.4 0			DIFF_BIO	0.67	-0.2	0.18	0.2 7
		UCA_NOBI Θ	5.06	20.8	-8.87	0.3 7			UCA_NOBI Θ	0.65	-0.7	0.19	0.4 2
		UCA_BIO	11.34	-50	-44.99	0.5 7			UCA_BIO	0.71	-0.8	-0.13	0.3 8
H	17-08-15	DIFF_NOBI Θ	1.57	4.4	0.01	0.3 0	-	-	-	-	-	-	
		DIFF_BIO	5.1	-23.1	-9.01	0.5 2							
		UCA_NOBI Θ	4.78	22.4	-7.99	0.1 2							
		UCA_BIO	8.66	-39.5	-28.02	0.6 3							

3.1 Stream hydrology

435 Across the 14 sampling campaigns, hourly streamflow ranged from 0 l/s to 116 l/s and from 2 l/s to 152 l/s at C5 and C6, respectively; and it was comparable to the temporal patterns observed during the whole ice-free period (C5: 0-150 l/s, C6: 2-200 l/s; Fig. 2). At both gauging stations, maximum streamflow occurred during the snowmelt, whereas minimum streamflow was observed during the artificial drought in summer 2017. As a result, the net gain in streamflow along the C5-C6 reach ranged from 8% (artificial flood, event G) to 90% (artificial drought, event H) (Fig. 2). During the other sampling campaigns, the net gain in streamflow along the reach was between 20% and 50%, with a mean of 37% (Fig. 2).

3.2 Stream DOC concentrations

440 During the study period, stream DOC concentrations ranged from 15 mg/l to 32 mg/l and varied over time as well as along the stream reach (Fig. 4). Seasonally, average DOC concentrations decreased over the three snowmelt periods (events A-E, J-L, and N-M). In summer 2017, stream DOC concentrations were relatively constant at C5 (19-20 mg/l), whereas they decreased during the same period at C6 (from 28 to 18 mg/l) (events F-I). Spatially, stream DOC concentrations generally decreased along the C5-C6 reach (8 out of 14 sampling campaigns) (Fig. 4). However, stream DOC concentrations clearly increased along the reach for the increasing limb of snowmelt 2017 (event B), the summer storm event (event F) and the artificial drought (event G). During the recession limb of the snowmelt peak 2017 (event D) and the lake flooding experiment (events H and I), stream DOC concentrations were relatively constant along the reach.

Abrupt changes in stream DOC concentrations occur in those sections affected by DRIPs (Fig. 4). During most snowmelt campaigns (events A-C, J-N) and summer base flow conditions (event E), stream DOC concentrations sharply decreased in

450 sections fed by DRIPs. The only exception was the section affected by the last DRIP, from which stream DOC concentrations tended to increase. Peaks in DOC concentrations immediately downstream DRIPs also occurred during the summer rain event and the experimental drought (events F-G). For the other sampling campaigns (events D, H and I), both increases and decreases in DOC concentrations occurred at DRIP locations.

3.3 Model simulations

455 The capacity of the models to simulate the magnitude and longitudinal patterns of stream DOC concentrations varied across sampling campaigns (Fig 4). For most sampling campaigns performed during the snow melt period, at least one of the models was able to capture either the magnitude or spatial variations of stream DOC concentrations (Fig. 4). For events B-D, K, and M-N, all models captured the magnitude of stream DOC concentrations (median PBias from -5 to 5%; Fig. 5), yet only for event K all of them were also able to simulate their longitudinal patterns (median $R > 0.80$; Fig. 6). Indeed, none of the models
460 captured spatial patterns for the events B, D and M (median $R < 0.50$), although the model Diff-Bio tended to perform better than the others (Fig. 6). For the event C, spatial patterns were captured by both the models Diff-Bio and UCA-Bio (median $R \sim 0.75$; Fig. 6), whereas the models UCA and UCA-Bio were able to simulate patterns of stream DOC concentrations for the event N (median $R \sim 0.70$, Fig. 6). For the three other field campaigns performed during the snow melt period (events A, J and L), the magnitude of stream DOC concentrations was only successfully captured by the models UCA and/or UCA-Bio (median
465 PBias $\sim 0\%$, Fig. 5), despite all models were able to simulate the spatial patterns of DOC concentrations ($R > 0.70$; Fig. 6).

For the sampling campaigns performed during summer 2017 (events E-I), there were large inconsistencies across models (Fig. 4). For summer base flow conditions (event E), the models Diff-Bio and UCA-Bio successfully simulated both the magnitude (PBias $< 3\%$) and spatial patterns ($R > 0.90$) of stream DOC concentrations (Fig. 5, Fig. 6). For the natural rain event (event F), all models underestimated stream DOC concentrations (PBias $< 0\%$) as well as failed to predict their spatial variation
470 (median $R < 0.35$). Yet the model UCA performed better than the others (Fig. 5, Fig. 6). None of the models was also able to capture spatial patterns during the lake flooding (event H, $R < 0.5$), even when all of them captured the overall magnitude of DOC concentrations (Fig 5, Fig 6). For the experimental drought (event G), Diff and UCA models successfully simulated spatial patterns of stream DOC concentrations ($R > 0.70$; Fig. 5), yet only the Diff model also accurately captured their magnitude (median PBias = 1%; Fig. 6). Similarly, only the model Diff was able to simulate both the magnitude and spatial
475 pattern of stream DOC concentrations for the post flooding campaign (event I; Fig. 4-6).

4 Discussion

Our observations showed that longitudinal 4.1 Modelling spatial patterns of stream DOC concentration

DRIPs are an important, and often primary, source of water and C to headwaters (Briggs and Hare, 2018; Demars et al., 2018), and can therefore play a major role in regulating spatial variation in stream DOC concentrations between the two gauging
480 stations, processing and exports. Our spatially explicit surveys revealed that longitudinal patterns of stream DOC concentrations varied spatially during different across flow conditions. While during some sampling campaigns stream DOC concentration was uniform. In general, DOC concentrations tended to decrease along the C5-C6 reach, indicating that DOC was generally diluted or taken up along the stream segment (around 20 mg/l), at other occasions it varied between 15 and 30 mg/l. Especially at DRIPs. However, we observed step changes in stream DOC concentrations, indicating that at DRIPs can
485 both decrease and increase stream DOC concentrations. We considered, indicating that these changes can be attributed to dilution and enrichment of DOC, as well as to in-locations play a key role for stream removal of DOC. To understand what controlled patterns of stream DOC concentrations at C exports. Similar patterns have been observed in other boreal headwaters

(Duvert et al., 2018; Lupon et al., 2019), yet our study is the various flow conditions, we simulated stream first to reveal the mechanisms by which DRIPs shape spatial patterns of DOC concentrations based on terrestrial DOC and fluxes and local in-stream DOC uptake. We compared four different model scenarios with the observed stream DOC profiles in these streams.

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, accounting for spatial variability in lateral groundwater inflows in the models (i.e. UCA) improved simulations of stream DOC concentrations for five out of the nine sampling campaigns performed during the snow melt period (events A, C, J, L and N), when groundwater inputs were high (> 20 l/s) and/or contributed significantly (>40%) to streamflow. During these events, sharp decreases in DOC concentrations were observed in sections fed by DRIPs, suggesting that these preferential groundwater flow paths mostly diluted the DOC concentrations in the stream. Further, UCA improved the simulations of stream DOC concentrations during the summer rain (event F), when the net gaining of streamflow along the reach was 46%. In this case, however, DOC concentrations increased in most DRIP locations, indicating that these flow paths were acting as important sources of C to the stream. Previous studies have observed that high groundwater tables associated with rain events often increase groundwater DOC concentrations by activating the dominant source layer (Ledesma et al., 2018), which might explain the observed increase in DOC concentrations along the reach observed for the event F. Regardless of the process (i.e. DOC source or dilution), these findings corroborate that the spatial variability in groundwater flow paths related to landscape topography has a major influence on stream C patterns when streams are mostly fed by groundwater flow (Covino et al., 2021; Dupas et al., 2021; Rocher-Ros et al., 2019).

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 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 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).

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 at the transition between low and high flows due to increases in labile DOC supply from terrestrial systems. However, our

530 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 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.

535 UCA did not improve models simulations for the sampling campaigns close to a snowmelt peak (events B, K and M) despite groundwater inputs being elevated (25-36 l/s). Our explanation is that during these events, increases in the groundwater level might homogenize groundwater inflows along the reach, potentially generating overland because of soil frost causing impervious conditions (Ploum et al., 2020). This might also explain the observed increase in DOC concentrations along the reach observed for the event B. Similarly, a potential homogenization of overland flow during the snowmelt can explain the decline in DOC concentrations during events K and M (Ploum et al., 2018; Laudon et al., 2011). In any case, from our work it is evident that model frameworks that integrate the spatial arrangement of groundwater flow paths (i.e. DRIPs) can help represent the variability in the hydrological connectivity along the stream.

545 Model simulations also revealed that accounting for in-stream uptake downstream of DRIPs improved predictions of longitudinal patterns of stream DOC concentration for the five sampling campaigns occurring from May to August (events C-E, H and M), but especially during summer low flow conditions (event E). It is likely that these results are explained by the seasonal pattern of microbial activity in boreal streams, which often mirror the temporal variation in water temperature (Burrows et al., 2017). However, in-stream uptake did not improve model simulations during those dates in summer showing very low (event G) or high flows (event I). These results concur with recent headwater studies (Lupon et al., 2019; Seybold and McGlynn, 2018; Demars, 2019), and suggest that aquatic biological activity is enhanced at the transition between low and high flows due to increases in labile DOC supply from terrestrial systems. Conversely, in-stream DOC uptake may be minimal during low flows due to C limitation (Burrows et al., 2017) or overwhelmed by low water residence times and physical disturbance during rain events (Raymond et al., 2016). Most importantly, our findings highlight that DRIPs are likely major locations of aquatic biological activity. Similarly, others have demonstrated that spatial patterns of DOC concentrations along headwaters are associated with biological activity and stream water permanence driven by terrestrial flow path organization (Lupon et al., 2019, Hale and Godsey, 2019). Collectively, these results suggest that DRIPs are important sources of DOC for stream biota and thus, the capacity for processing DOC of boreal headwater streams is closely tied to the spatial arrangement of lateral inputs of DOC from riparian zones.

555 4.2 Limitations of the model

560 Our model framework represented the source of lateral DOC inputs based on groundwater samples from a riparian well network that compared DRIP and non-DRIP groundwater chemistry (Ploum et al., 2020). This allowed us 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 than hydrology or in-stream uptake: during 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

570 ~~inputs~~For example, during the experimental drought (event G), the model Diff provided better simulations of both the magnitude and spatial patterns of stream DOC concentrations compared to the assumption of uniform inputs along the reach, suggesting that the representation of spatial variability in groundwater DOC concentrations was more important than hydrology or in-stream uptake. Hence, under these conditions, stream DOC patterns might not be directly related to groundwater fluxes, but rather to the thermal and chemical conditions that groundwater discharge creates at the local level (Briggs and Hare, 2018). However, ~~wethere are~~ also ~~see~~limitations ~~of~~in our groundwater sampling approach. For example, our groundwater sampling ~~campaigns werewas~~ not able to represent temporal DOC dynamics associated with variability in groundwater travel times (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).

580 Apart from the limitations of our groundwater sampling ~~campaigns~~, we identified ~~othersome~~ limitations in the hydrological ~~components and the in-stream uptake~~biogeochemical components of the model as well. The sampling campaign of ~~athe~~ ~~summer~~ rain event on 2017-08-02 (Fig. 3F(event F)) is a clear example of mismatch between our simulations and the observations: while stream DOC concentrations increased along the reach, ~~most of our model scenarios~~models simulated a decreasing pattern. ~~The observed step changes in stream DOC concentrations at~~Similarly, none of the DRIPs is in agreement with ~~models properly simulated~~ 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~~longitudinal patterns: our model scenarios produced a uniform DOC pattern, while the observations showed ~~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). ~~for two sampling campaigns performed around the snow melt peak (events B and M).~~ These examples ~~and the observed patterns that can be explained by our previous work,~~ suggest ~~ssuggest~~ that the model ~~framework and the data input have~~has some limitations representing the complex hydrologic and biogeochemical dynamics of ~~streamflow generation along the stream segment.~~ It is likely that there is discrepancy between our spatial distribution of ~~gained~~ streamflow based on UCA and the effective runoff to streams during different flow conditions ~~occurring in headwater streams~~ (Ambrose, 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 ~~For instance, our models~~ ~~do not account for local conditions affecting snow melt rates on hillslopes (i.e., shading, sun exposure) nor local variations in precipitation, interception or infiltration that are relevant during rain events~~ (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 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).

605 ~~For the in-stream uptake~~For the biogeochemical component of our model, we did not take into account processes that produce (i.e. resuspension) or remove (i.e., photodegradation, ~~adsorption~~adsorption, flocculation) DOC from the water column. (Droppo et al., 1998; Kaiser and Kalbitz, 2012). 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 et al., 2016). While the use of other values for V_f resulted in similar model output (Fig. S2S1), we cannot ~~discard~~rule out the idea that V_f 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., 2019, Hale and Godsey, 2019).~~To better understand the role of DRIPs on stream hydrology and biogeochemistry, future empirical studies testing how DRIPs affect specific processes are needed. Nevertheless, our study, even with its limitations, demonstrated that both lateral discrete and diffused inputs as well as biological activity are essential components of the DOC patterns in boreal streams. These findings shed a new light on the understanding of C dynamics across boreal aquatic-terrestrial interface.

Another major limitation of our models is their large uncertainty, especially during events with large groundwater contributions such as event B. For six events (A,B,C,G,J,L), all models showed large inconsistencies among runs, resulting in simulated DOC concentrations at C6 that vary over 10 mg/l. Moreover, the uncertainty in groundwater DOC concentrations was large, because not all stream sections were sampled and groundwater inputs of DOC had to be estimated based on means of the available DOC concentrations from non-DRIP wells. For future studies, we have identified two more directions that can be useful to improve ~~our~~the 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 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; Ploum et al., 2020). 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~~riparian zones to streams. A preliminary analysis indicated that the most optimal strategy to reduce model uncertainty was to 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

~~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-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~~

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).

650 This study provides new insight into the role of DRIPs on stream DOC concentrations in boreal headwater catchments. We showed that DRIPs influence longitudinal patterns of stream DOC concentrations at small spatial scales (few meters) by controlling both the hydrology and the biogeochemistry of the streams they feed. However, our study also shows that the role of DRIPs can change over time depending on the hydrologic conditions. During high flows, DRIPs control DOC concentrations by supplying or diluting the DOC. In contrast, in late-spring and summer, DRIPs can be important sources of C for stream
655 biota, delivering labile resources from their upstream contributing areas (UCA) and promoting local hot spots of in-stream DOC uptake downstream confluences. These results suggest that future changes in catchment hydrology associated with global change can affect DOC exports from boreal fluvial networks by shifting the dominant mechanisms by which DRIPs drive spatial patterns of DOC concentrations and processing along headwater streams. Thus, the identification and characterization of DRIPs is essential to understand the current and future mechanisms behind C fluxes from boreal fluvial networks.

660 **Data availability**

The presented data in this study can be requested through the first author. Krycklan data is openly available through the Svartberget database: <https://franklin.vfp.slu.se/>

Author contributions

665 AL and SP are shared first-authors. AL contributed to study concept, data collection, model framework, result interpretation and writing. 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 result interpretation and writing ~~process~~.

Competing interests

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

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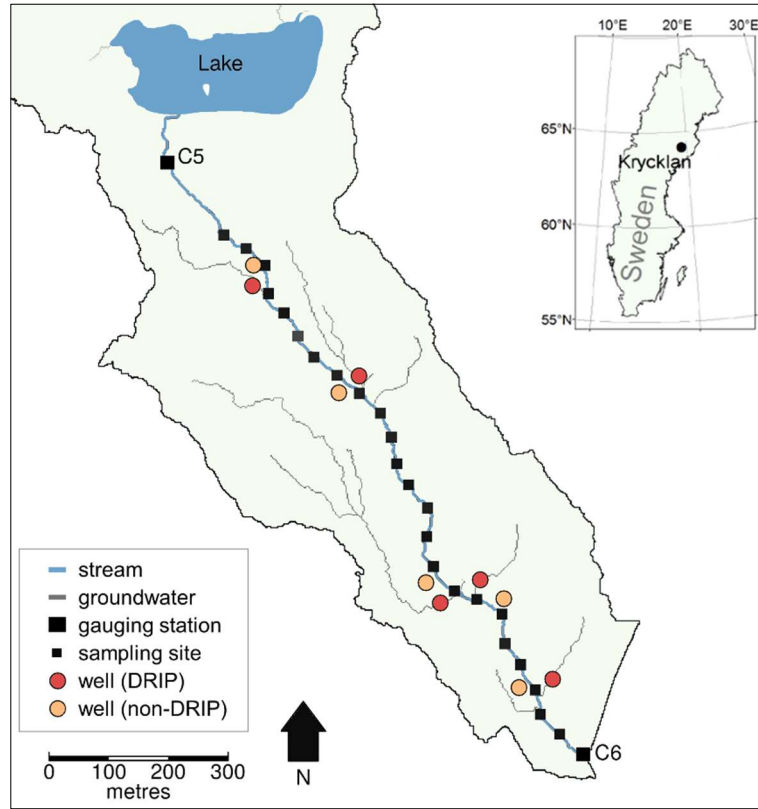
830

Tables and Figures

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 whether in-stream uptake of dissolved organic carbon (DOC) by biota is included.

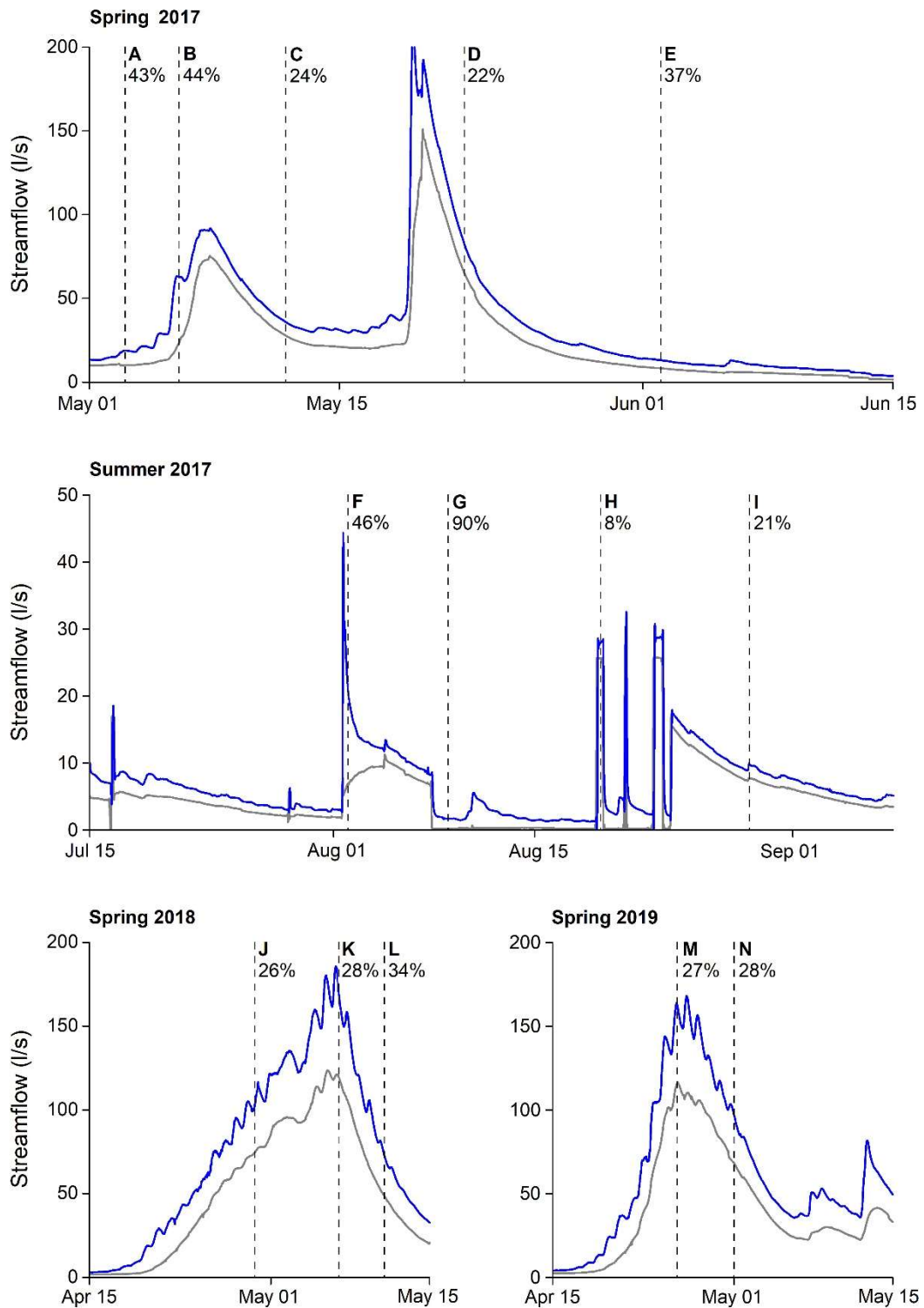
<u>Model Name</u>	<u>Hydrology</u>	<u>Biology</u>
<u>Diff</u>	<u>Diffuse</u>	<u>No in-stream uptake</u>
<u>Diff-Bio</u>	<u>Diffuse</u>	<u>Uptake downstream DRIPS</u>
<u>UCA</u>	<u>Upslope contributing area</u>	<u>No in-stream uptake</u>
<u>UCA-Bio</u>	<u>Upslope contributing area</u>	<u>Uptake downstream DRIPS</u>

835



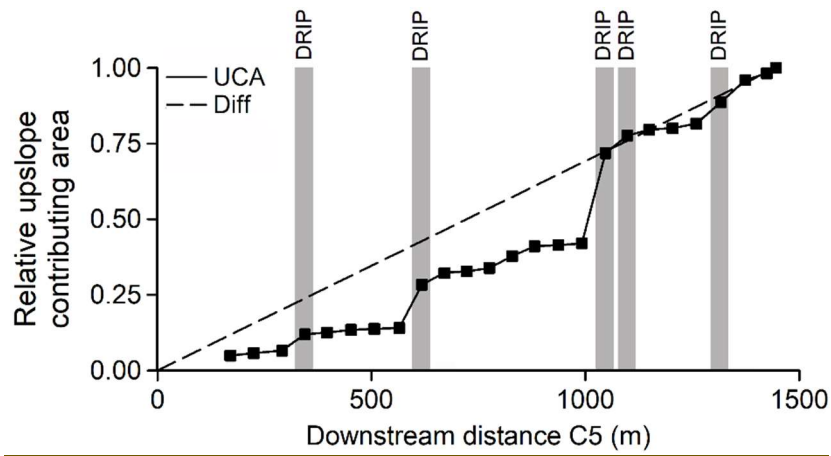
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Figure 1 The Stortjärnsbacken subcatchment in Krycklan, Sweden. The stream reach (blue line) starts at the outlet of lake Stortjärn (gauging station C5) and ends at the downstream gauging station C6. Stream sampling sites at approximately 50 meter increments are indicated with small black squares. Groundwater wells along the reach are indicated with red circles (DRIPs) and orange circles (non-DRIPs). At DRIPs, groundwater flow paths (grey lines) converge in the riparian zone.



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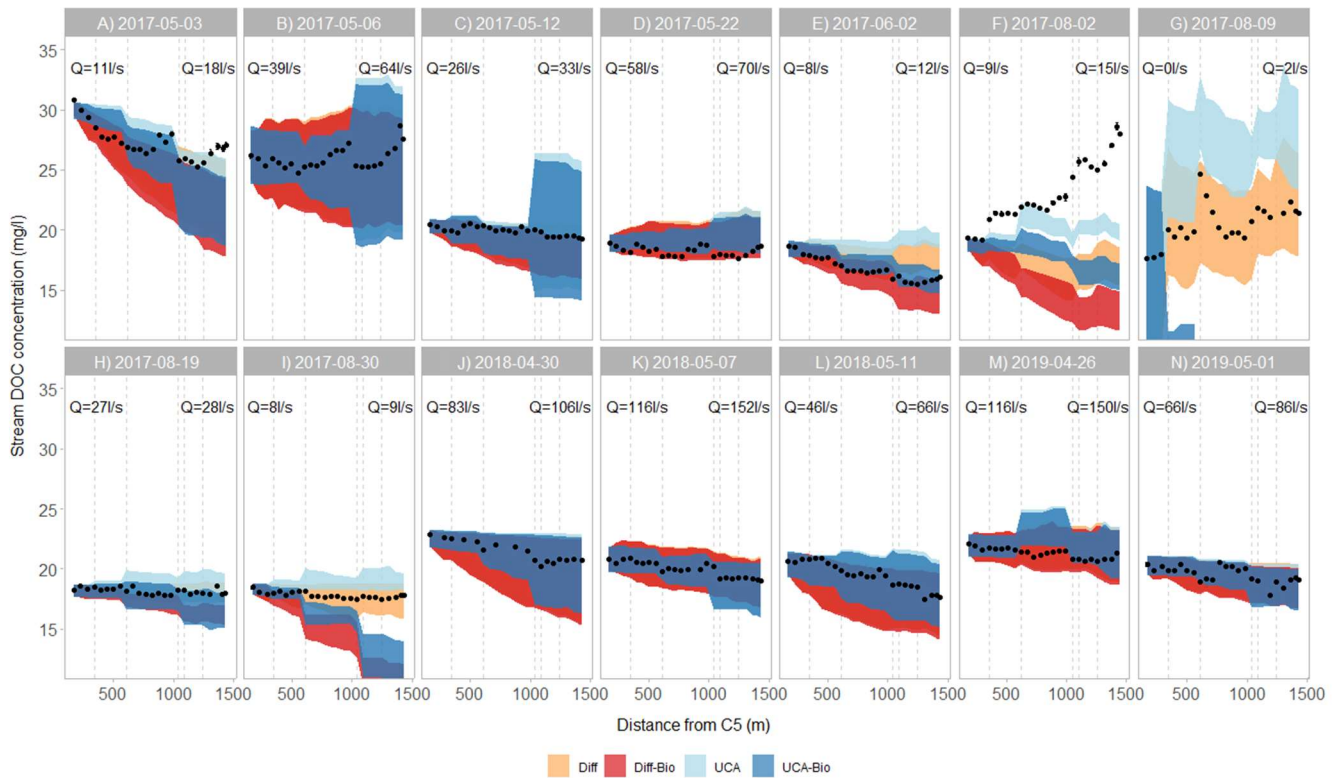
Figure 2 Hydrographs of the gauging stations C5 (grey) and C6 (blue) during the study period (spring 2017, summer 2017, spring 2018 and spring 2019). The vertical dashed lines and letters correspond to the 14 sampling campaigns. The percentages indicate the net gain in streamflow between the gauging stations C5 and C6.



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Figure3 Relative upslope contributing area along the stream reach. The solid line represents the UCA model, which assumes that the net gain in streamflow is proportional to the gain in upslope contributing area (UCA) between sampling sites (squares). The dashed line represents the Diff model, which assumes uniform, diffuse inflow of groundwater along the entire reach. Grey vertical bars indicate the location of discrete riparian inflow points (DRIP) along the stream reach, for which we sampled dissolved organic carbon (DOC) concentrations during the study period and in-stream DOC uptake was considered.

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860 **Figure 4** Longitudinal patterns of dissolved organic carbon (DOC) concentrations along the C5-C6 reach. 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 without wells (dashed). The streamflow (Q) at gauging stations C5 and C6 are shown for each sampling campaign.

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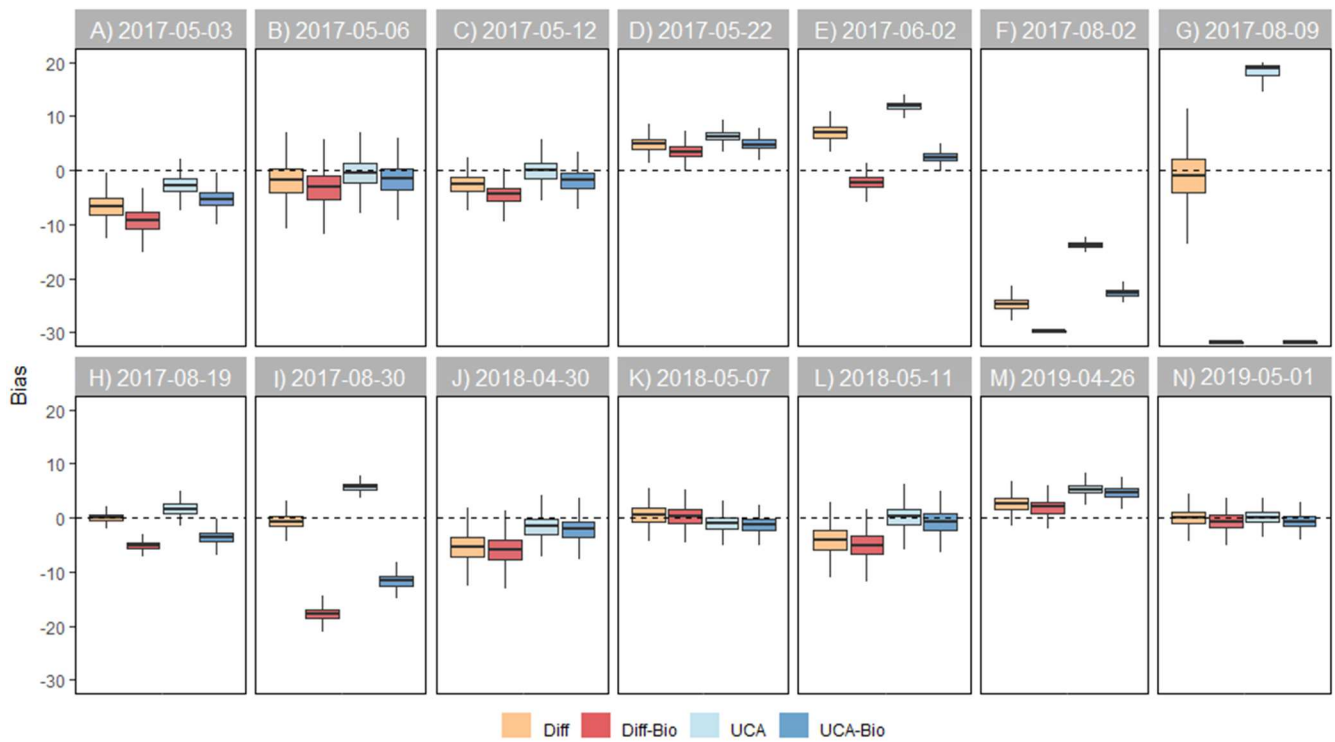


Figure 5. Relative bias (Bias) by model and sampling campaign. For each model, boxplots show the median, 25th and 75th percentiles, and whiskers extend to 10th and 90th percentiles of the 10,000 runs. Values close to 0 indicate that the model successfully simulate the magnitude of stream DOC concentrations. The horizontal line at Bias = 0 is shown as a reference.

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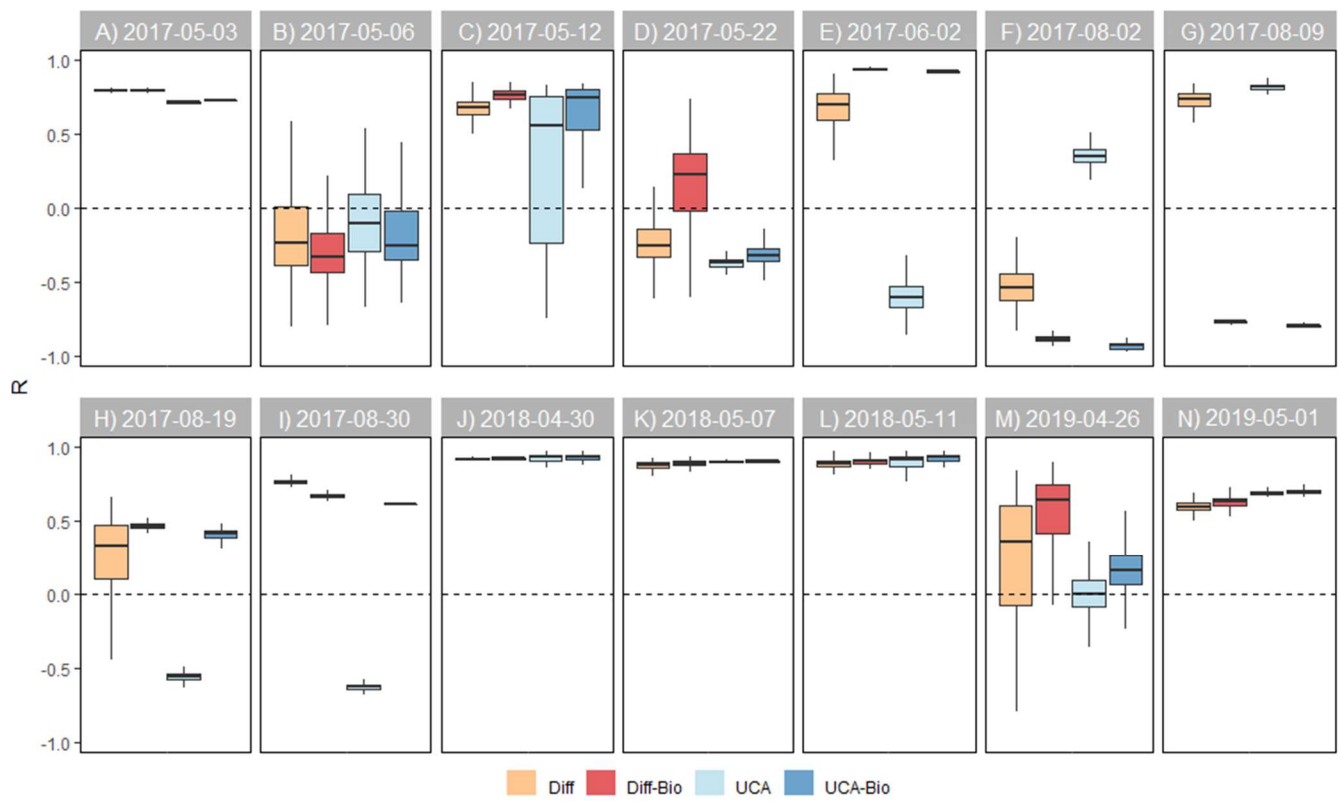


Figure 6. Spearman regression (R) by model and sampling campaign. For each model, boxplots show the median, 25th and 75th percentiles, and whiskers extend to 10th and 90th percentiles of the 10,000 runs. Values close to 1 indicate that the model successfully simulate the magnitude of stream DOC concentrations. The horizontal line at $R = 0$ is shown as a reference.

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