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Groundwater travel times predict DOC in streams and riparian soils across a heterogeneous boreal landscape

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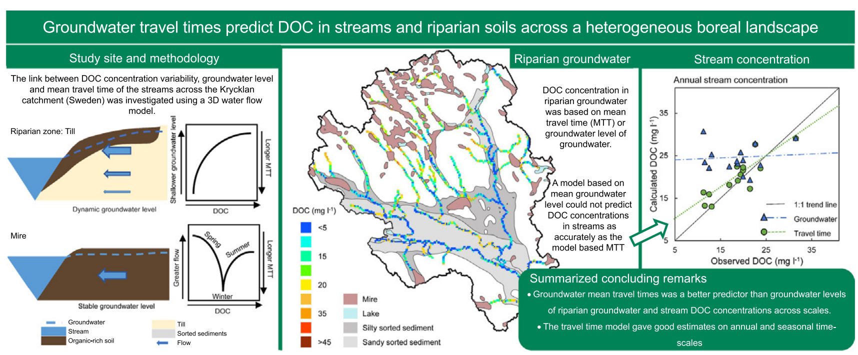
HIGHLIGHTS

- Modelling DOC concentration using a physically-based hydrological model.
- Testing the connection between DOC, groundwater level and mean travel time (MTT).
- Testing results against 14 long-term stream and 36 riparian groundwater observation locations.
- The MTT model can better predict stream and groundwater concentration of DOC.
- The MTT model gives good predictions on both annual and seasonal timescales.

GRAPHICAL ABSTRACT



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ABSTRACT

Dissolved organic carbon (DOC) in surface waters is an important component of the boreal landscape carbon budget and a critical variable in water quality. A dominant terrestrial DOC source in the boreal landscape is the riparian zone. These near stream areas play a key role in regulating DOC transport between land and aquatic ecosystems. The groundwater dynamics at this interface have been considered a major controlling variable for DOC export to streams. This study focuses on the regulating role of groundwater levels and mean travel times (MTT) on riparian DOC concentrations and, subsequently, stream DOC. This is done by comparing them as explanatory variables to capture the spatial and intra-annual variability of the stream and riparian groundwater DOC. We used a physically based 3D hydrological model, Mike SHE, to simulate DOC concentrations of the riparian zones for 14 sub-catchments within the Krycklan catchment (Sweden). The model concept assumes that DOC concentrations will be higher in groundwater moving through shallow flow paths. In the model, this can be linked to the position of the groundwater table at a point of observation or the travel time, which will generally be shorter for water that has travelled through shallow and more conductive soil layers. We compared the results with both observed stream and groundwater concentrations. The analysis revealed that the correlation between modelled and observed annual averages of stream DOC increased from $r = 0.08$ to $r = 0.87$ by using MTT instead of groundwater level. MTT also better captured the observed spatial variability in riparian DOC concentrations and more successfully represented seasonal variability of stream DOC. We, therefore, suggest that MTT is a better predictor than groundwater level for riparian DOC concentration because it can capture a greater variety of catchment heterogeneities, such as variation in soil properties, catchment size, and input from deep groundwater sources.

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1. Introduction

In northern latitudes, dissolved organic carbon (DOC) is the most abundant form of carbon in surface waters and an essential energy source for aquatic food webs (Jansson et al., 2007a; Meyer et al., 1998; Neff et al., 2006). Dissolved organic carbon also has important implications for surface water quality because of its impact on stream water pH and its key role in mobilising metals and organic pollutants (ElBishlawi and Jaffe, 2015; Hruška et al., 2003; Wei et al., 2008). The dynamics of DOC entering surface waters, including streams and lakes, is regulated by several factors such as soil temperature, rainfall-runoff response, and soil properties close to groundwater discharge areas (Clark et al., 2010; Kaiser et al., 2001; Wagner et al., 2008). In the boreal landscape, mires are considered dominant DOC source for streams and lakes (Ledesma et al., 2016; Ricker et al., 2013). However, groundwater entering the stream through the riparian zone provides a continuum of heterogeneous DOC inputs to river networks (Laudon and Sponseller, 2018). Representing these near stream areas to capture observed stream concentration variabilities of streams and rivers are therefore notoriously challenging.

The riparian zone is the interface between upland hillslopes and surface waters and is characterised by wet soil conditions, as well as groundwater levels that can rapidly increase and sustain near the surface. This difference in hydrological conditions compared to many upland soils translates to higher soil carbon content and plant communities favouring wet soil conditions (Ledesma et al., 2018; Ye et al., 2019). Cold climate and wet soil conditions reduce decomposition rates, resulting in the development and accumulation of soil organic matter (SOM) near streams (Fissore et al., 2017; Jansson et al., 2007b; Lidman et al., 2017). As such, the riparian zone is a critical carbon source for surface waters compared to upland soils, where much of the organic matter often is decomposed relatively fast, typically rendering these soils poor in organic matter (Ledesma et al., 2015; Vidon et al., 2019). The spatial variability in lateral transport of DOC from riparian zones to streams is largely associated with the relationship between groundwater levels and vertical variability in soil properties. Riparian soils typically have higher soil carbon content and hydraulic conductivity towards the surface. As a result, increasing lateral water fluxes are commonly positively correlate with higher DOC concentrations. However, the fluctuations in groundwater level and distribution of terrestrial SOM vary within the riparian zone, which leads to a spatial and temporal mosaic of DOC inputs to streams (Grabs et al., 2012). The underlying spatial variability in the soil properties and elevation results in a patchwork of different timing and DOC export rates across riparian zones (Dawson et al., 2008; Kuglerová et al., 2014; McClain et al., 2003; Mengistu et al., 2014), making it challenging to capture spatial variability in riparian DOC sources at catchment scales (Vidon et al., 2010, 2019). Finding and modelling such sources could have implications for our understanding of water quality and forest management, since they are closely connected to transport and regulation of nutrients, pollutants, and heavy metals to streams (Stutter et al., 2012; Harms and Ludwig, 2016).

Several model approaches have been developed to simulate stream DOC dynamics. Such attempts include simple process-based models linking variation in DOC concentration from hillslopes to streams (Birkel et al., 2014; Dick et al., 2015; Son et al., 2019) and semi-distributed hydrological models, including the use of SWAT (Meshesha et al., 2020). Xu et al. (2012) developed a model relating DOC transport to catchment water storage and runoff changes, which was further developed by Kasurinen et al. (2016) to account for catchment water storage and soil temperature. However, all these studies are based on variability in stream DOC concentrations which limits the representation of spatial variability in DOC inputs from riparian groundwater within stream networks. As such the dynamics of DOC mobilisation from terrestrial systems to the stream network are therefore not properly incorporated into model approaches (Ploum et al., 2021). Other studies have found a strong connection between groundwater level and variability in stream DOC (Abbott et al., 2018; Strohmenger et al., 2020; Thomas et al., 2016). One theoretical model approach that accounted for riparian DOC concentrations is the Riparian Integration Model (RIM) (Seibert et al., 2009). The RIM model assumes a strong connection between riparian DOC concentrations of the groundwater and the DOC stream variability, with high groundwater levels resulting in higher stream DOC concentrations. The model concept successfully predicted DOC concentration variability in the riparian zone for a stream draining a small till-dominated catchment (Seibert et al., 2009). Later, the RIM model approach describing variabilities of stream and riparian DOC concentrations has also been used to predict DOC variabilities in stream DOC concentrations and investigate important factors controlling DOC variability (Winterdahl et al., 2011a), such as soil temperature and soil moisture (Ågren et al., 2010; Humbert et al., 2015). However, the concept has mainly focused on modelling stream DOC in small till-dominated catchment and has not been applied for catchments with other soil types. Therefore, it remains uncertain if the riparian groundwater level alone may explain riparian DOC inputs to streams in various landscapes, or if other characteristics must be accounted for, such as catchment size and soil properties.

Recent studies show that hydrological pathways affect riparian and stream DOC through dilution from deep groundwater inputs (Tiwari et al., 2014; Strohmenger et al., 2020) and enrichment through shallow soil pathways (Ploum et al., 2020). Furthermore, hydrological pathways lead to differences in soil chemistry, vegetation patterns, and peat development in the riparian zone (Kuglerová et al., 2014, Ploum et al., 2021). Groundwater mean travel time (MTT) can be a potential predictor for the speed of flow and the hydrological pathways of riparian groundwater, thereby representing the heterogeneity of organic carbon accumulation and DOC export across catchments (Ågren et al., 2014; Jantze et al., 2015). In this context, MTT is the mean travel time of all groundwater from groundwater recharge to the time it takes to reach the riparian zone. A strong connection between DOC, travel time and groundwater level has been found. For example, Lessels et al. (2016) found that deep and old groundwater was connected to low DOC concentrations. Likewise, McDonough et al. (2020) and Birkel et al. (2020) showed a strong connection between DOC concentration and groundwater travel times. Lower DOC concentrations in streams are often associated with higher inputs of old groundwater sources (Ågren et al., 2014; Tiwari et al., 2017). In turn, in till dominated areas, groundwater levels are also associated with groundwater travel times because deep groundwater has longer MTTs, while shallow groundwater tends to have short MTTs due to new water inputs from rain or snowmelt (Peters et al., 2014; Tripler et al., 2006). Model studies using chloro-fluorocarbon and particle tracking support this idea, linking shallow and deep groundwater shorter and longer MTTs, respectively (Jutebring Sterte et al., 2021a; Kolbe et al., 2020). However, MTT may exhibit greater heterogeneity across scales than groundwater level since MTT can be affected by other factors such as soil properties (e.g., hydraulic conductivity) and the mixing of groundwater originating from old and young water sources (Hrachowitz et al., 2016). Therefore, the RIM model could potentially be adjusted to use groundwater MTTs as an alternative to groundwater levels. This would also provide a test to see if the information concerning DOC mobilisation content in MTT is higher than the information content of groundwater levels.

This study investigates whether a groundwater level (RIM) or MTT based methodology better can explain the heterogeneity of riparian DOC concentrations across the boreal landscape and predict the spatiotemporal DOC concentrations in stream water throughout the landscape. To do so, a fully distributed 3D model considering coupled surface and subsurface flow was used to simulate DOC concentrations. The DOC concentrations were based on both time-varying groundwater levels and travel times across a heterogeneous boreal landscape, in order to compare the two methodologies. Applying this model approach to the extensively studied Krycklan catchment in northern Sweden, the model was evaluated on both stream water and riparian soil water from 14 sub-catchments of different sizes and landscape configurations. The spatial distribution also allowed for evaluating DOC sources across individual catchments.

2. Method

2.1. Study site and flow model

The Krycklan catchment is a well-investigated research infrastructure situated in the boreal region, approximately 50 km northwest of Umeå, Sweden (64°23N, 19°46E) (Laudon et al., 2021). Mineral soils dominate the landscape, with mires distributed across the landscape. The main soil type at higher altitudes in the northwest consists primarily of glacial till, whereas sorted fluvial and glaciofluvial sediments dominate the landscape at lower altitudes to the southeast (Fig. 1). The till-soils are typical for the region with hydraulic conductivity decreasing exponentially with soil depth. However, in the sorted sediments soils, the hydraulic conductivity remains more constant with depth (Bishop et al., 2011; Seibert et al., 2009). Coniferous tree species dominate the catchment, including Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*). The catchment is divided into sub-catchments that are monitored for discharge and stream chemistry. Fourteen sub-catchments were included in this study with a mire proportion ranging from 0 % to 50 % (Table 1). Research and monitoring of hydrology and water quality, including DOC, have been ongoing at the site since the 1980s (Laudon et al., 2013). The monitoring data can be acquired from the open Krycklan database (www.slu.se/Krycklan), and more information about the long-time series, sample collection, and analysis can be found in Fork et al. (2020).

The hydrologic flow model used in this study is based on a previously developed distributed hydrological model for the Krycklan catchment consisting of a Mike SHE model (surface and groundwater flow) coupled to the Mike 11 model (streamflow). Mike SHE calculates transient daily groundwater and surface flow in a 3D space and water fluxes between different compartments (Graham and Butts, 2005). The compartments include overland, subsurface saturated, and unsaturated flow, which can be calculated with varying levels of complexity. In the present study, unsaturated flow is calculated in 1D using Richards's equation. Saturated flow is calculated in 3D using Darcy's equations, and 2D diffusive wave approximation in the Saint-Venant equations are used for overland flow. Mike 11, which handles streamflow, uses a high-order dynamic wave formulation of the Saint-Venant equations.

The horizontal resolution of the Mike SHE model is set to 50 × 50 m, extends to 100 m below the soil surface and is vertically divided into ten calculation layers in the saturated compartment and with a finer vertical

Table 1
Catchment characteristics. This study included the main catchment characteristics and the average (mean) annual DOC concentrations for each sub-catchment. The DOC stream observations comprised data from 2011 to 2014 (approximately 95 observation points for each station) and were acquired from The Krycklan Database (2013).

	Catchment size	Till-soils	Mire	Sorted sediments	Lakes	Stream DOC	
	km^2	%	%	%	%	$mg\ l^{-1}$	Number
C1	0.48	91	0	0	0	22	95
C2	0.12	79	0	0	0	20	93
C4	0.18	29	42	0	0	32	95
C5	0.65	47	46	0	6	23	94
C6	1.10	51	29	0	4	19	96
C7	0.47	68	16	0	0	24	96
C9	2.88	64	14	11	2	17	96
C10	3.36	64	28	1	0	20	96
C12	5.44	70	18	6	0	19	96
C13	7.00	60	10	18	1	19	96
C14	14.10	46	6	39	1	13	96
C15	19.13	64	15	10	2	13	96
C16	67.90	51	9	31	1	12	97
C20	1.45	55	9	28	0	11	93

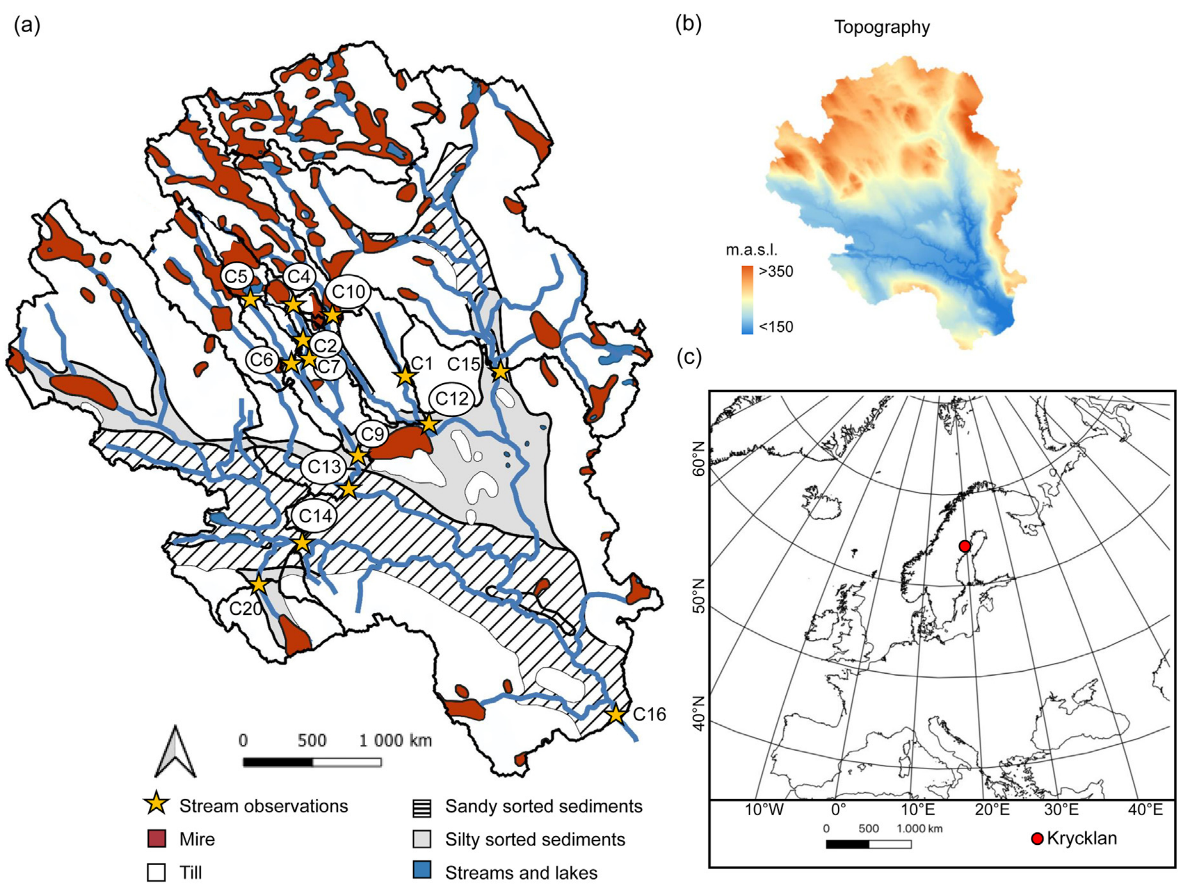

Fig. 1. The Krycklan catchment. (a) The figure shows the Krycklan catchments and the main soil properties considered in this study, including mires, till-soils and sorted sediments. (b) The catchment topography. (c) The catchment location, Sweden, Europe.

discretisation (cm to m) in the unsaturated compartment. The vertical layers follow the stratigraphy of the soil, with soil deposits being about 15–20 m thick at the upper elevations to the northwest, and 40–50 m thick to the southeast. The model spans 2009 to 2014 and uses topography, vegetation, soil properties, and time-varying climate inputs to calculate daily surface and groundwater flows. There is a no flow boundary condition at the topographical boundaries around the model domain, except for the sand deposit at the lower elevations of the cat catchments. Based on groundwater levels to the southeast, and lake levels to the west, groundwater is allowed to flow across the model boundaries at these locations. There is also a no-flow boundary condition at the bottom of the model at 100 m depth below the soil surface. The flow model, including specific soil properties, vertical discretisation is further described in Appendix 1 and Jutebring Sterte et al., 2021a, 2021b.

The flow model can reproduce accumulated stream discharge for 14 daily monitored streams across the catchment with a mean accumulated discharge error of 3 % (maximum 21 %), a r value (correlation constant) spanning from 0.82 to 0.94, and a standard deviation of the residuals spanning 0.8 × 10-3-0.34 $m^3 s^{-1}$ (2009–2014). The model can also able reproduce observed weekly to monthly groundwater levels for 15 wells across the catchment with a mean absolute error (MAE) of 0.1–0.9 m. Daily streamflow results for all 14 streams and groundwater results statistics are available from the open data store Safe Deposit (Jutebring Sterte et al., 2021d).

The flow model was recently used to investigate saturated groundwater MTT distributions in Krycklan (Jutebring Sterte et al., 2021a). Travel times are derived and transported similarly to solutes, using the advection-dispersion module in Mike SHE. Mike SHE can change the concentration of a solute by pre-established sources or by mixing (Butts et al., 2012), while pre-defined biogeochemical reactions are described with Mike ECO Lab, an external model coupled to Mike SHE. Groundwater recharge is given a travel time of zero days. The recharge is mixed with the groundwater, and in each 50 × 50 m cell in the saturated groundwater zone, at each time step, is assigned an average travel time of all water mixed at the location (MTT). Groundwater travel times are then moved by advection defined by the groundwater flow field, where velocities are calculated by dividing the Darcy velocity by the soil porosity. While moving through the saturated zone, the groundwater increases in age with one day per day and mixed with groundwater with other travel times, creating a spatial variation in MTT in each cell across the model domain. For initialisation, the modelled flow of surface and subsurface water from 2010 was repeated until stable MTT for the groundwater was reached. The model was then run for 2011–2014, allowing assessment of daily groundwater MTT for the groundwater across Krycklan. For details on the hydrological model used to generate travel times and groundwater levels in this study, see Jutebring Sterte et al. (2021a, 2021b).

The simulated daily groundwater levels and MTT in the riparian zone, defined here as the model cells directly adjacent to streams, were used as input to the DOC models (described below). In general, the modelled groundwater levels and MTTs are strongly correlated. That is, shorter travel time corresponds to higher groundwater levels while longer travel times correspond to lower groundwater levels. However, there is a variation in overall mean travel times among the sub-catchments, with some having shorter travel times overall, such as the sub-catchment of C2, compared to others, such as the sub-catchment of C20 (please see Appendix 3).

2.2. Groundwater DOC model

A mathematical model linking observed groundwater level and streamflow to the observed DOC concentration in the riparian zone of C2 (which is a small till-dominated catchment in Krycklan, Table 1) was established by Seibert et al. (2009). The so-called RIM model was based on an exponential function (Eq. (1), Fig. 2a), which links DOC to groundwater position according to Eq. (1):

$$\text{RIM}-\text{model}: C_{gw} = C_0 e^{-f*gw} (\text{mg l}^{-1}), \quad (1)$$

where C_{gw} (mg l^{-1}) denotes the groundwater DOC concentrations based on the current groundwater level (gw, meter), the concentration at the soil surface C_0 (mg l^{-1}) and the shape factor *f*. The equation assumes a correlation between DOC and groundwater level, i.e., the DOC concentration exponentially increases vertically with increasing groundwater level. In till-dominated Krycklan sub-catchments, the shallow groundwater, C_0, can vary between 20 mg l^{-1} and 80 mg l^{-1} and the shape factor, *f*, can vary from 0.5 to 4 (Seibert et al., 2009). Therefore, both C_0 and *f* must be calibrated for the specific site. This study tested the RIM model on the full Krycklan catchment using the Mike SHE flow model combined with Mike ECOLab (described above). This is the first time the RIM model has been tested with a full-scale distributed hydrological model on the landscape

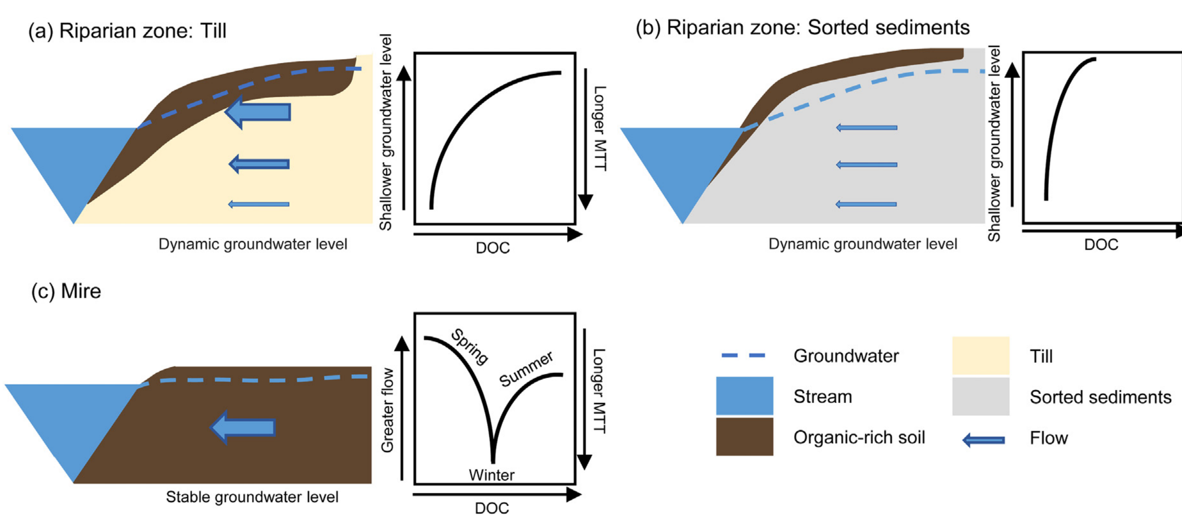

Fig. 2. Conceptual model. (a) Till-soils. The exponential decrease in hydraulic conductivity results in groundwater level becoming linked to flow velocity and DOC concentration. The groundwater level is connected to MTT since deeper groundwater generally is linked to longer and slower pathways. (b) Sorted sediments. A stable hydraulic conductivity with depth, potentially causing steadier flow regardless of groundwater level and less focusing of the flow to the uppermost saturated layers as in the till. Inputs from shallower groundwater become diluted by deeper groundwater sources to a greater extent. (c) Mire. The groundwater level is relatively stable near the surface. Here DOC concentrations are regulated by the flow. In spring, flushing results in low DOC concentrations, while the opposite occurs in summer, probably due to increased biological activity. Deep peat soils result in a high DOC concentration during winter baseflows.

level. Instead of inferring DOC from streamflow, the RIM model was applied directly to the riparian groundwater along the streams.

It has been pointed out that the hydrology of sorted sediments may function differently than till-soils (Tiwari et al., 2014; Ågren et al., 2014). A more constant hydraulic conductivity of sorted sediments with depth results in a greater fraction of deep and old groundwater (Fig. 2b). It has also been proposed that streams exiting larger catchments are influenced by a greater input of deep groundwater (Tiwari et al., 2017). Generally, shallower groundwater is derived from younger water entering the stream, reducing the MTT, especially during high flow events (Ågren et al., 2014; Jutebring Sterte et al., 2021a). Therefore, as suggested by Ågren et al. (2014) and observed by Jantze et al. (2015) and Birkel et al. (2020), MTT could be a valuable predictor of DOC variability in the riparian zone. For example, in till-soils, the main flow paths of till occur in the upper saturated half meter of the soil due to the decreasing hydraulic conductivity with depth. Since the content of soil organic matter increases towards the surface, young and shallow groundwater is linked to an increase in DOC. Assuming a strong relationship between the groundwater position and the mean travel time of the groundwater, Eq. (1) can be re-written as a function of the MTT to:

$$\text{MTT} - \text{model}: C_{gw} = C_0 e^{-f*MTT} \left(\text{mg l}^{-1}\right) \tag{2}$$

Hence, C_{gw}, in this case, describes the DOC concentration of riparian groundwater based on MTT (days), and C_0 is the DOC concentration of groundwater with shorter travel times. The equation assumes a negative correlation between DOC concentration and MTT, i.e., the DOC concentration exponentially decreases vertically with increasing MTT. As in Eq. (1), f denotes a shape factor that must be calibrated. Eqs. (1) and (2) are formulated to describe the behaviour of the riparian zone along stream channels. However, mires have been found to work differently. The deep accumulation of organic matter in mires causes high DOC concentrations even at low flow. The effect of mires can be exemplified using the observed DOC concentration and streamflow of C4, a sub-catchment in which most water enters the stream directly from a mire (Fig. 2c). In spring, the DOC concentration decreases significantly because of dilution from snowmelt and overland flow, thereby giving the groundwater the opposite relation to groundwater travel times compared to other riparian soils (Ågren et al., 2014; Laudon et al., 2011). In summer, younger water has a higher DOC concentration compared to old spring water, potentially due to high evapotranspiration, biogeochemical activity, and groundwater inputs from surrounding soils. Therefore, when implementing Eqs. (1) and (2) on the Krycklan catchment, the DOC concentration of water discharging from mires was defined as a set of varying monthly values based on the monthly average DOC concentration observed at C4 for 2011–2014 (Krycklan Database (2013)).

Seibert et al. (2009) and Winterdahl et al. (2011a) also suggested a strong seasonal variation in both the C_0 and f parameters (Eq. (1)). Generally, higher C_0 and greater f can be expected in July to October, whereas a lower C_0 and f can be expected in May and June. A strong seasonal DOC variation has also been reported by Kasurinen et al. (2016) using a model method developed by Rankinen et al. (2004) to predict soil temperatures and, in turn, stream DOC. The seasonality in the stream DOC concentration is assumed to be related to soil temperature, biological activity, and periodic flushing of the system with an increased release of DOC during summer and reduced release after the start of the spring snowmelt (Boyer et al., 2000; Hornberger et al., 1994; Winterdahl et al., 2011a). Therefore, different exponential functions would be expected for different seasons.

2.3. DOC model calibration and evaluation of model output

Based on the conceptual understanding of the site, three models were set up, run, and tested for 2011–2014. The three models, which were named RIM, MTT, and a seasonal version of the best working model (RIM or MTT), were applied directly to the groundwater of the riparian zones and calibrated using the DOC concentration of stream C2 (Table 1). The calibrated models were then applied and tested on all sub-catchments. The calibrated model parameters from C2, (C_0 and f) were applied across the entire model domain to test the models' abilities to capture spatial heterogeneity in DOC concentrations based solely on groundwater lever or MTT. First, the C_0 and f parameters for the RIM and MTT models were annually calibrated. After that, seasonal calibrations of C_0 and f were applied for the best working model. Based on the seasonal variations observed by Seibert et al. (2009), winter included Nov–April, spring included May–Jun, and summer included Jul–Oct.

The RIM and MTT models were manually calibrated to optimise the correlation coefficient (r) and mean error (ME) of simulated and observed stream DOC concentrations at C2. The Nash–Sutcliffe model efficiency coefficient (NSE) was also calculated to evaluate the final models further. The NSE coefficient has been used to test the predictive power of stream DOC models at the site before (Kasurinen et al., 2016; Oni et al., 2014). The NSE ranges from $-\infty$ to 1. A negative value indicates that the mean value of the observations is a better predictor than model calculations. In contrast, a value equal to 1 suggests a perfect agreement between model and observations (Nash and Sutcliffe, 1970).

In addition to stream observations, we also tested to what extent the RIM model and the final seasonal model could simulate the average annual DOC concentrations of riparian groundwater. The DOC concentration of each riparian cell (50 × 50), defined as all cells traversed by a stream, was simulated. Observed riparian groundwater DOC concentrations from 36 locations across the catchment were compared to the modelled DOC concentration at the same locations. The riparian groundwater observations included average DOC concentrations obtained from two well networks within the Krycklan catchment, Grabs et al. (2012) and Ploum et al. (2020). The observations by Grabs et al. (2012) represent riparian groundwater from various soil types (sorted sediments and till) and relatively small upslope contributing areas (12–1200 m^2). The observation averages stem from 12 sampling occasions at 14 locations between 2008 / May to October) and 2009 (June to September). The observations from Ploum et al. (2020) represent only till-dominated riparian soils, and groundwater samples were collected in the spring, summer and fall of hydrological years 2016 and 2017. The well network was designed for pairwise comparison between riparian areas with sustained groundwater discharge, and large upslope contributing areas (6000 m^2–77,000 m^2), referred to as DRIPs, (discrete riparian inflow points) and adjacent riparian areas with small upslope contributing areas (0–80 m^2) referred to as "non-DRIPs". These are used to emphasise the heterogeneity within riparian zones and their effects on stream biogeochemistry. A fluctuating groundwater level characterises non-DRIPS, while DRIPs are characterised by having more wetland-like features (e.g., high DOC concentrations and more constant high groundwater levels) (Ploum et al., 2020; Ploum et al., 2021). In comparing model output with observed riparian DOC concentrations, the locations of wells were used to select model cells (50 × 50 m). In ten cases, more than one well was located in the same cell, and therefore the observations from these groundwater wells shared the same model output. For MTTSeason and RIM, the modelled and observed riparian DOC concentrations were compared.

3. Results

3.1. RIM vs MTT performance across catchment streams

The RIM and MTT simulations resulted in comparable correlation coefficients (r) between modelled and observed stream DOC concentrations for all sub-catchments. For example, the correlation coefficient for RIM was ranging from 0.06 to 0.75 while the correlation coefficient was raining MTT ranging from 0.13 to 0.74 (Table 2). The calibrated parameters for both models became very similar, suggesting a strong connection between groundwater level and MTT at C2. However, the MTT model outperformed the RIM model at predicting annual stream averages for all sub-catchments: the RIM model ME ranged from -2.35 mg l^{-1} to 19.49 mg l^{-1}, with an average of 5.52 mg l^{-1}, and for MTT from -4.25 mg l^{-1} to 5.11 mg l^{-1},

Table 2
Statistical results: All sub-catchments, daily results, including the calibrated values of C_0 and f for each. The table includes daily statistical results, including the correlation coefficient (r), mean error (ME, mg l^{-1}) and Nash–Sutcliffe model efficiency coefficient (NSE) for all sub-catchments and all three models. C2 was the sub-catchment used for calibration. The mire DOC concentration was based on monthly variations of C4. RIM is based on Eq. (1), while MTT and 3 MTT_{Season} were based on Eq. (2). Seasonal variations of winter (W), spring (Sp) and summer (Su) were allowed in MTT_{Season}.

			RIM			MTT			MTT_{Season}		
									W	Sp	Su
Calibrated model parameters		C_0		50			50		50	30	60
		f		1.5			1.5		2	1.5	1.5
			r	ME	NSE	r	ME	NSE	r	ME	NSE
			Used for calibration and mire concentrations								
C2 (calibration)			0.44	0.12	−0.05	0.31	2.30	−0.29	0.57	−1.23	0.19
C4 (mire)			0.75	−2.35	0.50	0.74	−2.4	0.49	0.77	−2.17	0.53
	Lakes (%)	Sorted sediments (%)	An increasing proportion of sorted sediments								
C1	0	0	0.50	−2.19	−0.43	0.57	−4.25	−0.19	0.76	−3.62	0.15
C7	0	0	0.56	−0.98	0.25	0.55	−1.72	0.24	0.74	−3.45	0.28
C10	0	1	0.56	4.01	−0.05	0.54	1.59	0.21	0.65	0.17	0.38
C12	0	6	0.51	4.37	−0.29	0.46	0.33	0.17	0.61	0.33	0.26
C20	0	28	0.36	19.49	−10.88	0.27	5.10	−0.96	0.43	3.52	−0.38
C16	1	31	0.37	11.93	−7.06	0.56	1.70	0.15	0.65	0.52	0.39
C14	1	39	0.25	12.25	−6.97	0.33	−0.02	−0.11	0.53	−1.29	0.11
			An increasing proportion of lakes								
C13	1	18	0.40	6.39	−1.59	0.32	1.13	−0.11	0.56	−0.83	0.05
C9	2	11	0.62	5.54	−1.38	0.51	1.19	0.15	0.60	−0.43	0.11
C15	2	10	0.44	9.63	−9.72	0.38	3.43	−1.35	0.50	2.41	−0.85
C6	4	0	0.06	3.82	−2.53	0.14	5.11	−3.16	0.11	3.21	−2.70
C5	6	0	0.19	5.28	−2.68	0.13	5.04	−3.06	0.15	5.14	−3.57

with an average of 1.32 mg l^{-1} (Table 2). The NSE values did not exceed 0.5, which suggests that both the RIM and MTT model do not adequately represent daily variation in DOC concentration across the various catchments. However, annual, and seasonal stream concentration averages were captured by the MTT model across catchment scales (Fig. 3). The RIM model performed reasonably well for small headwater catchments (e.g., C1, C2 and C7). However, for catchments larger than ca. 0.5 km^2, which in this case also often contain a substantial fraction of sorted sediments, the RIM model overestimated the annual DOC concentration (Fig. 3). With an increasing proportion of sorted sediments, RIM model performance decreased (ME increased to 19 mg l^{-1}), while the MTT models remained within a 2 mg l^{-1} range, except for C20. Further, for lake-influenced catchments, both the RIM and the MTT model overestimated the stream DOC concentration and had low correlation coefficients (e.g., C5, Table 2). Overall, without re-calibrating the models for specific landscape characteristics, the MTT model outperformed the RIM – model when applied on various catchments.

3.2. Seasonal variability

The RIM and MTT models both captured the major summer and winter dynamics of the till-dominated headwater catchments C2 and C7 (Fig. 4a and b). However, both models overestimated the spring stream DOC concentrations. For larger catchments, this was also the case, but in addition, the winter baseflow DOC concentrations were overestimated as well (Figs. 3 and 4). Especially the RIM model consistently overestimated the DOC concentrations in the C20, C14 and C16 catchments, which all contain a substantial portion of sorted sediments.

Applying a seasonal variation of the overall best performing model (seasonal version of MTT-model, from now on called MTT_{season}) improved simulations of intra-annual concentrations (Table 2, Fig. 3). On an annual basis, the MTT and MTT_{Season} models were equally good at predicting DOC concentrations across the sub-catchments, with estimates close to the 1:1 trend line (Fig. 3). However, the MTT_{Season} model surpassed the MTT model on a seasonal basis, especially for spring and summer stream estimates. The correlation coefficients (r) and mean error (ME) improved for most sub-catchments, and the overprediction during summer was reduced (Fig. 3, MTT_{Season}). Still, stream DOC in lake-influenced catchments was overestimated (C5 and C6, Fig. 3). On a daily timescale, both versions of the MTT model had weaker predictive power for stream DOC concentrations than a seasonal time scale. However, most NSE values for the MTT_{Season} model were at least above zero, and the MTT_{Season} model had a stronger correlation to observations than the MTT model (Fig. 4 and Table 2). Small intra-annual variations of DOC concentration from the till-soils were not captured in either model, neither were all variations from the mire dominated sub-catchment (Fig. 4).

3.3. Modelling heterogeneity of riparian DOC concentrations

Within the riparian zones of individual sub-catchments, spatial variability was also simulated across distances in the order of 50 m (Fig. 5a and b). The observations of Grabs et al. (2012) and the non-DRIP sites from Ploum et al. (2020) (Fig. 5c and d, orange and dark green, respectively) mainly represented riparian zones with supposedly small upslope contributing areas. The DRIP observations by Ploum et al. (2020) represent riparian zones with extensive upslope contributing areas (Fig. 5c and d, light green), thereby representing longer travel times. The MTT_{Season} model was able to reproduce the spatial variability in DOC concentrations in riparian groundwater observed by Grabs et al. (2012) and Ploum et al. (2020) ($r = 0.53$, $p < 0.05$, Fig. 5c). For comparison, the RIM model only captured the concentrations within the 20–40 mg l^{-1} range ($r = 0.29$, $p > 0.05$, Fig. 5d). However, the MTT_{Season} model underestimated riparian DOC concentrations at DRIPs.

4. Discussion

In this study, we tested different hydrological approaches to model DOC concentrations of streams and riparian zones by implementing three different DOC source models into a well-calibrated 3D distributed hydrological model. The Riparian Integration Model (RIM; Seibert et al. (2009)) was compared to two MTT models, adapted from the RIM model, which used groundwater mean travel times (MTT) instead of groundwater level to account for the spatial heterogeneity of hydrological pathways. The RIM model assumes increasing riparian DOC concentration with increasing groundwater level, while the MTT model assumes an increasing DOC concentration with shorter MTT of the riparian groundwater. The results showed that using MTT instead of groundwater level improves stream DOC predictions on catchment and local scales while keeping the modelling

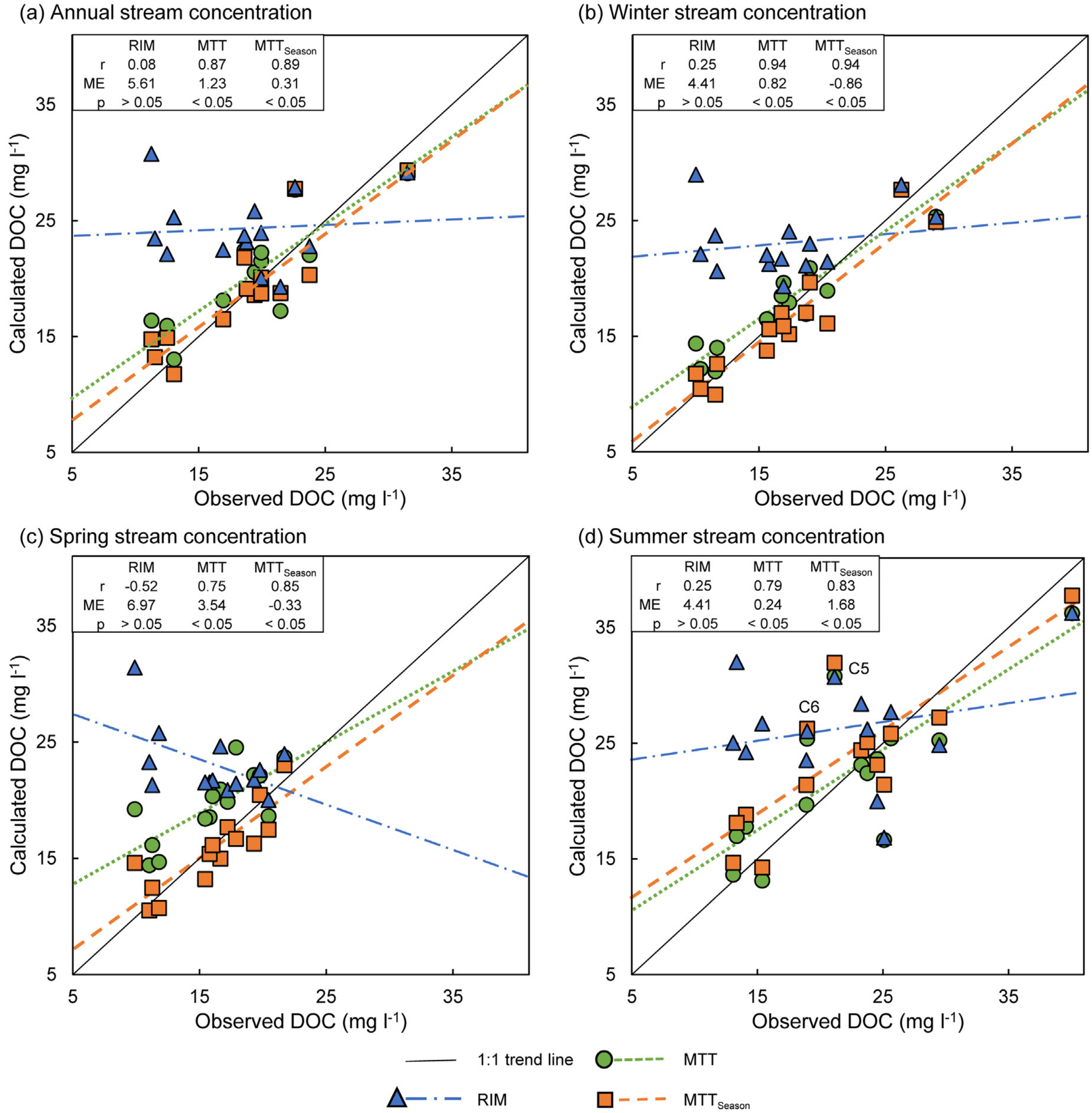

Fig. 3. Seasonal results, all 14 sub-catchments. The figures include annual and seasonal averages based on dates with observations, including RIM, MTT and MTT_{Season}: (a) annual catchment concentration, (b) winter season concentration (Nov–Apr), (c) spring (May–Jun), and (d) summer (Jul–Oct). In addition, the results include the 1:1 trend line (black), ME (mg l^{-1}) and the regression statistics. The size of the markers corresponds to the catchment size. Additional results for all three models can be found in Appendix 2.

of DOC concentration relatively simple (Eq. (2)). After optimising the MTT model with seasonal parameters, the stream DOC predictions became further improved (Fig. 4). Furthermore, the MTT model simulated spatial heterogeneity of riparian DOC concentrations across catchments with various soil types.

4.1. Stream DOC on spatial and temporal scales

Observations and modelling efforts have previously shown a strong link between the regulation of DOC and groundwater level in small till dominated areas (Seibert et al., 2009). An exponential vertical increase in DOC can be observed with increasing groundwater levels. MTT and groundwater levels are also closely correlated (Appendix 3), exemplified by similar and equally good DOC predictions for the small till dominated C2 area (Table 2, Fig. 3). However, when the close link between groundwater level and variations in DOC is lost, e.g., in more sedimentary areas, the MTT model outperforms the RIM model in capturing spatial variation in DOC regulation (Table 2, Fig. 4). For example, riparian groundwater observations at sorted sediments suggest much lower and more stable DOC concentrations regardless of groundwater position compared to till-soils (Grabs et al., 2012). The reason why the MTT model can outperform the RIM model of catchments with contrasting characteristics may be that the former indirectly considers more of the relevant physical factors for DOC concentrations. Such factors include the amount of water from deeper (and old) water inputs and the hydraulic conductivities of the soil, which implicitly contain information about the soil type and water pathways (Hrachowitz et al., 2016). Catchment heterogeneity has been suggested as the main reason behind the DOC variability between streams (Aitkenhead et al., 1999; Dawson et al., 2011), and studies on variability in DOC concentrations of discharging groundwater have been strongly connected to groundwater pathways and travel times (Birkel et al., 2020; Jantze et al., 2015; Lessels et al., 2016; Strohmenger et al., 2021). It is possible that the relationship between longer MTTs and low DOC concentrations, to some extent, also could reflect increased mineralisation of DOC and sorption to

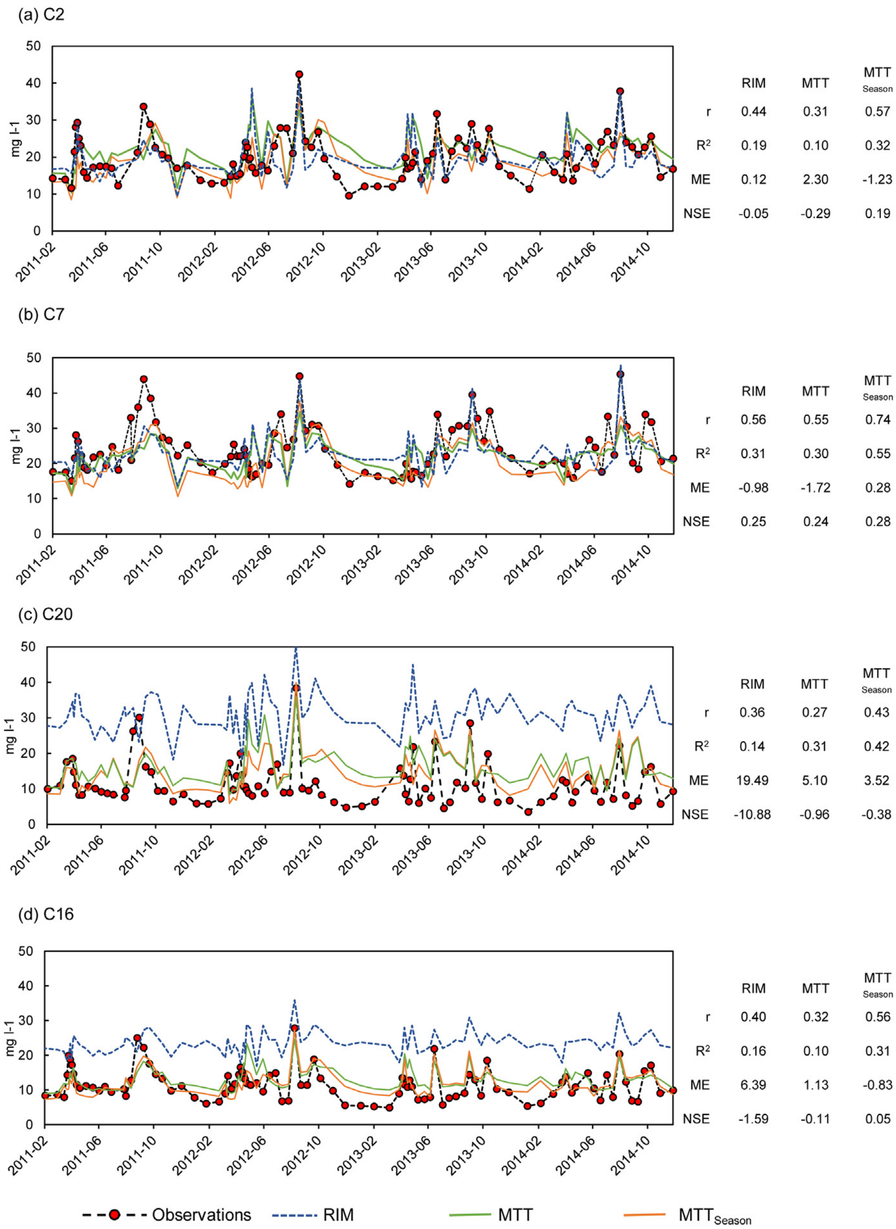

Fig. 4. Modelled stream DOC examples. The panels present examples of streams in increasing catchment size. The figure showcases the observed and modelled DOC from RIM, MTT and MTT_{Season}, including only dates with observations. (a) C2 till dominated sub-catchment, (b) C7 till dominated sub-catchment affected by the C4 mire, (c) C20 sub-catchment dominated by sorted sediments, (d) C16 the main catchment outlet. The figure includes the regression statistics and mean error (ME, mg l^{-1}). Note that these statistics also are included in Table 2 for all sub-catchments.

mineral surfaces along the flow paths of the groundwater (Klaminder et al., 2011). The present study further supports these findings, demonstrating that using MTT instead of groundwater level is an effective way to improve the model performance of catchments with different characteristics.

Annual and seasonal timescales were well predicted with the MTT model and partly improved with the MTT_{Season} model (Fig. 3). Additional parameters (e.g., soil moisture and temperature) have previously been used in other models to improve model performance (Kasurinen et al., 2016; Winterdahl et al., 2011b, 2016b). However, adding such parameters requires catchment-specific calibration, while replacing groundwater level with MTT avoids this need. As such, the use of MTT improves the general applicability of the model and provides the opportunity to assess spatiotemporal DOC dynamics of stream networks based on general catchment properties, such as travel times and water pathways (Birkel et al., 2017; Hrachowitz et al., 2013). The results suggest that advanced representation of biogeochemical processes, temperature or water saturation dependent parameters might not be necessary for annual and seasonal stream DOC estimates. MTT does implicitly regard the time for biogeochemical reactions, and MTT_{season} accounts for some seasonal temperature changes. Therefore, MTT or MTT_{Season} might be enough to represent such processes on such time long scales. Similar conclusions were presented by Strohmenger et al. (2021), testing a simple model dividing DOC inputs into deep (old) and shallow (young) groundwater sources. At any rate, on annual and seasonal timescales, hydrological transport has one of the most important roles in stream solute dynamics. MTT could therefore be a powerful tool to identify such dynamics and explain the variability of stream solutes, such as DOC, across scales (Benettin et al., 2017, 2020; Jutebring Sterte et al., 2021a; Harman, 2015).

However, all models in this study had a poorer ability to predict daily variability, as seen in the low or negative NSE values (Table 2). The poor representation of DOC dynamics on a daily timescale highlights that this model does not adequately represent some important short-timescales

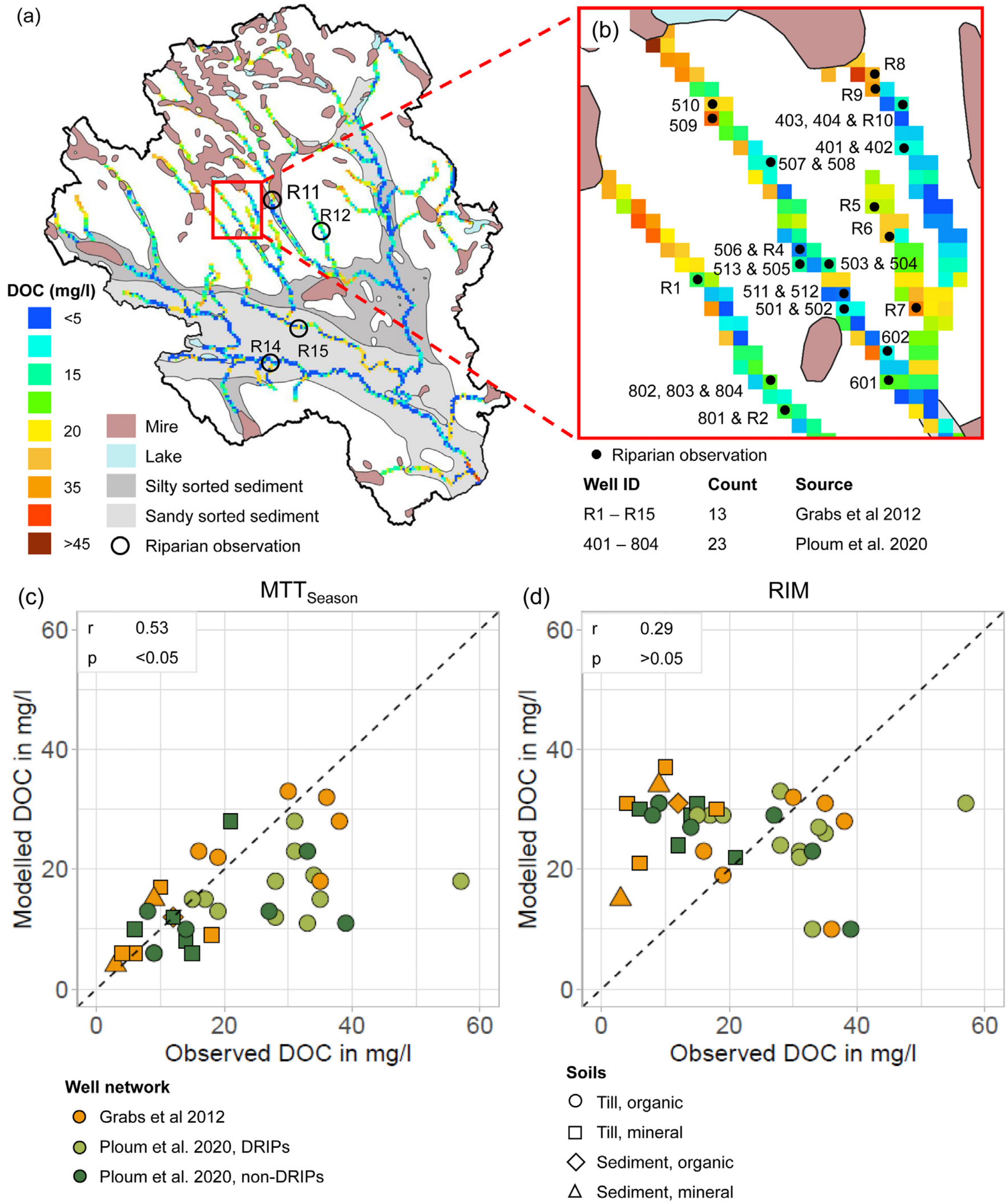

Fig. 5. Average annual DOC concentration in riparian cells along the Krycklan streams. (a) Average annual DOC concentration from MTT_{Season}, full catchment scale. Riparian observation wells are marked with black circles. (b) Magnification of the red area in (a). Riparian observations are marked with black dots. (c) Modelled (MTT_{Season}) and observed average DOC concentrations (d) Modelled (RIM) and observed average DOC concentrations. (c-d) Figures include the standard deviation of modelled values, the 1:1 trend line (black) and the regression statistics. Note: The observed and modelled data presented in (c) and (b) can also be found in Table B1, Appendix 2.

processes (Figs. 3 and 4). For example, sorption dynamics of soil, temperature sensitivity, and in-stream mineralisation are important processes that occur on short timescales and affect stream DOC concentrations (Cory et al., 2014; Kaiser, 2001; Köhler et al., 2008). It is also possible that some of the shortcomings stem from inaccuracies in the hydrological model. If the model mobilises the amount or timing of streamwater, the predicted concentration will also be wrong, even if the DOC model is flawless (Jutebring Sterte et al., 2021b). Furthermore, the spatial discretisation of the model (50 × 50 meter grid) and temporal resolution (daily time steps) can affect the representation of (sub-) daily, small scale processes. For example, Kasurinen et al. (2016), Winterdahl et al. (2011a) and Oni et al. (2014) showed greater predictive power of stream DOC concentration on a daily timescale using high resolution variations in sub-catchment water storage and soil temperature. As such, small scale processes both on land and in the streams are important to consider in stream biogeochemistry models with shorter than seasonal predictions. The relatively poor model performance in C5 and C6, especially during summer, also highlights the potential importance of internal stream and lake processes (Table 2, Fig. 3; Leach and Laudon, 2019; Lupon et al., 2019). Previous studies in Krycklan have shown that in-stream processes, such as photochemical and microbial processes, most likely are negligible due to the relatively short stream travel times (Ågren et al., 2007; Berggren et al., 2009;

Tiwari et al., 2014; Winterdahl et al., 2016a). Lake processes, however, are more important for regulating DOC concentrations because of the longer residence times, allowing more time for mineralisation and photo-oxidation (Vähätalo et al., 2000; Weyhenmeyer et al., 2012). Excluding lake processes have also led to poorer DOC estimates from lake influenced catchments in other studies (Kasurinen et al., 2016; Tiwari et al., 2014), while studies including these processes have presented better DOC predictions (Futter et al., 2007).

4.2. Riparian DOC heterogeneity

Besides the stream DOC dynamics, the MTT model also improved the predictions of DOC concentrations in riparian groundwater compared to the RIM model (Fig. 5). The MTT_{Season} model distinguished riparian zones with high and low average DOC concentrations on catchment and reach scales. Specific local heterogeneities in riparian DOC concentrations predicted by the MTT model corresponded to riparian groundwater observations across various riparian soil types and well networks (Fig. 5d). Local riparian conditions (vegetation, soil chemistry, soil moisture etc.) are important for riparian groundwater chemistry (Humbert et al., 2015; Lambert et al., 2013). Even though such conditions are important, the results suggest that MTTs still can predict the variability of riparian groundwater DOC.

In till-dominated areas with a strong mechanistic connection between groundwater level, MTT and DOC regulation, both the MTT and RIM model capture riparian groundwater DOC variations (Fig. 5). However, the connection between groundwater level and DOC concentration is lost in areas of other soil types, resulting in an overprediction of DOC in sorted sediment areas. Groundwater connections with the upland areas and hydrological pathways towards the riparian zone play a large role in creating these local riparian conditions (Kuglerová et al., 2014; Troch et al., 2013) which are better captured by the MTT model across spatial scales.

However, DOC concentrations were underestimated at confluences of hydrological pathways (DRIPs) (Fig. 5d), suggesting other factors might affect groundwater DOC concentrations at such sites. One such factor is that the model cannot predict the extent of the DOC sources. Given that at DRIPs, peat extends beyond the riparian zone into the upland and to a deeper depth, it has been proposed that these parts of the riparian zone share hydrochemical characteristics with mires and might deviate from typical riparian till hydrology (Fig. 2, Ploum et al., 2021). The extensive peat development, creating micro-mires, are associated with high DOC concentrations along with parts of the stream (Ploum et al., 2021). The extent of the peat at such sites would result in higher DOC concentrations even for groundwater originating from deeper and older groundwater sources. Explicit consideration of DRIPs as smaller mires could potentially improve model estimates of riparian DOC concentrations and the subsequent predictions of stream chemistry (Briggs and Hare, 2018). For example, Barclay et al. (2020) concluded using a distributed hydrological model that this type of implementation is important to consider in catchment models but that they remain a challenge.

4.3. Potential future model developments

In the future, there are possibilities to develop the MTT model further in several aspects. Potential improvements include seasonally dependent parameters and mire, lake, and instream processes. The result of this study showed that on an annual basis, MTT and MTT_{Season} were equally good at predicting stream DOC concentration. However, on a seasonal and intra-annual basis, MTT_{Season} outperformed MTT in predictive power (Fig. 3). The results suggest that further developing the model to be more dependent on seasonal parameters could improve intra-annual variations of stream DOC. Such parameters include soil temperature, biological activity, water storage, pH, the solubility of DOC and carbon mobilisation changes, affecting riparian DOC (Hood et al., 2006; Mulholland and Hill, 1997; Wilson et al., 2013).

A second potential improvement is to include in-stream and lake processes. The extent of the impact of in-stream processes on catchments is associated with uncertainties (Anderson et al., 2019; Mineau et al., 2016). However, for annual estimates of DOC for streams associated with longer instream travel times or larger lakes, such processes could be important to include.

A third potential improvement is to have a better way of defining mires and to add mire processes. Mire processes and potential micro-mires (DRIPs) are overlooked in the current model setup (Fig. 5). In this study, mires are handled using a monthly mean concentration, while DRIPs are handled like mineral soil. However, the interaction between hydrology and the regulation of DOC functions differently in mires (Fig. 2). Firstly, groundwater levels are often more stable in mires than elsewhere, resulting in DOC regulation being more related to the speed of flow (Fig. 2). Secondly, mires have generally high DOC concentrations regardless of the riparian groundwater originating from deep (old) or shallow (young) sources, resulting in a different connection to MTTs compared to riparian zones. The high DOC concentrations are caused by peat accumulation extending beyond the riparian zone into the upland and to a deeper depth than elsewhere; thereby, even winter baseflow becomes DOC-rich (Fig. 2). Hence, it is not surprising that another modelling approach would be needed to include mires, for example, the methods presented by Yurova et al. (2008), including adsorption, desorption, microbial production, and microbial mineralisation. An alternative approach could be to include a spatially variable peat depth across the catchment and allow the MTT model to gradually change from mineral soils to micro-mires and true mires, using special subroutines to model mires and mire-like formations. Where the groundwater is in contact with the peat, even at low flows (situations with longer MTTs), the DOC concentration could be kept high. Such a method might allow the MTT model method to be used even for mires and reduce the underestimation of local micro-mires (DRIPs).

5. Concluding remarks

This study presents a novel model method to base DOC concentration on groundwater MTTs and demonstrates that a model based on MTTs can strongly predict stream and riparian groundwater DOC variability across heterogeneous catchments on seasonal and annual timescales. We found a strong connection between MTT, DOC-rich riparian zones and stream DOC concentration dynamics of 14 investigated catchments. The study supports the findings that groundwater travel times and pathways are important factors controlling DOC concentrations of the riparian zone, suggesting that an advanced description of biogeochemical reactions might not be necessary at such timescales. This study provides a simple yet useful tool to initially predict stream DOC concentrations and the location of DOC rich sources within catchments. The model approach could, in the future, be developed to better include soil temperatures, mires, stream and lake processes for improved representation of a daily variation of DOC concentration and allow the enhanced representation of lake and mire dominated areas.

Data and code availability

At Svartberget's open database: the Krycklan Catchment Study (www.slu.se/Krycklan), GIS, environmental and chemistry data can be found. The software, including Mike 11 and Mike SHE, is available online (https://www.mikepoweredbydhi.com/). All input files and the setup for the flow model can be acquired from the open database Safe Deposit (Jutebring Sterte et al., 2021c). Additionally, the DOC model setup and all sub-catchment results regarding DOC stream concentrations can be acquired from the open database Safe Deposit (Jutebring Sterte et al., 2022).

CRediT authorship contribution statement

Elin Jutebring Sterte (EJS) conceptualised the study with support from Hjalmar Laudon (HL) and Fredrik Lidman (FL). EJS, HJ and FL designed the model experiment and evaluated the results with input from all other co-authors. EJS led the writing of the paper with contributions from all co-authors. EJS, together with Stefan W Ploum and Ylva Sjöberg, conducted the preparation of figures with input from all co-authors.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix 1

This section presents the soil properties assigned to the flow model. These are the same as in Jutebring Sterte et al. (2021b). The soil type is the same as shown in Fig. 1 and Table 1.

Table A1
Soil properties in flow model (Jutebring Sterte et al., 2021b).

Soil type surface	Depth below ground (m)	Soil type	Horizontal hydraulic conductivity (m s^{-1})	Vertical hydraulic conductivity (m s^{-1})	Porosity
Till	2.5	Till	2×10^{-5}	2×10^{-6}	0.3
	To bedrock	Fine till	1×10^{-6}	1×10^{-7}	0.3
	Bedrock		1×10^{-9}	1×10^{-9}	0.0001
Mire	5	Peat	1×10^{-5}	5×10^{-5}	0.5
	7	Clay	1×10^{-9}	1×10^{-9}	0.55
	To bedrock	Fine till	1×10^{-6}	1×10^{-7}	0.3
	Bedrock		1×10^{-9}	1×10^{-9}	0.0001
Silty sediments	3	Silt/clay	1×10^{-7}	1×10^{-7}	0.55
	To bedrock	Fine till	1×10^{-6}	1×10^{-7}	0.3
	Bedrock		1×10^{-9}	1×10^{-9}	0.0001
Sandy sediments	0.8	Silt/Sand	1×10^{-7}	1×10^{-7}	0.45
	2.8	Silt/clay	1×10^{-8}	1×10^{-7}	0.55
	0.9 × max depth	Sand	3×10^{-4}	3×10^{-5}	0.35
	To bedrock	Gravel	1×10^{-4}	1×10^{-4}	0.32
	Bedrock		1×10^{-9}	1×10^{-9}	0.0001

Appendix 2

In this section, the supporting results for Figs. 3 and 5 can be found (Table B1). The results include annual and seasonal stream results from RIM, MTT and MTT_{Season}, as well as observed and modelled DOC concentrations of the riparian groundwater.

Table B1
Supporting results of Figs. 3 (a) and 5 (b). (a) The table includes observed and modelled annual and seasonal DOC averages and observed averages of the 14 Krycklan streams (mg l^{-1}). The table includes RIM, MTT and MTT_{Season}. (b) The table includes annual observed and modelled averages (mg l^{-1}) shown in Fig. 5, including data from observations, RIM and MTT_{season}. Observations are data from Ploum et al. (2020) and Grabs et al. (2012).

(a) Supporting results Fig. 3								
	Annual				Winter			
	Observed	RIM	MTT	MTT_{Season}	Observed	RIM	MTT	MTT_{Season}
C2	20	20	22	19	17	19	20	16
C1	21	19	17	19	19	21	17	17
C4	32	29	29	29	29	25	25	25
C5	23	28	28	28	26	28	28	28
C6	19	24	22	22	19	23	21	20
C7	24	23	22	20	20	21	19	16
C9	17	22	18	16	16	22	16	14
C10	20	24	22	20	17	22	18	17
C12	19	23	19	19	16	21	16	16
C13	19	26	21	19	17	24	18	15
C14	13	25	13	12	12	24	12	10
C15	12	22	16	15	12	21	14	13
C16	12	23	13	13	10	22	12	10
C20	11	31	16	15	10	29	14	12
	Spring				Summer			
	Observed	RIM	MTT	MTT_{Season}	Observed	RIM	MTT	MTT_{Season}
C2	18	21	25	17	25	20	24	23
C1	20	20	19	17	25	17	17	21
C4	22	24	24	23	40	36	36	38
C5	20	23	22	20	21	31	31	32
C6	17	21	20	18	19	26	25	26
C7	19	22	22	16	29	25	25	27
C9	15	22	18	13	19	24	20	21

(continued on next page)

Table B1 (*continued*)

(a) Supporting results Fig. 3

C10	16	22	20	16	26	28	25	26
C12	16	22	19	15	24	26	22	25
C13	17	25	21	15	23	28	23	24
C14	12	26	15	11	15	27	13	14
C15	11	21	16	12	14	24	18	19
C16	11	23	14	11	13	25	14	15
C20	10	31	19	15	13	32	17	18

(b) Supporting results Fig. 4

Well ID	401	402	403	404	501	502	503	504	505	506	507	508	509	510	511	512	513	601
Observed	33	39	31	33	28	6	35	14	17	15	28	12	31	21	9	9	15	34
RIM	10	10	23	23	30	30	26	29	29	31	24	24	6	22	31	31	29	27
MTT_{Season}	11	11	23	23	10	10	15	8	15	6	12	12	38	28	6	6	15	19
Well ID	602	801	802	803	804	R4	R12	R1	R9	R7	R10	R6	R5	R2	R15	R14	R8	R11
Observed	14	57	27	19	8	4	6	10	18	36	16	38	19	35	9	3	30	12
RIM	27	31	29	29	29	31	21	37	30	10	23	28	19	31	34	15	32	31
MTT_{Season}	10	18	13	13	13	6	6	17	9	32	23	28	22	18	15	4	33	12

Appendix 3

In this section, the correlation between modelled MTT and groundwater levels of the riparian zone (not including mires) are presented (Fig. C1). The plots showcase the daily averages for the cells representing the riparian zone for each respective sub-catchment. That is, there is variability in both MTT and groundwater levels for each point, and the table does not reflect how much water entering the streams at each individual cell. Two representative catchments have been chosen, C2 and C20. C2 is the stream of the catchment used for calibration (Fig. C1a). Overall, the shallowest and deepest recorded groundwater level for C2 is 0.0 and 3 m, respectively. This can be compared to the shortest and longest MTT of less than a week to 7 years. C20 is the stream of the catchment with longest recorded MTT (Fig. C1b, Jutebring Sterte et al., 2021a, 2021b, 2021c, 2021d). Overall, the shallowest and deepest recorded groundwater level for C2 is 0.0 and 3 m, respectively. This can be compared to the shortest and longest MTT of less than a week to 24 years. The correlation between groundwater level and MTT in both cases is strong. However, the main difference is that C2 cowcases a genareal greater depth diversety than C20, while C20 showcases generally longer MTTs.

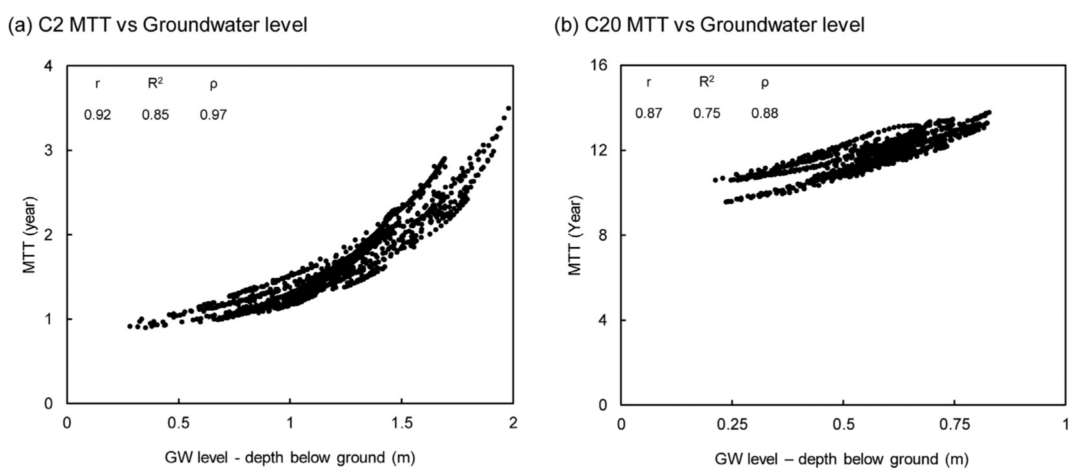

Fig. C1. The daily average MTT (year) and groundwater level (depth below ground (m)) for the riparian cells upstream the outlet of C2 and C20. The figures also include the general statistics such as the correlation coefficient (r) and the Spearman's rank correlation coefficient (ρ).

References

Abbott, B.W., Moatar, F., Gauthier, O., Fovet, O., Antoine, V., Ragueneau, O., 2018. Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France. Sci. Total Environ. 624, 845–858. https://doi.org/10.1016/j.scitotenv.2017.12.176.

Ågren, A., Buffam, I., Jansson, M., Laudon, H., 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. J. Geophys. Res. Biogeosci. 112, G03003. https://doi.org/10.1029/2006JG000381.

Ågren, A., Haei, M., Köhler, S.J., Bishop, K., Laudon, H., 2010. Regulation of stream water dissolved organic carbon (DOC) concentrations during snowmelt; the role of discharge, winter climate and memory effects. Biogeosciences 7, 2901–2913. https://doi.org/10.5194/bg-7-2901-2010.

Ågren, A.M., Buffam, I., Cooper, D.M., Tiwari, T., Evans, C.D., Laudon, H., 2014. Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements? Biogeosciences 11 (4), 1199–1213. https://doi.org/10.5194/bg-11-1199-2014.

Aitkenhead, J.A., Hope, D., Billett, M.F., 1999. The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. Hydrol. Process. 13 (8), 1289–1302. https://doi.org/10.1002/(SICI)1099-1085(19990615)13:8<1289::AID-HYP766>3.0.CO;2-M.

Anderson, T.R., Rowe, E.C., Polimene, L., Tipping, E., Evans, C.D., Barry, C.D.G., Hansell, D.A., Kaiser, K., Kitidis, V., Lapworth, D.J., Mayor, D.J., Monteith, D.T., Pickard, A.E., Sanders, R.J., Spears, B.M., Torres, R., Tye, A.M., Wade, A.J., Waska, H., 2019. Unified concepts for understanding and modelling turnover of dissolved organic matter from freshwaters to the ocean: the UniDOM model. Biogeochemistry https://doi.org/10.1007/s10533-019-00621-1.

Barclay, J.R., Starn, J.J., Briggs, M.A., Helton, A.M., 2020. Improved prediction of management-relevant groundwater discharge characteristics throughout river networks. Water Resour. Res. 56, e2020WR028027. https://doi.org/10.1029/2020WR028027.

Benettin, P., Soulsby, C., Birkel, C., Tetzlaff, D., Botter, G., Rinaldo, A., 2017. Using SAS functions and high-resolution isotope data to unravel travel time distributions in headwater catchments. Water Resour. Res. 53 (3), 1864–1878. https://doi.org/10.1002/2016WR020117.

Benettin, P., Fovet, O., Li, L., 2020. Nitrate removal and young stream water fractions at the catchment scale. Hydrol. Process. 34 (12), 2725–2738. https://doi.org/10.1002/hyp.13781.
Berggren, M., Laudon, H., Jansson, M., 2009. Hydrological control of organic carbon support for bacterial growth in boreal headwater streams. Microb. Ecol. 57 (1), 170–178. https://doi.org/10.1007/s00248-008-9423-6.
Birkel, C., Soulsby, C., Tetzlaff, D., 2014. Integrating parsimonious models of hydrological connectivity and soil biogeochemistry to simulate stream DOC dynamics. J. Geophys. Res. Biogeosci. 119 (5), 1030–1047. https://doi.org/10.1002/2013JG002551.
Birkel, C., Broder, T., Biester, H., 2017. Nonlinear and threshold-dominated runoff generation controls DOC export in a small peat catchment. J. Geophys. Res.-Biogeosci. 122 (3), 498–513. https://doi.org/10.1002/2016JG003621.
Birkel, C., Duvert, C., Correa, A., Munksgaard, N.C., Maher, D.T., Hutley, L.B., 2020. Tracer-aided modeling in the low-relief, wet-dry tropics suggests water ages and DOC export are driven by seasonal wetlands and deep groundwater. Water Resour. Res. 56 (4). https://doi.org/10.1029/2019WR026175.
Bishop, K., Seibert, J., Nyberg, L., Rodhe, A., 2011. Water storage in a till catchment. II: implications of transmissivity feedback for flow paths and turnover times. Hydrol. Process. 25 (25), 3950–3959. https://doi.org/10.1002/hyp.8355 John Wiley & Sons Ltd.
Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 2000. Effects of asynchronous snowmelt on flushing of dissolved organic carbon: a mixing model approach. Hydrol. Process. 14, 3291–3308. https://doi.org/10.1002/1099-1085(20001230)14:18<3291::AID-HYP202>3.0.CO;2-2.
Briggs, M.A., Hare, D.K., 2018. Explicit consideration of preferential groundwater discharges as surface water ecosystem control points. Hydrol. Process. 32, 2435–2440. https://doi.org/10.1002/hyp.13178.
Butts, M., Loinaz, M., Gottwein, P.B., Unnasch, R., Gross, D., 2012. Mike SheEcolab—an integrated catchment-scale eco-hydrological modelling tool XIX International Conference on Water Recourses CMWR 2012 University of Illinois at Urbana-Champaign, June 17–22, 2012.
Clark, J.M., Bottrell, S.H., Evans, C.D., Monteith, D.T., Bartlett, R., Rose, R., Newton, R.J., Chapman, P.J., 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. Sci. Total Environ. 408 (13), 2768–2775. https://doi.org/10.1016/j.scitotenv.2010.02.046.
Cory, R.M., Ward, C.P., Crump, B.C., Kling, G.W., 2014. Sunlight controls water column processing of carbon in arctic fresh waters. Science. https://doi.org/10.1126/science.1253119.
Dawson, J.J., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S.M., Malcolm, I.A., 2008. Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. Biogeochemistry 90 (1), 93–113. https://doi.org/10.1007/s10533-008-9234-3.
Dawson, J.J.C., Tetzlaff, D., Speed, M., Hrachowitz, M., Soulsby, C., 2011. Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. Hydrol. Process. 25, 1647–1658. https://doi.org/10.1002/hyp.7925.
Dick, J.J., Tetzlaff, D., Birkel, C., Soulsby, C., 2015. Modelling landscape controls on dissolved organic carbon sources and fluxes to streams. Biogeochemistry 122 (2), 361–374. https://doi.org/10.1007/s10533-014-0046-3.
ElBishlawi, H., Jaffe, P.R., 2015. Characterisation of dissolved organic matter from a restored urban marsh and its role in the mobilisation of trace metals. Chemosphere 127, 144–151. https://doi.org/10.1016/j.chemosphere.2014.12.080.
Fissore, C., Dalzell, B.J., Berhe, A.A., Voegtle, M., Evans, M., Wu, A., 2017. Influence of topography on soil organic carbon dynamics in a Southern California grassland. Catena 149, 140–149. https://doi.org/10.1016/j.catena.2016.09.016.
Fork, M., Sponseller, R.A., Laudon, H., 2020. Changing source-transport dynamics drive differential browning trends in a boreal stream network. Water Resour. Res. https://doi.org/10.1029/2019WR026336.
Futter, M.N., Butterfield, D., Cosby, B.J., Dillon, P.J., Wade, A.J., Whitehead, P.G., 2007. Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. Water Resour. Res. 43 (2). https://doi.org/10.1029/2006WR004960.
Grabs, T., Bishop, K., Laudon, H., Lyon, S.W., Seibert, J., 2012. Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports. Biogeosciences 9 (10), 3901–3916. https://doi.org/10.5194/bg-9-3901-2012.
Graham, D.N., Butts, M.B., 2005. Flexible, integrated watershed modelling with MIKE SHE. Watershed Models 849336090, 245–272.
Harman, C.J., 2015. Time-variable transit time distributions and transport: theory and application to storage-dependent transport of chloride in a watershed. Water Resour.Res. 51, 1–30. https://doi.org/10.1002/2014WR015707.
Harms, T.K., Ludwig, S.M., 2016. Retention and removal of nitrogen and phosphorus in saturated soils of arctic hillslopes. Biogeochemistry 127, 291–304. https://doi.org/10.1007/s10533-016-0181-0.
Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds,Oregon. J. Geophys. Res. 111 (G1), G01007. https://doi.org/10.1029/2005JG000082.
Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1994. Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma,Colorado. Biogeochemistry 25 (3), 147–165. https://doi.org/10.1007/BF00024390.
Hrachowitz, M., Savenije, H., Bogaard, T., Tetzlaff, D., Soulsby, C., 2013. What can flux tracking teach us about water age distribution patterns and their temporal dynamics? Hydrol. Earth Syst. Sci. 7 (2), 533–564. https://doi.org/10.5194/hess-17-533-2013.
Hrachowitz, M., Benettin, P., van Breukelen, B.M., Fovet, O., Howden, N.J.K., Ruiz, L., van der Velde, Y., Wade, A.J., 2016. Transit times—the link between hydrology and water quality at the catchment scale. Wiley Interdiscip. Rev. Water 3 (5), 629–657. https://doi.org/10.1002/wat2.1155.
Hruška, J., Köhler, S., Laudon, H., Bishop, K., 2003. Is a universal model of organic acidity possible: comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. Environ. Sci. Technol. 37 (9), 1726–1730. https://doi.org/10.1021/es0201552 American Chemical Society.
Humbert, G., Jaffrezic, A., Fovet, O., Gruau, G., Durand, P., 2015. Dry-season length and runoff control annual variability in stream DOC dynamics in a small, shallow groundwater-dominated agricultural watershed. Water Resour. Res. 51 (10), 7860–7877. https://doi.org/10.1002/2015WR017336.
Jansson, M., Persson, L., De Roos, A.M., Jones, R.I., Tranvik, L.J., 2007a. Terrestrial carbon and intraspecific size-variation shape lake ecosystems. Trends Ecol. Evol. 22 (6), 316–322. https://doi.org/10.1016/j.tree.2007.02.015.
Jansson, R., Laudon, H., Johansson, E., Augspurger, C., 2007b. The importance of groundwater discharge for plant species number in riparian zones. Ecology, 131–139 https://doi.org/10.1890/0012-9658(2007)88[131:TIOGDF]2.0.CO;2.
Jantze, E.J., Laudon, H., Dahlke, H.E., Lyon, S.W., 2015. Spatial variability of dissolved organic and inorganic carbon in subarctic headwater streams. Arct. Antarct. Alp. Res. 47 (3), 529–546. https://doi.org/10.1657/AAAR0014-044 Taylor & Francis.
Jutebring Sterte, E., Lidman, F., Lindborg, E., Sjöberg, Y., Laudon, H., 2021a. How catchment characteristics influence hydrological pathways and travel times in a boreal landscape. Hydrol. Earth Syst. Sci. 25 (4), 2133–2158. https://doi.org/10.5194/hess-25-2133-2021.
Jutebring Sterte, E., Lidman, F., Balbarini, N., Lindborg, E., Sjöberg, Y., Selroos, J.O., Laudon, H., 2021b. Hydrological control of water quality – modelling base cation weathering and dynamics across heterogeneous boreal catchments. Sci. Total Environ. 799, 149101. https://doi.org/10.1016/j.scitotenv.2021.149101.
Jutebring Sterte, E., Sjöberg, Y., Lindborg, E., Lidman, F., Laudon, H., Karlsen, R.Huseby, 2021. Surface-ground water interaction: from watershed processes to hyporheic exchange: Mike SHE Model 2022 Mike SHE Model 2022 DOC (2022) (Accessed 10 Jun 2021). [online]. Available from: https://www.safedeposit.se/projects/166.
Jutebring Sterte, E., Sjöberg, Y., Lindborg, E., Lidman, F., Laudon, H., Huseby Karlsen, R., 2021. Surface-ground water interaction: from watershed processes to hyporheic exchange: Mike SHE Model 2021 Weathering and Flow Results (Accessed 10 Jun 2021). [online]. Available from: https.
Jutebring Sterte, E., Sjöberg, Y., Lindborg, E., Lidman, F., Laudon, H., Karlsen, R.Huseby, 2022. Surface-ground water interaction: from watershed processes to hyporheic exchange: Mike SHE Model 2022 DOC (2022) (Accessed 12 Feb 2022). [online]. Available from: https://www.safedeposit.se/projects/166.
Kaiser, K., 2001. Dissolved organic phosphorus and sulphur as influenced by sorptive interactions with mineral subsoil horizons. Eur. J. Soil Sci. 52 (3), 489–493. https://doi.org/10.1046/j.1365-2389.2001.00396.x John Wiley & Sons, Ltd (10.1111).
Kaiser, K., Kaupenjohann, M., Zech, W., 2001b. Sorption of dissolved organic carbon in soils: effects of soil sample storage, soil-to-solution ratio, and temperature. Geoderma 99 (3), 317–328. https://doi.org/10.1016/S0016-7061(00)00077-X.
Kasurinen, V., Alfredsen, K., Ojala, A., Pumpanen, J., Weyhenmeyer, G.A., Futter, M.N., Laudon, H., Berninger, F., 2016. Modeling nonlinear responses of DOC transport in boreal catchments in Sweden. Water Resour. Res. 52 (7), 4970–4989. https://doi.org/10.1002/2015WR018343.
Klaminder, J., Grip, H., Mörth, C.M., Laudon, H., 2011. Carbon mineralization and pyrite oxidation in groundwater: importance for silicate weathering in boreal forest soils and stream base-flow chemistry. Appl. Geochem. 26 (3), 319–325.
Köhler, S.J., Buffam, I., Laudon, H., Bishop, K.H., 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements. J. Geophys. Res. 113, G03012. https://doi.org/10.1029/2007JG000629.
Kolbe, T., Marçais, J., de Dreuzy, J.R., Labasque, T., Bishop, K., 2020. Lagged rejuvenation of groundwater indicates internal flow structures and hydrological connectivity. Hydrol. Process. 34 (10), 2176–2189. https://doi.org/10.1002/hyp.13753.
Krycklan Database, 2013. Hydrological Research at Krycklan Catchment Study.Available at: https://www.slu.se/krycklan (Accessed: 18 June 2021).
Kuglerová, L., Jansson, R., Ågren, A., Laudon, H., Malm-Renöfält, B., 2014. Groundwater discharge creates hotspots of riparian plant species richness in a boreal forest stream network. Ecology 95 (3), 715–725. https://doi.org/10.1890/13-0363.1 Wiley Online Library.
Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J.-N., Jeanneau, L., 2013. Hydrologically driven seasonal changes in the sources and production mechanisms of dissolved organic carbon in a small lowland catchment. Water Resour. Res. 49 (9), 5792–5803. https://doi.org/10.1002/wrcr.20466.
Laudon, H., Sponseller, R.A., 2018. How landscape organisation and scale shape catchment hydrology and biogeochemistry: insights from a long-term catchment study. WIREs Water 5, e1265. https://doi.org/10.1002/wat2.1265.
Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., Köhler, S., 2011. Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling. Ecosystems 14 (6), 880–893. https://doi.org/10.1007/s10021-011-9452-8.
Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., Bishop, K., 2013. The krycklan catchment study - a flagship infrastructure for hydrology, biogeochemistry, and climate research in the boreal landscape. Water Resour. Res. 49 (10), 7154–7158. https://doi.org/10.1002/wrcr.20520.
Laudon, H., Hasselquist, E.M., Peichl, M., Lindgren, K., Sponseller, R., Lidman, F., Kuglerová, L., Hasselquist, N.J., Bishop, K., Nilsson, M.B., Ågren, A.M., 2021. Northern landscapes in transition: evidence, approach and ways forward using the Krycklan Catchment Study. Hydrol. Process. 35 (4), e14170. https://doi.org/10.1002/hyp.14170.
Leach, J.A., Laudon, H., 2019. Headwater lakes and their influence on downstream discharge. Limnol. Oceanogr. 4, 105–112. https://doi.org/10.1002/lol2.10110.
Ledesma, J.L.J., Grabs, T., Bishop, K.H., Schiff, S.L., Köhler, S.J., 2015. Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. Glob. Chang. Biol. 21 (8), 2963–2979. https://doi.org/10.1111/gcb.12872.
Ledesma, J.L., Futter, M.N., Laudon, H., Evans, C.D., Köhler, S.J., 2016. Boreal forest riparian zones regulate stream sulfate and dissolved organic carbon. Sci. Total Environ. 560–561, 110–122. https://doi.org/10.1016/j.scitotenv.2016.03.230.

Ledesma, J.L., Futter, M.N., Blackburn, M., Lidman, F., Grabs, T., Sponseller, R.A., Laudon, H., Bishop, K.H., Köhler, S.J., 2018. Towards an improved conceptualisation of riparian zones in boreal forest headwaters. Ecosystems 21, 297–315. https://doi.org/10.1007/s10021-017-0149-5.

Lessels, J.S., Tetzlaff, D., Birkel, C., Dick, J., Soulsby, C., 2016. Water sources and mixing in riparian wetlands revealed by tracers and geospatial analysis. Water Resour. Res. 52 (1), 456–470. https://doi.org/10.1002/2015WR017519.

Lidman, F., Boily, Å., Laudon, H., Köhler, S.J., 2017. From soil water to surface water - how the riparian zone controls element transport from a boreal forest to a stream. Biogeosciences 14 (12), 3001–3014. https://doi.org/10.5194/bg-14-3001-2017.

Lupon, A., Denfeld, B.A., Laudon, H., Leach, J., Karlsson, J., Sponseller, R.A., 2019. Groundwater inflows control patterns and sources of greenhouse gas emissions from streams. Limnol. Oceanogr. 64, 1545–1557. https://doi.org/10.1002/lno.11134.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G., 2003. Biogeochemical hot spots and hot moments at the Interface of terrestrial and aquatic ecosystems. Ecosystems 6 (4), 301–312. https://doi.org/10.1007/s10021-003-0161-9.

McDonough, L.K., Santos, I.R., Andersen, M.S., O'Carroll, D.M., Rutlidge, H., Meredith, K., Oudone, P., Bridgeman, J., Gooddy, D.C., Sorensen, J.P.R., Lapworth, D.J., MacDonald, A.M., Ward, J., Baker, A., 2020. Changes in global groundwater organic carbon driven by climate change and urbanisation. Nat. Commun. 11 (1), 1279. https://doi.org/10.1038/s41467-020-14946-1.

Mengistu, S.G., Creed, I.F., Webster, K.L., Enanga, E., Beall, F.D., 2014. Searching for similarity in topographic controls on carbon, nitrogen and phosphorus export from forested headwater catchments. Hydrol. Process. 28, 3201–3216. https://doi.org/10.1002/hyp.9862.

Meshesha, T.W., Wang, J., Melaku, N.D., 2020. Modelling spatiotemporal patterns of water quality and its impacts on aquatic ecosystem in the cold climate region of Alberta, Canada. J. Hydrol. 587, 124952. https://doi.org/10.1016/j.jhydrol.2020.124952.

Meyer, J.L., Wallace, J.B., Eggert, S.L., 1998. Leaf litter as a source of dissolved organic carbon in streams. Ecosystems 1 (3), 240–249. https://doi.org/10.1007/s100219900019.

Mineau, M.M., Wollheim, W.M., Buffam, I., Findlay, S.E.G., Hall, R.O., Hotchkiss, E.R., Koenig, L.E., McDowell, W.H., Parr, T.B., 2016. Dissolved organic carbon uptake in streams: a review and assessment of reach-scale measurements. J. Geophys. Res. Biogeosci. 121, 2019–2029. https://doi.org/10.1002/2015JG003204.

Mulholland, P.J., Hill, W.R., 1997. Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: separating catchment flow path and in-stream effects. Water Resour. Res. 33 (6), 1297–1306. https://doi.org/10.1029/97WR00490.

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I — a discussion of principles. J. Hydrol. 10 (3), 282–290. https://doi.org/10.1016/0022-1694(70)90255-6.

Neff, J.C., Finlay, J.C., Zimov, S.A., Davydov, S.P., Carrasco, J.J., Schuur, E.A.G., Davydova, A.I., 2006. Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. Geophys. Res. Lett. 33, L23401. https://doi.org/10.1029/2006GL028222.

Oni, S.K., Futter, M.N., Teutschbein, C., Laudon, H., 2014. Cross-scale ensemble projections of dissolved organic carbon dynamics in boreal forest streams. Clim. Dyn. 42 (9), 2305–2321. https://doi.org/10.1007/s00382-014-2124-6.

Peters, N.E., Burns, D.A., Aulenbach, B.T., 2014. Evaluation of high-frequency mean streamwater transit-time estimates using groundwater age and dissolved silica concentrations in a small forested watershed. Aquat. Geochem. 20 (2), 183–202. https://doi.org/10.1007/s10498-013-9207-6.

Ploum, S.W., Laudon, H., Peralta-Tapia, A., Kuglerová, L., 2020. Are dissolved organic carbon concentrations in riparian groundwater linked to hydrological pathways in the boreal forest? Hydrol. Earth Syst. Sci. 24, 1709–1720. https://doi.org/10.5194/hess-24-1709-2020.

Ploum, S.W., Leach, J.A., Laudon, H., Kuglerová, L., 2021. Groundwater, soil, and vegetation interactions at discrete riparian inflow points (DRIPs) and implications for boreal streams. Front. Water 3, 669007. https://doi.org/10.3389/frwa.2021.669007.

Rankinen, K., Karvonen, T., Butterfield, D., 2004. A simple model for predicting soil temperature in snow-covered and seasonally frozen soil: model description and testing. Hydrol. Earth Syst. Sci. 8, 706–716. https://doi.org/10.5194/hess-8-706-2004.

Ricker, M.C., Stolt, M.H., Donohue, S.W., Blazejewski, G.A., Zavada, M.S., 2013. Soil organic carbon pools in riparian landscapes of southern New England. Soil Sci. Soc. Am. J. 77, 1070–1079. https://doi.org/10.2136/sssaj2012.0297.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., Bishop, K., 2009. Linking soil- and stream-water chemistry based on a riparian flow-concentration integration model. Hydrol. Earth Syst. Sci. 13 (12), 2287–2297. https://doi.org/10.5194/hess-13-2287-2009.

Son, K., Lin, L., Band, L., Owens, E.M., 2019. Modelling the interaction of climate, forest ecosystem, and hydrology to estimate catchment dissolved organic carbon export. Hydrol. Process. 33 (10), 1448–1464. https://doi.org/10.1002/hyp.13412.

Strohmenger, L., Fovet, O., Akkal-Corfini, N., Dupas, R., Durand, P., Faucheux, M., Gruau, G., Hamon, Y., Jaffrézic, A., Minaudo, C., Petitjean, P., 2020. Multitemporal relationships between the hydroclimate and exports of carbon, nitrogen, and phosphorus in a small agricultural watershed. Water Resour. Res. 56 (7), e2019WR026323.

Strohmenger, L., Fovet, O., Hrachowitz, M., Salmon-Monviola, J., Gascuel-Odoux, C., 2021. Is a simple model based on two mixing reservoirs able to reproduce the intra-annual dynamics of DOC and NO3 stream concentrations in an agricultural headwater catchment? Sci. Total Environ. 794, 148715. https://doi.org/10.1016/j.scitotenv.2021.148715.

Stutter, M.I., Chardon, W.J., Kronvang, B., 2012. Riparian buffer strips as a multifunctional management tool in agricultural landscapes: introduction. J. Environ. Qual. 41, 297–303. https://doi.org/10.2134/jeq2011.0439.

Thomas, Z., Abbott, B.W., Troccaz, O., Baudry, J., Pinay, G., 2016. Proximate and ultimate controls on carbon and nutrient dynamics of small agricultural catchments. Biogeosciences 13 (6), 1863–1875. https://doi.org/10.5194/bg-13-1863-2016.

Tiwari, T., Laudon, H., Beven, K., Ågren, A.M., 2014. Downstream changes in DOC: inferring contributions in the face of model uncertainties. Water Resour. Res. https://doi.org/10.1002/2013WR014275.

Tiwari, T., Buffam, I., Sponseller, R.A., Laudon, H., 2017. Inferring scale-dependent processes influencing stream water biogeochemistry from headwater to sea. Limnol. Oceanogr. https://doi.org/10.1002/lno.10738.

Tripler, C.E., Kaushal, S.S., Likens, G.E., Todd Walter, M., 2006. Patterns in potassium dynamics in forest ecosystems. Ecol. Lett. 9 (4), 451–466. https://doi.org/10.1111/j.1461-0248.2006.00891.x.

Troch, P.A., Carrillo, G., Sivapalan, M., Wagener, T., Sawicz, K., 2013. Climate-vegetation-soil interactions and long-term hydrologic partitioning: signatures of catchment co-evolution. Hydrol. Earth Syst. Sci. 17, 2209–2217. https://doi.org/10.5194/hess-17-2209-2013.

Vähätalo, A.V., Salkinoja-Salonen, M., Taalas, P., Salonen, K., 2000. Spectrum of the quantum yield for photochemical mineralisation of dissolved organic carbon in a humic lake. Limnol. Oceanogr. 45 (3), 664–676. https://doi.org/10.4319/lo.2000.45.3.0664.

Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot spots and hot moments in riparian zones: potential for improved water quality management. JAWRA J.Am.Water Resour.Assoc. 46, 278–298. https://doi.org/10.1111/j.1752-1688.2010.00420.x.

Vidon, P.G., Welsh, M.K., Hassanzadeh, Y.T., 2019. Twenty years of riparian zone research (1997–2017): where to next? J. Environ. Qual. 48 (2), 248–260. https://doi.org/10.2134/jeq2018.01.0009.

Wagner, L.E., Vidon, P., Tedesco, L.P., Gray, M., 2008. Stream nitrate and DOC dynamics during three spring storms across land uses in glaciated landscapes of the Midwest. J. Hydrol. 362 (3), 177–190. https://doi.org/10.1016/j.jhydrol.2008.08.013.

Wei, Q.S., Feng, C.H., Wang, D.S., Shi, B.Y., Zhang, L.T., Wei, Q., Tang, H.X., 2008. Seasonal variations of chemical and physical characteristics of dissolved organic matter and trihalomethane precursors in a reservoir: a case study. J. Hazard. Mater. 150 (2), 257–264. https://doi.org/10.1016/j.jhazmat.2007.04.096.

Weyhenmeyer, G.A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., Tranvik, L.J., 2012. Selective decay of terrestrial organic carbon during transport from land to sea. Glob Change Biol. 18, 349–355. https://doi.org/10.1111/j.1365-2486.2011.02544.x.

Wilson, H.F., Saiers, J.E., Raymond, P.A., Sobczak, W.V., 2013. Hydrologic drivers and seasonality of dissolved organic carbon concentration, nitrogen content, bioavailability, and export in a forested New England stream. Ecosystems 16, 604–616. https://doi.org/10.1007/s10021-013-9635-6.

Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., Bishop, K., 2011a. Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. Water Resour. Res. 47 (8). https://doi.org/10.1029/2010WR010235.

Winterdahl, M., Temnerud, J., Futter, M.N., Löfgren, S., Moldan, F., Bishop, K., 2011b. Riparian zone influence on stream water dissolved organic carbon concentrations at the Swedish integrated monitoring sites. Ambio 40, 920–930. https://doi.org/10.1007/s13280-011-0199-4.

Winterdahl, M., Wallin, M.B., Karlsen, R.H., Laudon, H., Öquist, M., Lyon, S.W., 2016a. Decoupling of carbon dioxide and dissolved organic carbon in boreal headwater streams. J. Geophys. Res. Biogeosci. 121 (10), 2630–2651. https://doi.org/10.1002/2016JG003420.

Winterdahl, M., Laudon, H., Lyon, S.W., Pers, C., Bishop, K., 2016b. Sensitivity of stream dissolved organic carbon to temperature and discharge: implications of future climates. J. Geophys. Res. Biogeosci. 121 (1), 126–144. https://doi.org/10.1002/2015JG002922.

Xu, N., Saiers, J.E., Wilson, H.F., Raymond, P.A., 2012. Simulating streamflow and dissolved organic matter export from a forested watershed. Water Resour. Res. 48, W05519. https://doi.org/10.1029/2011WR011423.

Ye, F., Ma, M.H., Wu, S.J., Jiang, Y., Zhu, G.B., Zhang, H., Wang, Y., 2019. Soil properties and distribution in the riparian zone: the effects of fluctuations in water and anthropogenic disturbances. Eur. J. Soil Sci. 70 (3), 664–673. https://doi.org/10.1111/ejss.12756.</p>

Yurova, A., Sirin, A., Buffam, I., Bishop, K., Laudon, H., 2008. Modeling the dissolved organic carbon output from a boreal mire using the convection-dispersion equation: importance of representing sorption. water resourRes. 44 (7). https://doi.org/10.1029/2007WR006523.