1 2	Seasonal and interannual Dissolved Organic Carbon transport process dynamics in a subarctic headwater catchment revealed by high-resolution measurements.
3 4	Danny Croghan ¹ , Pertti Ala-Aho ² , Jeffrey Welker ^{1,3,4} , Kaisa-Riikka Mustonen ¹ , Kieran Khamis ⁵ , David M. Hannah ⁵ , Jussi Vuorenmaa ⁶ , Bjørn Kløve ² , and Hannu Marttila ²
5 6 7 8 9 10 11 12 13	 Ecology and Genetics Research Unit, University of Oulu, Oulu, Finland Water, Energy and Environmental Engineering Research Unit, University of Oulu, Oulu Finland Department of Biological Sciences, University of Alaska Anchorage, USA UArctic, Rovaniemi, Finland School of Geography, Earth and Environmental Sciences, University of Birmingham Birmingham, UK Finnish Environment Institute, Finland
14	Corresponding Author: Danny Croghan (danny.croghan@oulu.fi)
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25	
2627	
28	
29	
30	
31	
32	
33	

<u>Abstract</u>

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64

Dissolved organic carbon (DOC) dynamics are evolving in the rapidly changing Arctic and a comprehensive understanding of the controlling processes is urgently required. For example, the transport processes governing DOC dynamics are prone to climate driven alteration given their strong seasonal nature. Hence, high-resolution and long-term studies are required to assess potential seasonal and inter-annual changes in DOC transport processes. In this study, we monitored DOC at a 30-minute resolution from September 2018 to December 2022 in a headwater peatland-influenced stream in Northern Finland (Pallas catchment, 68° N). To-Temporal variability in assess-transport processes was assessed using multiple methods, specifically were used: concentration – discharge (C-Q) slope for seasonal analysis, a modified hysteresis index for event analysis, yield analysis, and random forest regression models to determine the hydroclimatic controls on transport. The findings reveal the following distinct patterns: (a) the slope of the C-Q relationship displayed a strong seasonal trend, indicating increasing transport limitation each month after snowmelt beginsbegan; (b) the hysteresis index decreases decreased post-snowmelt, signifying the influence of distal sources and DOC mobilization through slower pathways; and (c) interannual variations in these metrics are were generally low, often smaller than month-tomonth fluctuations. These results highlight the importance of long-term and detailed monitoring to enable separation of inter and intra annual variability to better understand the complexities of DOC transport. This study contributes to a broader comprehension of DOC transport dynamics in the Arctic because knowledge gained regarding the dominant transport mechanisms and their, specifically quantifying seasonal variations variability and associated mechanistic drivers, which is is-vital for predicting evaluating how the carbon cycle is likely to will change in the future in Arctic ecosystems.

65

66

1. Introduction

67 The dynamics of Dissolved Organic Carbon (DOC) in Arctic catchments are undergoing profound transformations due to the impacts of climate change, recovery from acidification, 68 69 and land-use change (Anderson et al., 2023; de Wit et al., 2016; Liu et al., 2022; McGuire et al., 2018; Shogren et al., 2021; Tank et al., 2016). Notably, the Arctic region has experienced a 70 71 fourfold increase in warming compared to the global average since 1979 (Rantanen et al., 2022), fostering substantial changes in hydrological processes, particularly in terms of 72 73 transport mechanisms (Liu et al., 2022). Climate change-induced alterations are occurring in 74 permafrost extent (Koch et al., 2022), snowpack water storage (Bokhorst et al., 2016; 75 Pulliainen et al., 2020), snowpack duration (Bowering et al., 2023), snowmelt timing (Tan et 76 al., 2011), and hydrological seasonality (Osuch et al., 2022), which have been significantly 77 affecting DOC dynamics (Liu et al., 2022; Shogren et al., 2021). Consequently, these shifts have triggered rapid and consequential transformations within both the Arctic water and 78 carbon cycles that are both climatically sensitive (Bintanja and Andry, 2017; Bruhwiler et al., 79 2021; Mcguire et al., 2009; Vihma et al., 2016). 80 81 DOC transport processes (referring to the mobilization of DOC from catchment sources to 82 the stream through differing flow paths) in the Arctic exhibit pronounced seasonality and are highly susceptible to change (Bowering et al., 2023; Csank et al., 2019; Shatilla and 83 84 Carey, 2019). Among the various transport mechanisms, the spring snowmelt flood is the main event and control on annual DOC flux in Arctic catchments (Croghan et al., 2023). 85 86 Several studies have demonstrated its contribution ranging from 37% to 82% of the annual DOC load, albeit with considerable variations between catchments and years (Dyson et al., 87 2011; Finlay et al., 2006; Prokushkin et al., 2011). However, in the Arctic, climate change is 88 89 reducing snow cover duration and increasing the fraction of precipitation in the liquid phase 90 (Bintanja and Andry, 2017). Consequently, storm events are emerging as increasingly 91 important mechanisms for the export of DOC from terrestrial ecosystems (i.e. soils) 92 catchments to streams stream networks (Day and Hodges, 2018; Speetjens et al., 2022). 93 Furthermore, the lengthening growing seasons, accompanied by potential increases in DOC source supply, are further exacerbating the impact of summer and autumn storm events on 94 DOC dynamics in the Arctic region (Bowering et al., 2020; Pearson et al., 2013). Additionally, 95

while the significance of shoulder seasons (defined in the Arctic as the transitional period 96 between the end of plant senescence and the freezing of the headwaters, and after the 97 onset of thaw till the end of snowmelt) for DOC export has been acknowledged in recent 98 99 years, their characterization remains limited. Therefore, there is a pressing need for more 100 extensive documentation to elucidate the influence of shifting climate on DOC dynamics in 101 the Arctic (Shogren et al., 2020). 102 Headwater catchments play a crucial role in the transport of DOC into streams (Fork et al., 103 2020; Lambert et al., 2014). These catchments constitute approximately 90% of the total 104 global stream length and serve as the primary connection for carbon transport between 105 terrestrial landscapes and oceans (Argerich et al., 2016; Li et al., 2021). Allochthonous inputs 106 into the stream, driven by rain and snowmelt events, dominate the dynamics of headwater 107 catchments (Billett et al., 2006; Laudon et al., 2004). Headwater wetland mires are especially abundant in northern latitudes and are significant contributors of carbon to the 108 109 stream, often exhibiting higher concentrations compared to other landscape types (Campeau and del Giorgio, 2014; Dick et al., 2015; Gómez-Gener et al., 2021). Furthermore, 110 111 the seasonal dynamics of carbon transfer processes in headwater wetlands differ significantly depending on the season. During snowmelt, rapid superficial pathways are 112 113 observed, which later evolve into more complex pathways in the landscape during the 114 summer and autumn (Croghan et al., 2023; Laudon et al., 2011). Additionally, headwater 115 catchments are highly vulnerable to the impacts of hydrological extremes (Koch et al., 2022), and they are expected to undergo significant changes due to climate change (Ward et 116 al., 2020). The increasing hydrological stochasticity in Arctic catchments (e.g. occurrence 117 and magnitude of extremes) highlight the need to better understand inter-annual variability 118 119 using more highly resolved data to characterize event dynamics (Bring et al., 2016). Consequently, longer term and higher frequency study of sensitive headwater catchments is 120 121 essential to better understand their functioning and response to environmental changes, 122 especially in high latitude conditions (Bruhwiler et al., 2021; Marttila et al., 2022, 2021). 123 To comprehensively investigate the transport processes of DOC across seasons, it is essential to employ high-resolution, long-term monitoring approaches (Shogren et al., 124 2020). This need is particularly pronounced in headwater environments, where the majority 125 126 of the DOC input into streams occurs during storm events and snowmelt (Billett et al.,

2006). Only through high-frequency monitoring can we adequately identify and understand 127 the transport processes and characteristics associated with sudden episodic and 128 unpredictable storm and snowmelt events, capturing the necessary resolutions for 129 130 improved process understanding (Blaen et al., 2016). Furthermore, higher-resolution data 131 collection can facilitate the use of multiple analytical techniques, such as hysteresis analysis, 132 which can offer deeper insights into DOC transport dynamics (Croghan et al., 2023; Lloyd et al., 2016b). Historically, limited spatial and temporal field sampling has led to biases in our 133 134 understanding of the impacts of climate change in Arctic regions (Metcalfe et al., 2018; 135 Shogren et al., 2020). Additionally, high-frequency DOC measurements in the Arctic remain 136 relatively rare, especially datasets that cover the shoulder seasons and encompass multi-137 year measurements for assessing inter-annual differences (Beel et al., 2021; Shogren et al., 138 2021). Hence, there is an urgent need to integrate high-frequency monitoring sites in 139 subarctic, low Arctic, and high Arctic regions, particularly for evaluating the ongoing 140 evolution of the Arctic carbon and water cycles (Laudon et al., 2017; Marttila et al., 2021; 141 Pedron et al., 2023). The rapid evolution of controlling DOC processes due to climate change necessitates 142 aemphasizes pressing the need to document transport processes in understudied high-143 144 latitude headwater catchments (Shatilla et al., 2023). The scarcity of multi-year, high-145 frequency datasets in these high-latitude catchments has impeded our understanding of seasonal and inter-annual DOC dynamics. As the underlying drivers of DOC transport 146 147 processes are undergoing substantial changes, there is a need to understand baseline levels of variability (Shatilla and Carey, 2019; Shogren et al., 2021). This is particularly essential for 148 assessing the dynamic evolution of the Arctic carbon and water cycles, underscoring the 149 150 need for a concerted effort to address these knowledge gaps. (Laudon et al., 2017; Marttila 151 et al., 2021; Pedron et al., 2023). To address key knowledge gaps in Arctic headwater DOC 152 transport, our study focused on a peatland-influenced headwater catchment located in 153 subarctic, Northern Finland (68°N), with the overarching aim to identify the primary drivers of <u>DOC</u> transport processes of DOC and explore their seasonal and interannual dynamics. 154 155 We utilized a unique four-year high-resolution dataset of DOC, allowing us to conduct high-156 frequencyundertake varied analyses. To enhance understanding of DOC transport processes

157 158	questions were addressed:
159	1) How do the main drivers of DOC transport processes vary across different seasons?
160	2) To what extent do DOC transport processes and their drivers vary inter-annually?
161	We hypothesized that:
162 163	H ₁ At the intra annual scale, DOC transport processes would significantly differ between snow melt, snow free, and snow cover seasons;
164 165	$\underline{H_2}$ At the inter annual scale, the metrics of DOC transport processes would significantly differ between years with the most different hydrometeorological conditions.
166 167 168 169	2.0 Methods 2.1 Site Description
170	The research was conducted within the Lompolojängänoja catchment, also referred to as
171	the Pallas catchment (Marttila et al., 2021), situated in a peatland-influenced headwater
172	stream (Figure 1). This catchment is located in Northern Finland (68°02'N, 24°16'W) within
173	the Pallas-Yllästunturi National Park. Encompassing a total area of 4.42 km², the Pallas
174	catchment exhibits elevations ranging from 268 m to 375 m above sea level.
175	The stream location is strongly influenced by a peatland, which comprises fens, mires,
176	paludified forest and floodplains. This peatland exerts significant control over the flow
177	dynamics within the catchment, contributing most of the flow at the headwater location
178	(Marttila et al., 2021). Within the broader catchment area, coniferous forests account for
179	79% of the land classification, followed by mixed forests (9%) and peatbogs (8%).
180	The Pallas catchment is categorized as subarctic, characterized by long winters with
181	substantial snowfall and short, rainy summers. Notably, despite its northern latitude, the
182	catchment lacks a permafrost layer, making it one of the most northern research
183	catchments without permafrost (Marttila et al., 2021). The mean annual rainfall in the
184	catchment amounts to 521 mm, with 42% of that precipitation occurring as snowfall.
185	Typically, snowmelt occurs towards the end of April or early May and concludes by late May
186	or early June. Permanent snow cover in the catchment typically commences around late

October, though it can extend into late November. For further comprehensive descriptions of the Pallas catchment's characteristics, please refer to Marttila et al., (2021).

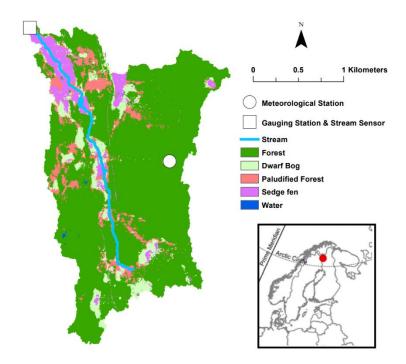


Figure 1 – Map of the study location (inset), catchment and measurement locations within the catchment. Classification of vegetation in the catchment was derived from (Räsänen et al., 2021)

2.2 Stream Monitoring

The monitoring of stream variables was conducted during the period from 18th September 2018 to 31st December 2022. To measure these variables, a multiparameter sonde (YSI-EXO3; Excitation 365 nm, Emission 480 nm) was deployed at the catchment outlet in the Lompolojängänoja stream (Figure 1). The sonde collected data at 30-minute intervals, measuring fluorescent dissolved organic matter (FDOM), electrical conductivity, turbidity, water temperature, and pH. The Finnish Environment Institute (SYKE) installed, calibrated, and maintained the sensor throughout the study duration. Stream flow was measured at the same location using a pressure transducer at a 120° V-notch weir, and records were logged at the same temporal resolution.

The FDOM measurements from the sonde were used to model the concentration of DOC.

The instrument internally corrected for temperature effects (i.e. thermal quenching), and

FDOM <u>required</u> for turbidity <u>effects</u> (Downing et al., 2012).

206 <u>Corrections for turbidity were undertaken</u> using the following equation <u>which was derived</u>
207 <u>using internal lab calibration of the instrument</u>:

$$DOC_{corrected} = \left(\frac{0.117*fDOM}{1-(1.1\cdot Turbidty)/(120+Turbidity)}\right)$$
(1)

Here, the value 0.117 represents the slope obtained from the lab sample DOC against instrument FDOM. To ensure data accuracy, regular grab samples were taken throughout the study (Supplementary Figure 1). No correction was applied to the instrument for inner-filter effects, as there was no observed deviation from linearity in the relationship between in-stream Absorbance 254nm and stream DOC. The instrument underwent regular manual cleaning every two weeks to prevent fouling, while the sensor also had a self-brushing antifouling system. No fouling was apparent over the course of the study.

The calculation of DOC load during the study period was performed using the following equation:

$$C_{l}=C_{c}\cdot Q \tag{2}$$

Where C_l is the carbon load (mg h⁻¹), C_c is the carbon concentration (mg L⁻¹), and Q is the stream flow (L h⁻¹).

Throughout the study, various meteorological measurements were collected. A meteorological station located at the Kenttärova forest site (Figure 1) was utilized to record precipitation, snow depth, and air temperature in 10 minutes resolution. The maintenance of the meteorological station was carried out by the Finnish Meteorological Institute (FMI).

2.3 Data Analysis

The 4-year dataset was transformed into hourly data by calculating hourly means. In our analysis, we delineated three distinct seasonal periods: the snowmelt season, snow-free season, and snow cover season.

The snowmelt season was defined as the period starting from the onset of snowmelt, indicated by a decline in snow depth-concurrent with a concurrent n-increase in flow, until there was no remaining snow cover at the Kenttärova site reached 0 cm (Fig. 1). The spring

snowmelt season was classified using both snow depth and flow as snow depth alone varies 233 for reasons not due to melting (e.g. snowpack consolidation). -The snow cover season 234 235 referred to the period when <u>permanent snow cover occurred</u> (i.e. the point of the year 236 snow depth was > 0 cm till the spring snowmelt)snow cover was present and persisted until 237 the subsequent. snowmelt season. The snow free season referred to the period between 238 the snowmelt and snow cover seasons where snow depth was 0 cm. All analyses were 239 performed using R in RStudio (version 2023.03.0). 240 To conduct event-based analysis, we extracted specific events from the dataset. Events 241 were defined as periods where discharge had to exceed baseflow by 10% for a duration of at least 24 hours, following definitions used in previous studies (Shogren et al., 2021; 242 Vaughan et al., 2017). Baseflow was computed using a Lyne-Hollick baseflow filter 243 244 implemented in the R package "grwat". In total, 92 events were identified and extracted from the dataset. Among these events, 18 occurred during the snowmelt period, 63 took 245 place during the snow-free period, and 11 events were observed within the snow cover 246 247 period. Concentration-Discharge (C-Q) analysis was performed to examine variations in transfer 248 249 processes at seasonal scales. We calculated the slope (β) of the logarithmic relationship 250 between DOC and streamflow (Q) for each year and each monthseason of the study. The 251 months of December to March were not included in the seasonal analysis as flow remained 252 at baseflow during these months throughout the study. A positive slope ($\beta > 0$) suggests a 253 transport-limited relationship, indicating that the concentration of DOC is primarily 254 controlled by the transport processes. Conversely, a negative slope (β < 0) suggests a 255 source-limited relationship, indicating that the concentration of DOC is primarily influenced by the sources within the catchment. A slope of zero ($\beta = 0$) indicates chemostasis, 256 257 indicating no significant change in DOC concentration with variations in streamflow. C-Q 258 slopes have been widely employed to assess the extent of transport or source limitation in 259 catchments (Godsey et al., 2009; Zarnetske et al., 2018). The coefficient of variation (CV) for monthly DOC was also calculated alongside monthly C-Q slopes to identify the amount of 260 variation in DOC relative to changes in C-Q slope.". 261 Hysteresis analysis was conducted to gain insights into flow pathways and transport 262 processes at event scale. The Modified Hysteresis Index (HI) was calculated following Lloyd 263

et al., (2016b). Briefly, the HI is calculated by subtracting the falling limb standardised DOC value from the rising limb standardised DOC value at each 20th flow percentile across the loop. The HI is then calculated as the average HI of the loop for each event. Only singlepeak events, where the flow returned to at or near baseflow, were selected for analysis For each event, individual peaks were treated as separate events to allow the HI to be calculated across the rising and falling limb of the flow. Therefore, for multi-peak events, multiple HI were calculated. The HI yielded values between -1 and 1 for each event. Positive values (> 0) indicate clockwise hysteresis, where the peak concentration of DOC occurs on the rising limb of the event. This pattern suggests the presence of near-stream sources or rapid transport of DOC. Negative values (< 0) indicate anticlockwise hysteresis, where the peak concentration of DOC occurs on the falling limb of the event. This pattern indicates the influence of distal sources or slow transport of DOC (Lloyd et al., 2016b; Williams, 1989). DOC load yields and event water yields were calculated for each event by totalling the sum of DOC (measured in kg per km²) and water (measured in mm), and subsequent linear regressions were performed to assess the variability between DOC and event water yields across seasons and years (Vaughan et al., 2017). For comparisons between years, 2018 was excluded as data collection only began in September 2018. Differences in the linear regression relationships signify variations in transport <u>limitation</u> and source <u>activation</u> dynamics among seasons and years. Furthermore, the Yield Ratio, defined as the ratio of event DOC load yield to event water yield, was computed to identify potential variations between months, indicating differences in transport processes (Vaughan et al., 2017). To identify the best performing hydrometeorological predictors drivers of event-based metrics, we employed a machine learning method (Random Forest regression) using the R package "randomForest". This approach was chosen due to observed non-linearity in some of the relationships. We considered a set of hydrometeorological predictors based on their potential significance in prior studies examining stream nutrient concentrations transport processes across seasonal timescales (Blaen et al., 2017). The selected predictor variables included maximum discharge, 7-day antecedent rainfall, average air temperature during the event, average water temperature during the event, and total rainfall during the event. The Random Forest regressions were conducted using the entire dataset, as the aim was to identify the most informative predictors. Models (names in brackets) were created to assess

264

265

266

267

268

269

270

271

272

273

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

the best predictors of Maximum event DOC (MaxDOC), the percentage of change of DOC during events (DOC Change), event C-Q slope (Slope), event hysteresis index (HI), and event Yield Ratio (Yield Ratio). We present the output of the models for the best predictors, as determined by node purity. Higher node purity values indicate better prediction performance. Additionally, we report the variance explained and the mean of squared residuals for each model. These metrics provide insights into the predictive power and goodness of fit of the selected predictors. Only models with variance explained > 10% are featured. Resultantly, no HI models are featured, as they did not meet this threshold.

Flow exhibited a pronounced seasonal pattern (Fig. 2a). Each year, the highest flow occurred

3.0 Results

303304305

306

307

308

309

310

311

312

313

314

315

316

317

318

319

320

321

322

323

324

295

296

297

298

299

300

301

302

3.1 <u>Time Series</u>

during the snowmelt season. In the snow-free season, flow was primarily driven by episodic precipitation events. During the early snow cover season, flow was responsive to some precipitation events, but remained at baseflow for most of the snow cover season (Table 1). DOC concentrations (Fig. 2b; Table 1) generally exhibited a consistent rise throughout the snowmelt season, and remained elevated throughout the snow-free period, albeit with frequent event-driven peaks. During the snow cover period, DOC levels initially declined and then stabilized. DOC load, on the other hand, mirrored the dynamics of flow, and the highest loads occurred during the snowmelt season, with smaller event-driven peaks during the snow-free season. Air temperature (Fig. 2c; Table 1) during the snowmelt season exhibited a positive trend, with some variation around 0 °C meaning regular fluctuation between melting and freezing in the snowmelt season. In the snow-free season, temperatures increased until August and then declined. At the onset of the snow cover season, temperatures dropped below zero. Snow cover typically began in mid-October and reached its peak in March or early April. Water temperature (Fig. 2d; Table 1) remained relatively stable during most of the snowmelt season and gradually increased towards the end of the period. Throughout the snow-free season, water temperature closely tracked air temperature. During the snow cover season, water temperature hovered around 0 °C. Turbidity, on the other hand, peaked during the snowmelt season due to initial flushes, but also reached high levels during large summer events in the snow-free season.

325

326

327

328

329

330

331

332

333

334

335

336

337

338

When considering the total annual cumulative DOC load averaged across the study (Fig. 2e; Table 1), the $^{\sim}$ 6 week snowmelt period contributed around 33.4% of the total annual DOC load. In contrast, the snow-free season contributed approximately 59% of the total annual DOC load, while the snow cover season contributed around 7.6%.

Table 1 – Hydrometeorological variables in the snow cover, snow melt, and snow free seasons. Values are presented as Mean, except for precipitation, which is shown as the total for each season. ± Standard Deviation.

<u>Year</u>	Season	Turbidity (NTU)	DOC (mg L ⁻¹)	DOC Load (kg h ⁻¹)	Flow (L s-1 km ⁻ 2)	Precipitation (mm)	Snow Depth (m)	Water Temp (°C)	Air Temp (°C)
2018	SnowCover	0.86	4.11	0.32	3.90	<u>98.7</u>	<u>0.17</u>	0.25	<u>-4.78</u>
<u>2018</u>	<u>SnowFree</u>	0.90	<u>6.82</u>	0.94	<u>7.16</u>	<u>58</u>	<u>0.02</u>	<u>2.33</u>	<u>1.47</u>
<u>2019</u>	SnowCover	<u>1.31</u>	<u>3.90</u>	0.23	<u>3.10</u>	<u>295.5</u>	<u>0.59</u>	0.19	<u>-7.80</u>
<u>2019</u>	<u>SnowFree</u>	<u>0.68</u>	<u>7.92</u>	<u>2.06</u>	<u>12.81</u>	<u>335.6</u>	0.00	<u>8.39</u>	9.07
<u>2019</u>	<u>SnowMelt</u>	<u>1.60</u>	<u>6.57</u>	<u>3.41</u>	<u>26.76</u>	<u>37.8</u>	<u>0.42</u>	<u>1.70</u>	4.30
<u>2020</u>	<u>SnowCover</u>	<u>0.75</u>	<u>4.30</u>	<u>0.46</u>	<u>4.77</u>	<u>348.4</u>	<u>0.74</u>	0.17	<u>-4.94</u>
<u>2020</u>	<u>SnowFree</u>	<u>0.62</u>	<u>6.88</u>	<u>2.06</u>	<u>13.61</u>	<u>310.6</u>	0.00	<u>10.41</u>	10.51
<u>2020</u>	<u>SnowMelt</u>	<u>1.11</u>	<u>7.20</u>	<u>7.27</u>	<u>47.20</u>	<u>17.5</u>	<u>0.81</u>	<u>1.9</u> 4	<u>5.14</u>
<u>2021</u>	<u>SnowCover</u>	<u>0.46</u>	<u>4.58</u>	<u>0.73</u>	<u>6.76</u>	<u>304.2</u>	<u>0.63</u>	0.17	<u>-8.21</u>
<u>2021</u>	<u>SnowFree</u>	<u>0.83</u>	<u>6.31</u>	<u>1.21</u>	<u>9.19</u>	<u>289.2</u>	0.00	<u>9.81</u>	10.55
<u>2021</u>	<u>SnowMelt</u>	<u>1.43</u>	<u>6.21</u>	<u>3.92</u>	<u>30.55</u>	<u>74.1</u>	<u>0.67</u>	<u>1.65</u>	<u>2.31</u>
2022	<u>SnowCover</u>	<u>0.98</u>	<u>3.48</u>	<u>0.37</u>	<u>5.63</u>	<u>229.1</u>	<u>0.65</u>	0.17	<u>-6.90</u>
2022	<u>SnowFree</u>	<u>0.89</u>	<u>6.45</u>	<u>1.70</u>	<u>13.50</u>	<u>350.4</u>	0.00	<u> 10.26</u>	10.00
2022	<u>SnowMelt</u>	<u>1.31</u>	<u>5.76</u>	<u>4.36</u>	<u>35.11</u>	<u>42.3</u>	<u>0.76</u>	<u>1.79</u>	3.44
Measurem		Snow	Snow Cover			Snow Melt	Snow Free		
Flow (L s-1	-km²)	4.89	4.89 ± 4.06			34.38 ± 35.77 12.05 ±		0.90	

DOC Concentration (mg L-1) 4.03 ± 0.99 6.39 ± 1.12 6.84 ± 1.47 DOC Load (kg h⁻¹) 0.41 ± 0.50 1.71 ± 1.98 4.62 ± 5.26 Air Temperature (°C) -6.74 ± 6.03 3.62 ± 5.37 9.51 ± 6.08 Water Temperature (°C) 0.18 ± 0.14 9.31 ± 4.31 1.76 ± 3.14 **Turbidity (NTU)** 0.91 ± 0.62 1.37 ± 0.88 0.77 ± 0.52

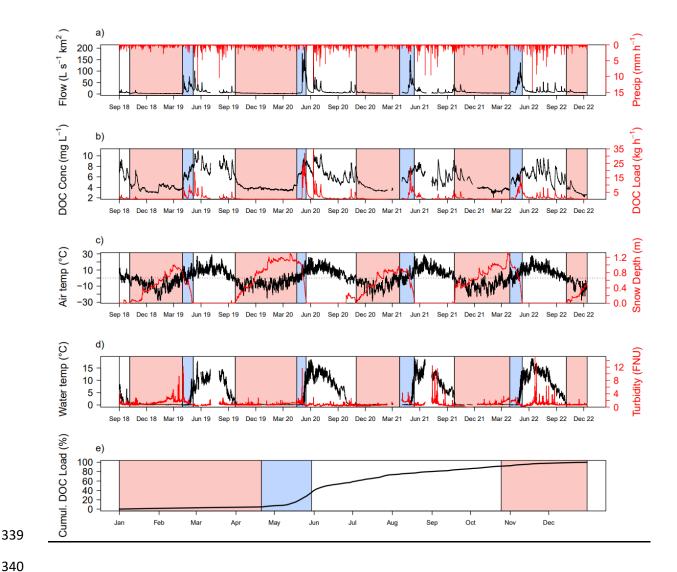
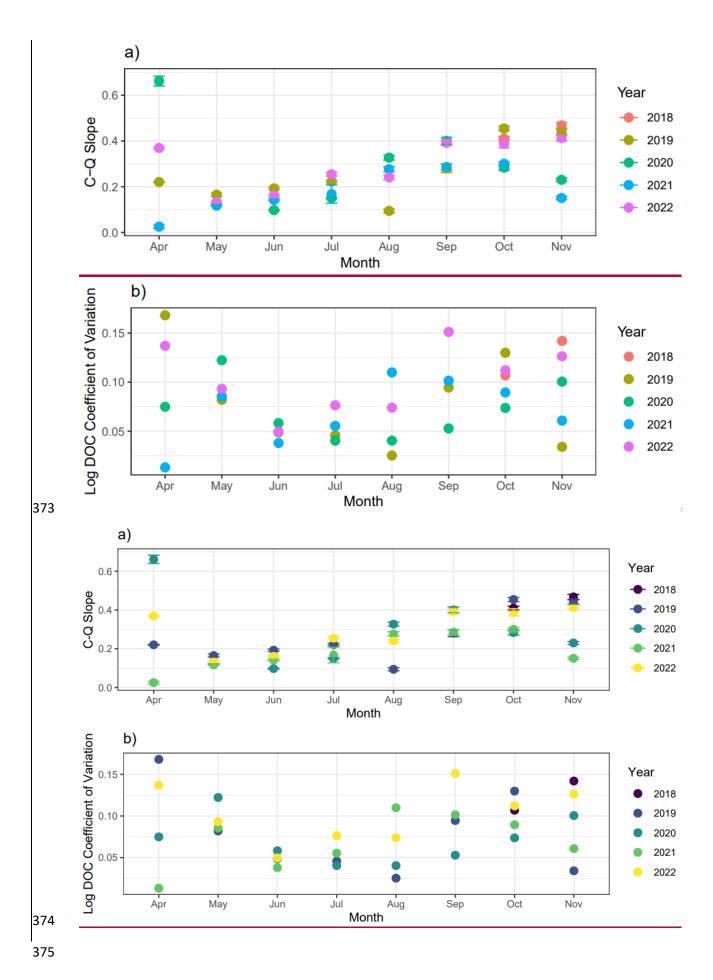


Figure 2 – Time series depicting: a) Flow (black) and Precipitation (red), b) DOC concentration (black) and DOC load (red), c) Air temperature (black) and snow depth (red), d) Water temperature (black) and Turbidity (red), and e) Average cumulative DOC load for the study period. The background shading indicates the different seasons: white background represents the snow-free season, red background represents the snow cover season, and blue background represents the snow-free, permanent snow cover, and snowmelt seasons.

3.2 Concentration-discharge (C-Q) relationships

The analysis of the C-Q relationship revealed consistent positive slopes across all months and years, indicating transport limitation (Fig. 3a). A pronounced seasonal trend in slope was observed throughout the study period. From May to November, the slope exhibited a consistent increase. In April, substantial variation in slopes was observed, primarily driven by minimal flow changes in most years. Occasional outliers were noted in August 2019, and November 2020 and 2021; but these were attributable to minimal range in flow in those

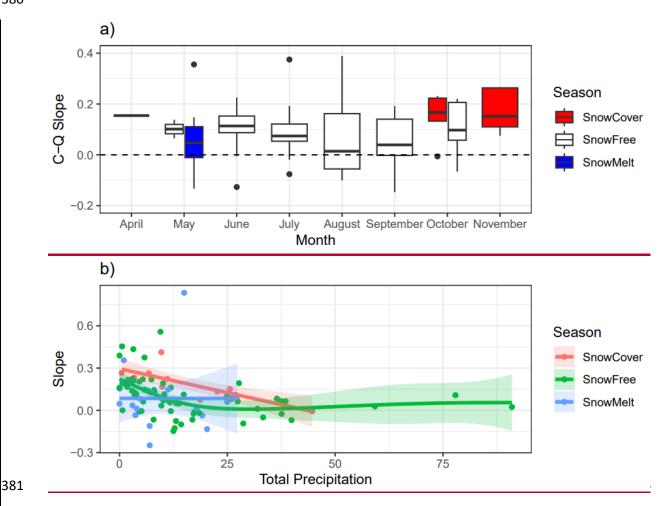
months. Notably, the variation between years was relatively small and generally smaller 355 than the month-to-month differences. The coefficient of variance data shows strong 356 357 seasonal and between years differences in variation of the DOC data (Fig. 3b). The largest 358 variation of DOC between years occurred during April and May, while in the summer months of June to August, variation was continuously the lowest, before subsequently 359 360 increasing again in the Autumn months. 361 In contrast, when considering events only, the C-Q slope showed less pronounced seasonal 362 variation (Fig. 4a). No significant differences were found between months ($\frac{df = 7}{f}$) F = 0.77, P \Rightarrow 0.6205) or seasons (df = 2, F = 1.54, P \Rightarrow 0.2205), although the slope during snow cover 363 exhibited slightly higher values compared to other months. Notably, non-linear relationships 364 365 emerged between the C-Q slope and 7-day antecedent precipitation for flow events (Fig. 366 4b). During the snow-free season, the slope was significantly negatively correlated with 367 antecedent precipitation up to approximately 20 mm ($R^2 = 0.26$, P = < 0.0006001), beyond which the slope relationship plateaued around 0 despite increasing antecedent 368 precipitation. A similar significant relationship was observed during the snow cover season 369 $(R^2 = 0.57, P < 0.0041)$. However, a no significant relationship was observed during the 370 snowmelt season ($R^2 = 0.00$, P = 0.99 > 0.05). Interestingly, the C-Q slope consistently 371 372 exhibited higher values during the snow cover season compared to the snow-free season.

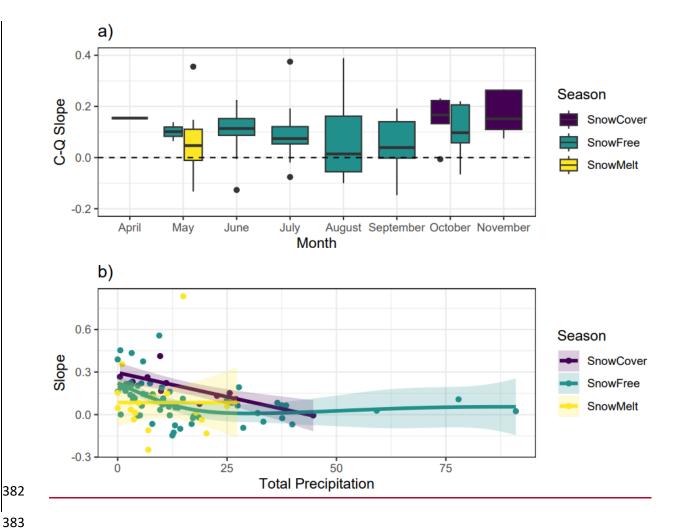




376

377





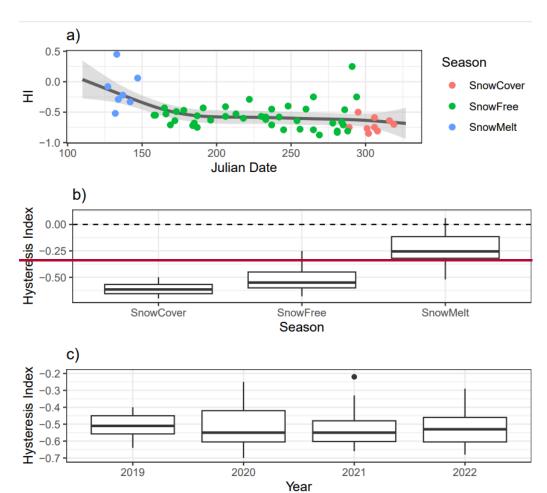
<u>Figure 4 – C-Q</u> slope analysis for individual events. A) Boxplot of C-Q slope for events by month, b) Relationship of slope of C-Q relationship with 7-day antecedent precipitation. Shading shows the standard error. Dot colours show season of event, and the line shows the fitted General Additive Model.

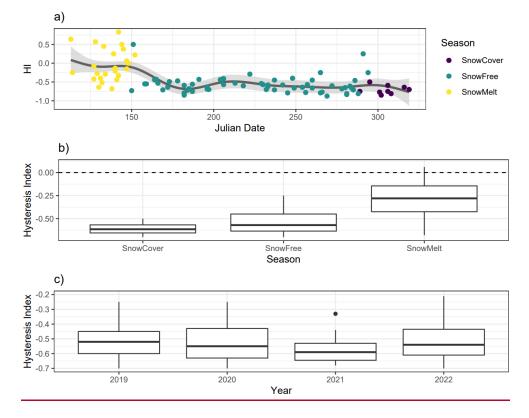
Hysteresis patterns

In the Hysteresis analysis, the HI exhibited significant ($R^2 = 0.4128$, P = < 0.00010.001) and distinct seasonal patterns (Fig. 5a). During the snowmelt season, HI values were generally highest, ranging from postiveweakly positive to weakly negative. However, as the season progressed and transitioned into the snow-free season, HI values showed a rapid decline and remained relatively consistent around -0.5. Throughout the snow cover season, HI exhibited a relatively stable pattern. Notably, a single positive outlier with an HI value of 0.26 was observed during the snow-free season, which can be attributed to a rare event characterized by heavy early snowfall followed by subsequent rainfall.

Significant differences were found between the snowmelt season and snow free season (\underline{t} ∓ = $\underline{7.755.15}$, P =< < 0.0010.001), and the snowmelt season and snow cover season (\underline{t} ∓ = 5.9846, P < 0.0011; Fig. 5b), indicating distinct hysteresis patterns during different periods. However, no significant difference was observed between the snow cover season and the snow-free season (\underline{t} ∓ = 1.3176, P = 0.38>0.05), suggesting similar hysteresis behaviour during these periods. Furthermore, there were no significant differences in HI between different years of the study ($\underline{df} = 4$, F = 0.8751, P => 0.4805; Fig. 5c), indicating consistent hysteresis patterns across the study duration.







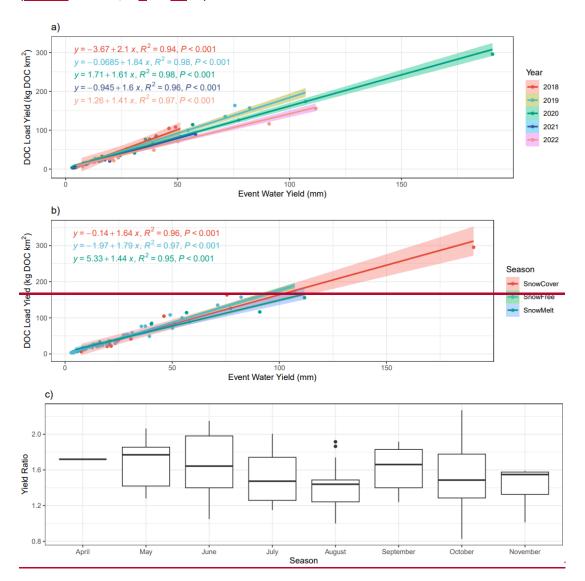
<u>Figure 5 –</u> a) Time series of Hysteresis Index against Julian Date with the fitted general additive model. Dot colours show seasons. Shading shows the standard error of the predictions from the general additive model B) Boxplot showing Hysteresis Index variation by season. C) Boxplot showing Hysteresis Index variation by year.

3.3 DOC load and event water yields relationships

The analysis of event yield revealed significant inter-annual variations in the relationship between DOC load yield and Event Water Yield (Fig. 6a; df = 3, F = 9.707.95, P < 0.0001). Specifically, the regressions for 2018 and for 2019 was significantly steeper than 2020 (2018 -2020: T = 3.04, P < 0.05 and 2019 - 2020: T = 3.3524, P = 0.0075) and 2022 (2018 -2022: T = 4.10, P < 0.01; T = 2019 - 2022: T = 5.3819, T = 0.0001), while 2020 was also significantly steeper than 2022 (T = 2.77, T = 0.035), indicating differences in the transport and source dynamics between these years. Additionally, significant differences were observed between seasons (T = 2.71), T = 0.001), where the snowfree season had a significantly higher regression than the snowmelt season (T = 3.77), T = 0.0008). However, no significant differences were observed between the seasons during the study (T = 0.27), T > 0.05; Fig. 6b).

Across all years and seasons, the relationship between DOC load yield and Event Water Yield $\frac{\text{were}}{\text{remained}}$ strongly linear (all P = < 0.001; R² = 0.961 - 0.98). This suggests a consistent

and predictable relationship between the amount of <u>DOC dissolved organic carbon</u> and event water yield. Furthermore, the analysis of the yield ratio across months showed no apparent seasonal trends (Fig. 6c), with no significant differences observed between months $(\underline{df} = 7, F = 1.07; P \Rightarrow 0.3805)$.



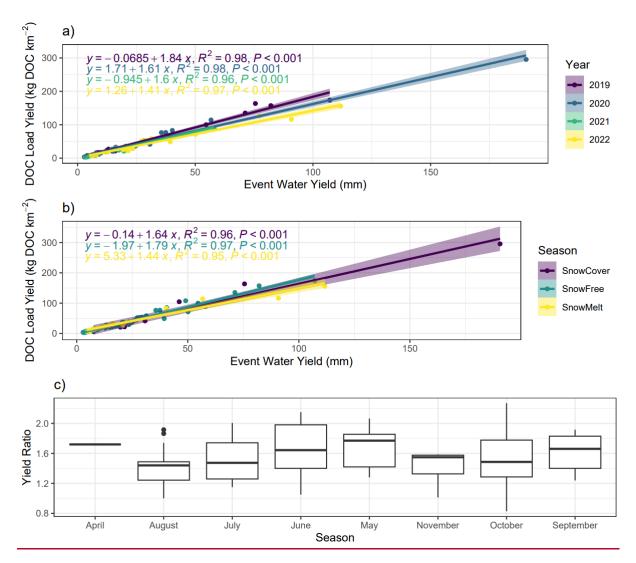


Figure 6 – Event yield analysis figures showing a) Linear regression of DOC load yield vs Event Water Yield separated by year, b) Linear regression of DOC load yield vs Event Water Yield separated by season, c) Boxplot of yield ratio for different months in study.

Additionally, DOC load yield vs event water yield separated by yield only featuring events with event water yield <50 mm (i.e. removing extreme events) is featured in Supplementary Figure 2.

3.4 Predictors of Seasonal Variation

During the snowmelt season (Table 2a), the hydrometeorological predictors did not account for a significant amount of variation. Maximum discharge emerged as the most important predictor for both the Maximum DOC and C-Q slope models, but the predictive value of these models was relatively low (19.81% and 10.52% of variance explained, respectively). In contrast, during the snow-free season (Table 2b), the predictors explained a relatively high amount of variance (55.2%) in the Maximum DOC model, with maximum discharge identified as the most important predictor (node purity = 50.19). However, for the models of

DOC percentage change and yield ratio, 7-day antecedent precipitation was found to be the most important predictor, although the predictive value of these models was weak (17.68% and 11.67% of variance explained, respectively).

For the snow cover season (Table 2c), maximum discharge remained an important predictor for the Maximum DOC model. However, for the C-Q slope model, average water temperature and event rainfall emerged as the strongest predictors. Both the Maximum DOC and C-Q slope models showed moderate explanatory capability during the snow cover season, explaining 34.822% and 32.6555% of the variance, respectively.

<u>Table 2 —</u> Random Forest regression prediction results for target variables for a) Snow Melt Events, b) Snow Free Events, and c) Snow Cover Events. The predictor abbreviations are as follows: MaxDis = Maximum Discharge, AvgWTemp = Average Water Temperature, AvgATemp = Average Air Temperature, AntPre = 7-day antecedent precipitation, and EventPre = Total Event Precipitation. The target variables were Maximum DOC value in events (MaxDOC), the percentage DOC changed from its starting value (DOC Change), the C-Q slope of events (Slope), the Hysteresis Index (HI), and the Yield Ratio (Yield Ratio). The value in the predictors column represents the node purity. Additionally, the table presents the variance explained (%var) and the mean of squared residuals for each model (Res Mean). NS = Not significant.

			a) Snov	v Melt			
	Predictors					Model	
Target	MaxDis	AvgW	AvgA	AntPre	EventPre	%Var	Res
		Temp	Temp				Mean
MaxDOC	3.18	2.80	2.70	2.15	1.06	19.81	0.61
DOC						NS	
Change							
Slope	0.227	0.14	0.15	0.07	0.04	10.52	0.04
Yield						NS	
Ratio							
			b) Snov	v Free			
		Predictors Model					odel
Target	MaxDis	AvgW	AvgA	AntPre	EventPre	%Var	Res
		Temp	Temp				Mean
MaxDOC	50.19	17.45	15.12	21.51	30.21	55.2	1.04
DOC	6712.51	5572.31	5767.61	9270.8	6113.33	17.68	523.9
Change							
Slope						NS	
Yield	1.06	0.95	0.92	1.17	0.96	11.67	0.08
Ratio							
	•	•	c) Snow	Cover	•	•	•
			Predictor	·s		М	odel

Target	MaxDis	AvgW	AvgA	AntPre	EventPre	%Var	Res
		Temp	Temp				Mean
MaxDOC	1069.83	1035.79	885.8	585.89	531.53	34.82	285.6
DOC						NS	
Change							
Slope	0.01	0.02	0.01	0.01	0.02	32.55	0.01
Yield						NS	
Ratio							

464

465

466

467

468

469

470

471

472

473

474

475

476

477

478

479

480

481

482

483

484

485

486

487

488

489

4.0 Discussion

4.1 Seasonal Variation in DOC Transport Processes

Distinct seasonal variations were evident in the DOC transport processes, shedding light on their changing characteristics during different periods. Notably, the snowmelt season exhibited the lowest C-Q slope (Fig. 3a), albeit still positive, indicating a relatively lower degree of transport limitation compared to other seasons (Gómez-Gener et al., 2021). This can be attributed to the limited availability of sources during the snowmelt season (Ruckhaus et al., 2023; Shogren et al., 2021). The theory of less source availability during snowmelt is further supported by fact that the regression between snowmelt DOC load yield and event water yield (Fig. 6b) was significantly lower compared to the snow free period. This suggests during snow melt there is less DOC transported per unit of water, possibly reflecting the reduced amount of DOC sources in the snowmelt season compared to the snow free period (Shatilla et al., 2023; Vaughan et al., 2017).-During the snowmelt, isotope separation indicated approximately 60% of the stream water is comprised of event water, i.e., the melting snowpack (Noor et al., 2023)(Noor et al in review). The onset of snowmelt is characterized by more rapid melting in the peatland compared to the hillslopes, while surface pathways dominate and facilitate rapid DOC transport compared to later in the year (Laudon et al., 2004). This observation is further supported by the high (positive) HI values during the snowmelt season, indicating the connectivity of new near-stream sources and the rapid flushing of DOC from the catchment during this period (Croghan et al., 2023; Shatilla et al., 2023)(Croghan et al., 2023). However, when exclusively examining event flows rather than encompassing all flow conditions (Fig. 4a), no significant disparity was observed between snowmelt conditions and other months. In contrast, C-Q slope values exhibited a general reduction across all months, when compared to slope values for all flow conditions. This reduction may suggest that transport limitation reduces, and increased source

490 depletion occurs relatively quickly after flow increases beyond baseflow conditions across all 491 seasons. 492 In contrast, the relationship between snowmelt DOC load yield and event water yield (Fig. 493 6b) did not exhibit significant variation compared to other seasons. This (Shatilla et al., 494 2023) suggests that although the transport processes differed, the overall amount of DOC relative to the unit of water remained relatively consistent. Thus, despite variations in 495 496 sources and transport mechanisms, a sustained supply of DOC was observed without deviating from linearity, implying a readily available reservoir of DOC in the catchment 497 during the snowmelt season. This was possibly because of an accumulation of DOC on the 498 top soil surface during winter (Billett et al., 2006; Dyson et al., 2011). In Pallas, soil frost is 499 500 relatively minimal in the peatlands and soil temperature remains above zero during early 501 winter which allows for the production of DOC (Marttila et al., 2021). Furthermore, in a previous study in Pallas, top soil water (up to 1 m) has been noted to be replaced two times 502 annually (Muhic et al., 2023) - firstly during the snow melt and then secondly during the 503 late summer. This also primes conditions for DOC transport from the soil column during 504 these periods, supporting our observations from the stream. 505 506 During the snow-free season, the C-Q slopes became consistently more transport-limited as 507 the season progressed (Fig. 3a), likely due to increased source availability as the catchment 508 gradually wetted up, activating pathways and connectivity (Birkel et al., 2017; Gómez-Gener 509 et al., 2021). Additionally, enhanced microbial activity and increased vegetation breakdown throughout the growing season could provide more abundant sources of DOC (Campbell et 510 al., 2022), and may also be an explanatory factor in the higher DOC yield during snow free 511 512 events compared to the snowmelt period. This interpretation is partially supported by the HI, which consistently revealed strong anti-clockwise hysteresis, indicative of likely distal 513 514 sources and slow DOC transport (Ducharme et al., 2021). However, the HI did not show 515 significant seasonal variation across the snow-free season. Notably, a steeper linear 516 relationship between DOC yield and event yield was observed during the snow-free season 517 compared to the snowmelt season (Fig. 6b), suggesting a greater supply of DOC per unit of water during events (Vaughan et al., 2017). Furthermore, while maximum discharge 518 consistently influenced DOC dynamics in all seasons, antecedent precipitation emerged as 519 520 an important predictor during the snowmelt season, highlighting the role of prior rainfall in

supporting transport dynamics (Blaen et al., 2017; Tiefenbacher et al., 2021). For the C-Q slope (Fig. 3c), higher antecedent rainfall led to reduced transport limitation, suggesting the exhaustion of certain sources to some extent. Interestingly, the relationship was non-linear, and with high antecedent rainfall, no further change in the relationship was observed, possibly indicating that high antecedent rainfall enables the transport of new sources of DOC, preventing the system from becoming source limited, even under extremely high antecedent precipitation or large events. Surprisingly, the snow cover season (late October, November) exhibited the highest values for the C-Q slope, indicating that increasing source limitation did not occur despite the presence of snow cover (Fig. 3A), possibly resultant from due to the decay of organic matter providing a large source of DOCdominating after the end of the growing season. Interestingly, the C-Q slope was also consistently higher with antecedent rainfall during the snow cover season, compared to the snow free season. This suggests that antecedent rainfall had a lesser impact on reducing source supply during this period. The antecedent rainfall may also come as snow, and the snowmelt vs rainfall contribution to discharge in the early snow season are difficult to identify. One possible explanation is that the snow cover season begins in the hills and forests, where the snow depth is recorded (Kenttärova station Fig. 1), while the snow cover on the peatland occurs later (Croghan et al., 2023; Marttila et al., 2021). Consequently, during the snow cover season, the hillslopes, which likely contribute less carbon per unit of water, are cut off, while the carbon-enriched peatlands make an increased contribution to streamflow during events compared to other seasons (Gómez-Gener et al., 2021; Rosset et al., 2019). However, neither the HI nor yield analysis showed significant variation during the snow cover season. The use of spatially distributed hydrological models in future studies would be valuable in identifying source contributors and further investigating if the differences in source contributions during the snow cover season drive the observed variations in C-Q relationships (Ala-aho et al., 2018; Birkel et al., 2017). 4.2 Inter-Annual Variation in Transport Processes

521

522

523

524

525

526

527

528

529

530

531

532

533

534

535

536

537

538

539

540

541

542

543

544

545

546

547

548

549

550

551

Despite significant year-to-year variations in hydrometeorological conditions, including snow cover onset and snowmelt conditions, we found limited inter-annual variation in the C-Q slope and HI (Fig. 3-5), However, exceptions were noted in the shoulder months of April 552 and November, where variations in inter-annual transport metric values stemmed from the fact that, in certain years, minimal flow variation occurred due to the catchment remaining 553 554 in frozen conditions, whereas in other years, large events occurred during these months. 555 While there were some differences in C-Q slopes between years, the month-to-month 556 variation generally outweighed the year-to-year variation, suggesting a remarkable 557 consistency in the degree of seasonality in transport limitation throughout the study. This consistency implies activation of consistent sources and flow pathways from year to year 558 559 (Vaughan et al., 2017; Zarnetske et al., 2018; Shatilla et al., 2023)(Vaughan et al., 2017; 560 Zarnetske et al., 2018). Similarly, the HI values showed no discernible differences on an annual 561 basis, indicating flow path stability in this system (Lloyd et al., 2016b). Source activation and 562 transport processes have a strong seasonal pattern; however, the differences between 563 years may not have been pronounced enough to drive substantial changes, underscoring 564 the need for longer-term data series for a comprehensive understanding. 565 In contrast, the yield analysis revealed variations between years. Specifically, we observed steeper regressions for 2018 and 2019 compared to 2020 and 2022, and for 2020 relative to 566 2022, indicating a higher transport of DOC per unit of water during these years, however 567 when extreme events were removed from the analysis (Supplementary Figure 2), 568 569 differences between the years disappeared. Thus, though source activation processes do 570 not appear to be changing year on year, thethe relationship between DOC yield and event water yield appears to be consistent between years does, which highlights the need to 571 572 understand how changes in water source contribution drive changes in both processes and yield<u>with differences between years driven by differences in the extent of annual extreme</u> 573 574 events. While previous long-term studies have suggested that warmer years lead to 575 increased mobilization of DOC, possibly due to reduced snowpack duration which creates more potential for soil C to be mobilised and a greater potential breakdown of the humic 576 577 layer (Bowering et al., 2023, 2020), we did not find notable differences between years for 578 the amount of mobilization of DOC per unit of water, suggesting a strong consistency between the amount of DOC produced year on year, despite differing climatic conditions. 579 Possibly this is because although there were climatic differences between years, they were 580 581 not strong enough to drive differences in DOC production. Differences were instead driven by the extent of extreme events, thus the expected increase in occurrence and magnitude 582

of extreme rainfall events in the Arctic is likely to be a substantial driver of differences in DOC mobilization in the future (Beel et al., 2021; McCrystall et al., 2021)_-Although 2019 was not an exceptionally warmer year, we did observe a quicker onset of snowmelt peaks (Croghan et al., 2023). Consequently, years with rapid snowmelt onset may result in a greater mobilization of DOC per unit of water. In the longer term, differences in annual trends may be more apparent as the warming climate will also impact vegetation and peatland formation patterns (Sallinen et al., 2023), which eventually impact also flow paths, connectivity and DOC transport. Thus, highlighting the need to maintain critical environmental monitoring infrastructure in high latitudes.

5.0 Conclusions

583

584

585

586

587

588

589

590

591

592

593

594

595

596

597

598

599

600

601

602

603

604

605

606

607

608

609

610

611

612

613

Our study provides valuable insights into the seasonal and inter-annual variations in DOC transport processes in the Arctic, stressing the need for comprehensive monitoring across all seasons. By examining various transport metrics, we observed distinct patterns that enhance our understanding of carbon dynamics in Arctic ecosystems. The observed seasonal variations in C-Q slopes indicate a progressive increase in transport limitation as the year progresses from snowmelt to snow-free season to snow-covered season due to increased source supply. The decline in hysteresis index after the snowmelt season highlights the rapid flushing of DOC from the catchment during this period. Importantly, the relationship between DOC yield and event water yield remained consistent across seasons, suggesting a stable supply of DOC per unit of water. However, high-resolution DOC monitoring is needed for improvingto unravel seasonal variability in DOC storage and transport process and responses to extreme events-understanding. Interestingly, despite significant year-to-year variations in hydrometeorological conditions, the intra-annual variation in transport processes was relatively low. This suggests a remarkable consistency in the activation and deactivation of sources and flow pathways over the study period. However, longer-term records are necessary to fully comprehend the impacts of climate change on DOC transport processes as headwater are anticipated to warm and experienced greater and more regular <u>extreme events, which will cause shits in</u> water sources and paths shift. Our findings emphasize the vulnerability sensitivity of DOC transport processes to change with changing snow and snowmelt seasonality in response to climate change. Our study highlights the importance of long-term monitoring to assess the long-term impacts on DOC

614	transport. To further enhance our understanding, future research should focus on better
615	understanding how DOM compositional changes impact DOC fate in headwater catchments,
616	establishingand establishing causal relationships between transport metrics, in-stream
617	<u>processing</u> and <u>empirical</u> indicators of sources and transport <u>processes</u> <u>pathways. A</u>
618	promising avenue for further research involves, integrating high-resolution stable water
619	isotope monitoring and spatially distributed hydrological modelling with in-situ DOC
620	monitoring of quantity and quality (e.g. combined fluorescence and absorbance
621	measurements)gThis work contributes to advancing our knowledge of DOC transport
622	processes in Arctic ecosystems, providing valuable information for informed decision-
623	making and effective management of these fragile environments in the face of climate
624	change.
625	Data Availability
626	Data supporting this study are available from the corresponding author upon request.
627	<u>Author Contribution</u>
628 629 630	Conceptualization: DC, HM, PAA, KK, DMH. Formal Analysis: DC, Funding Acquisition: HM, JW, BK, Investigation: DC, Resources: HM, BK, JW, JV, Visualization: DC, Writing – original draft preparation: DC, Writing – review & editing: DC, PAA, JW, KRM, KK, DMH, JV, BK, HM.
631	Competing Interests
632	The authors declare that they have no conflict of interest.
633	<u>Acknowledgements</u>
634 635 636 637 638	The study was supported by the Maa-ja Vesitekniikan Tuki ry, the K. H. Renlund Foundation, the Academy of Finland (projects: 316349, 316014, 308511, 318930, 312559, and 337552), the Strategic Research Council, JMW's UArctic Research Chairship, and the University of Oulu Kvantum Institute. The study is part of the activities of the National Freshwater Competence Centre (FWCC).
640	References
641 642 643 644	Ala-aho, P., Soulsby, C., Pokrovsky, O. S., Kirpotin, S. N., Karlsson, J., Serikova, S., Vorobyev, S. N., Manasypov, R. M., Loiko, S., and Tetzlaff, D.: Using stable isotopes to assess surface water source dynamics and hydrological connectivity in a high-latitude wetland and permafrost influenced landscape, Journal of Hydrology, 556, 279–293, https://doi.org/10.1016/J.JHYDROL.2017.11.024,

- Anderson, L. E., DeMont, I., Dunnington, D. D., Bjorndahl, P., Redden, D. J., Brophy, M. J., and
- 647 Gagnon, G. A.: A review of long-term change in surface water natural organic matter concentration
- 648 in the northern hemisphere and the implications for drinking water treatment, Science of The Total
- 649 Environment, 858, 159699, https://doi.org/10.1016/j.scitotenv.2022.159699, 2023.
- Argerich, A., Haggerty, R., Johnson, S. L., Wondzell, S. M., Dosch, N., Corson-Rikert, H., Ashkenas, L.
- R., Pennington, R., and Thomas, C. K.: Comprehensive multiyear carbon budget of a temperate
- headwater stream, Journal of Geophysical Research: Biogeosciences, 121, 1306–1315,
- 653 https://doi.org/10.1002/2015JG003050, 2016.
- 654 Beel, C. R., Heslop, J. K., Orwin, J. F., Pope, M. A., Schevers, A. J., Hung, J. K. Y., Lafrenière, M. J., and
- 655 Lamoureux, S. F.: Emerging dominance of summer rainfall driving High Arctic terrestrial-aquatic
- 656 connectivity, Nature Communications, 12, 1–9, https://doi.org/10.1038/s41467-021-21759-3, 2021.
- 657 Billett, M. F., Deacon, C. M., Palmer, S. M., Dawson, J. J. C., and Hope, D.: Connecting organic carbon
- in stream water and soils in a peatland catchment, Journal of Geophysical Research: Biogeosciences,
- 659 111, https://doi.org/10.1029/2005JG000065, 2006.
- Bintanja, R. and Andry, O.: Towards a rain-dominated Arctic, Nature Climate Change, 7, 263–267,
- https://doi.org/10.1038/nclimate3240, 2017.
- Birkel, C., Broder, T., and Biester, H.: Nonlinear and threshold-dominated runoff generation controls
- 663 DOC export in a small peat catchment, Journal of Geophysical Research: Biogeosciences, 122, 498–
- 664 513, https://doi.org/10.1002/2016JG003621, 2017.
- 665 Blaen, P. J., Khamis, K., Lloyd, C. E. M., Bradley, C., Hannah, D., and Krause, S.: Real-time monitoring
- 666 of nutrients and dissolved organic matter in rivers: Capturing event dynamics, technological
- opportunities and future directions, Science of The Total Environment, 569–570, 647–660,
- 668 https://doi.org/10.1016/J.SCITOTENV.2016.06.116, 2016.
- Blaen, P. J., Khamis, K., Lloyd, C., Comer-Warner, S., Ciocca, F., Thomas, R. M., MacKenzie, A. R., and
- 670 Krause, S.: High-frequency monitoring of catchment nutrient exports reveals highly variable storm
- 671 event responses and dynamic source zone activation, Journal of Geophysical Research:
- 672 Biogeosciences, 122, 2265–2281, https://doi.org/10.1002/2017JG003904, 2017.
- Bokhorst, S., Pedersen, S. H., Brucker, L., Anisimov, O., Bjerke, J. W., Brown, R. D., Ehrich, D., Essery,
- R. L. H., Heilig, A., Ingvander, S., Johansson, C., Johansson, M., Jónsdóttir, I. S., Inga, N., Luojus, K.,
- Macelloni, G., Mariash, H., McLennan, D., Rosqvist, G. N., Sato, A., Savela, H., Schneebeli, M.,
- 676 Sokolov, A., Sokratov, S. A., Terzago, S., Vikhamar-Schuler, D., Williamson, S., Qiu, Y., and Callaghan,
- 677 T. V.: Changing Arctic snow cover: A review of recent developments and assessment of future needs
- for observations, modelling, and impacts, Ambio, 45, 516–537, https://doi.org/10.1007/s13280-016-
- 679 0770-0, 2016.
- Bowering, K. L., Edwards, K. A., Prestegaard, K., Zhu, X., and Ziegler, S. E.: Dissolved organic carbon
- 681 mobilized from organic horizons of mature and harvested black spruce plots in a mesic boreal
- 682 region, Biogeosciences, 17, 581–595, https://doi.org/10.5194/bg-17-581-2020, 2020.
- Bowering, K. L., Edwards, K. A., Wiersma, Y. F., Billings, S. A., Warren, J., Skinner, A., and Ziegler, S. E.:
- Dissolved Organic Carbon Mobilization Across a Climate Transect of Mesic Boreal Forests Is
- 685 Explained by Air Temperature and Snowpack Duration, Ecosystems, 26, 55–71,
- 686 https://doi.org/10.1007/s10021-022-00741-0, 2023.

- Bring, A., Fedorova, I., Dibike, Y., Hinzman, L., Mård, J., Mernild, S. H., Prowse, T., Semenova, O.,
- 688 Stuefer, S. L., and Woo, M.-K.: Arctic terrestrial hydrology: A synthesis of processes, regional effects,
- and research challenges, Journal of Geophysical Research: Biogeosciences, 121, 621–649,
- 690 https://doi.org/10.1002/2015JG003131, 2016.
- 691 Bruhwiler, L., Parmentier, F. J. W., Crill, P., Leonard, M., and Palmer, P. I.: The Arctic Carbon Cycle
- and Its Response to Changing Climate, Current Climate Change Reports, 7, 14–34,
- 693 https://doi.org/10.1007/s40641-020-00169-5, 2021.
- 694 Campbell, T. P., Ulrich, D. E. M., Toyoda, J., Thompson, J., Munsky, B., Albright, M. B. N., Bailey, V. L.,
- 695 Tfaily, M. M., and Dunbar, J.: Microbial Communities Influence Soil Dissolved Organic Carbon
- 696 Concentration by Altering Metabolite Composition, Frontiers in Microbiology, 12, 2022.
- 697 Campeau, A. and del Giorgio, P. A.: Patterns in CH4 and CO2 concentrations across boreal rivers:
- 698 Major drivers and implications for fluvial greenhouse emissions under climate change scenarios,
- 699 Global Change Biology, 20, 1075–1088, https://doi.org/10.1111/gcb.12479, 2014.
- 700 Croghan, D., Ala-Aho, P., Lohila, A., Welker, J., Vuorenmaa, J., Kløve, B., Mustonen, K.-R., Aurela, M.,
- and Marttila, H.: Coupling of Water-Carbon Interactions During Snowmelt in an Arctic Finland
- 702 Catchment, Water Resources Research, 59, e2022WR032892,
- 703 https://doi.org/10.1029/2022WR032892, 2023.
- 704 Csank, A. Z., Czimczik, C. I., Xu, X., and Welker, J. M.: Seasonal Patterns of Riverine Carbon Sources
- and Export in NW Greenland, Journal of Geophysical Research: Biogeosciences, 124, 840–856,
- 706 https://doi.org/10.1029/2018JG004895, 2019.
- Day, J. J. and Hodges, K. I.: Growing Land-Sea Temperature Contrast and the Intensification of Arctic
- 708 Cyclones, Geophysical Research Letters, 45, 3673–3681, https://doi.org/10.1029/2018GL077587,
- 709 2018.
- 710 Dick, J. J., Tetzlaff, D., Birkel, C., and Soulsby, C.: Modelling landscape controls on dissolved organic
- 711 carbon sources and fluxes to streams, Biogeochemistry, 122, 361–374,
- 712 https://doi.org/10.1007/s10533-014-0046-3, 2015.
- 713 Downing, B. D., Pellerin, B. A., Bergamaschi, B. A., Saraceno, J. F., and Kraus, T. E. C.: Seeing the light:
- The effects of particles, dissolved materials, and temperature on in situ measurements of DOM
- 715 fluorescence in rivers and streams, Limnology and Oceanography: Methods, 10, 767–775,
- 716 https://doi.org/10.4319/lom.2012.10.767, 2012.
- Ducharme, A. A., Casson, N. J., Higgins, S. N., and Friesen-Hughes, K.: Hydrological and catchment
- controls on event-scale dissolved organic carbon dynamics in boreal headwater streams,
- 719 Hydrological Processes, 35, e14279, https://doi.org/10.1002/HYP.14279, 2021.
- 720 Dyson, K. E., Billett, M. F., Dinsmore, K. J., Harvey, F., Thomson, A. M., Piirainen, S., and Kortelainen,
- 721 P.: Release of aquatic carbon from two peatland catchments in E. Finland during the spring
- 722 snowmelt period, Biogeochemistry, 103, 125–142, https://doi.org/10.1007/s10533-010-9452-3,
- 723 2011.
- 724 Finlay, J., Neff, J., Zimov, S., Davydova, A., and Davydov, S.: Snowmelt dominance of dissolved
- organic carbon in high-latitute watersheds: Implications for characterization and flux of river DOC,
- 726 Geophysical Research Letters, 33, https://doi.org/10.1029/2006GL025754, 2006.

- 727 Fork, M. L., Sponseller, R. A., and Laudon, H.: Changing Source-Transport Dynamics Drive Differential
- 728 Browning Trends in a Boreal Stream Network, Water Resources Research, 56, e2019WR026336,
- 729 https://doi.org/10.1029/2019WR026336, 2020.
- 730 Godsey, S. E., Kirchner, J. W., and Clow, D. W.: Concentration-discharge relationships reflect
- 731 chemostatic characteristics of US catchments, Hydrological Processes, 23, 1844–1864,
- 732 https://doi.org/10.1002/hyp.7315, 2009.
- 733 Gómez-Gener, L., Hotchkiss, E. R., Laudon, H., and Sponseller, R. A.: Integrating Discharge-
- 734 Concentration Dynamics Across Carbon Forms in a Boreal Landscape, Water Resources Research, 57,
- 735 e2020WR028806, https://doi.org/10.1029/2020WR028806, 2021.
- 736 Koch, J. C., Sjöberg, Y., O'Donnell, J. A., Carey, M. P., Sullivan, P. F., and Terskaia, A.: Sensitivity of
- headwater streamflow to thawing permafrost and vegetation change in a warming Arctic, Environ.
- 738 Res. Lett., 17, 044074, https://doi.org/10.1088/1748-9326/ac5f2d, 2022.
- 739 Lambert, T., Pierson-Wickmann, A.-C., Gruau, G., Jaffrezic, A., Petitjean, P., Thibault, J. N., and
- 740 Jeanneau, L.: DOC sources and DOC transport pathways in a small headwater catchment as revealed
- by carbon isotope fluctuation during storm events, Biogeosciences, 11, 3043–3056,
- 742 https://doi.org/10.5194/bg-11-3043-2014, 2014.
- 743 Laudon, H., Köhler, S., and Buffam, I.: Seasonal TOC export from seven boreal catchments in
- 744 northern Sweden, Aquat. Sci., 66, 223–230, https://doi.org/10.1007/s00027-004-0700-2, 2004.
- Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and Köhler, S.:
- Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes,
- 747 Connectivity, and Scaling, Ecosystems, 14, 880–893, https://doi.org/10.1007/s10021-011-9452-8,
- 748 2011.
- Laudon, H., Spence, C., Buttle, J., Carey, S. K., McDonnell, J. J., McNamara, J. P., Soulsby, C., and
- 750 Tetzlaff, D.: Save northern high-latitude catchments, Nature Geoscience, 10, 324–325,
- 751 https://doi.org/10.1038/ngeo2947, 2017.
- Li, M., Peng, C., Zhang, K., Xu, L., Wang, J., Yang, Y., Li, P., Liu, Z., and He, N.: Headwater stream
- ecosystem: an important source of greenhouse gases to the atmosphere, Water Research, 190,
- 754 116738, https://doi.org/10.1016/J.WATRES.2020.116738, 2021.
- Liu, S., Wang, P., Huang, Q., Yu, J., Pozdniakov, S. P., and Kazak, E. S.: Seasonal and spatial variations
- 756 in riverine DOC exports in permafrost-dominated Arctic river basins, Journal of Hydrology, 612,
- 757 128060, https://doi.org/10.1016/j.jhydrol.2022.128060, 2022.
- 758 Lloyd, C. E. M., Freer, J. E., Johnes, P. J., and Collins, A. L.: Technical Note: Testing an improved index
- 759 for analysing storm discharge-concentration hysteresis, Hydrol. Earth Syst. Sci, 20, 625–632,
- 760 https://doi.org/10.5194/hess-20-625-2016, 2016a.
- 761 Lloyd, C. E. M., Freer, J. E., Johnes, P. J., and Collins, A. L.: Using hysteresis analysis of high-resolution
- 762 water quality monitoring data, including uncertainty, to infer controls on nutrient and sediment
- transfer in catchments, Science of The Total Environment, 543, 388–404,
- 764 https://doi.org/10.1016/J.SCITOTENV.2015.11.028, 2016b.
- 765 Marttila, H., Lohila, A., Ala-Aho, P., Noor, K., Welker, J. M., Croghan, D., Mustonen, K., Meriö, L.-J.,
- Autio, A., Muhic, F., Bailey, H., Aurela, M., Vuorenmaa, J., Penttilä, T., Hyöky, V., Klein, E., Kuzmin, A.,
- 767 Korpelainen, P., Kumpula, T., Rauhala, A., and Kløve, B.: Subarctic catchment water storage and

- 768 carbon cycling leading the way for future studies using integrated datasets at Pallas, Finland,
- 769 Hydrological Processes, https://doi.org/10.1002/HYP.14350, 2021.
- 770 Marttila, H., Laudon, H., Tallaksen, L. M., Jaramillo, F., Alfredsen, K., Ronkanen, A.-K., Kronvang, B.,
- 771 Lotsari, E., Kämäri, M., Ala-Aho, P., Nousu, J., Silander, J., Koivusalo, H., and Kløve, B.: Nordic
- hydrological frontier in the 21st century, Hydrology Research, 53, 700–715,
- 773 https://doi.org/10.2166/nh.2022.120, 2022.
- McCrystall, M. R., Stroeve, J., Serreze, M., Forbes, B. C., and Screen, J. A.: New climate models reveal
- faster and larger increases in Arctic precipitation than previously projected, Nat Commun, 12, 6765,
- 776 https://doi.org/10.1038/s41467-021-27031-y, 2021.
- 777 Mcguire, A. D., Anderson, L. G., Christensen, T. R., Scott, D., Laodong, G., Hayes, D. J., Martin, H.,
- Lorenson, T. D., Macdonald, R. W., and Nigel, R.: Sensitivity of the carbon cycle in the Arctic to
- 779 climate change, Ecological Monographs, 79, 523–555, https://doi.org/10.1890/08-2025.1, 2009.
- 780 McGuire, A. D., Lawrence, D. M., Koven, C., Clein, J. S., Burke, E., Chen, G., Jafarov, E., MacDougall, A.
- 781 H., Marchenko, S., Nicolsky, D., Peng, S., Rinke, A., Ciais, P., Gouttevin, I., Hayes, D. J., Ji, D., Krinner,
- 782 G., Moore, J. C., Romanovsky, V., Schädel, C., Schaefer, K., Schuur, E. A. G., and Zhuang, Q.:
- 783 Dependence of the evolution of carbon dynamics in the northern permafrost region on the
- 784 trajectory of climate change, Proceedings of the National Academy of Sciences of the United States
- 785 of America, 115, 3882–3887, https://doi.org/10.1073/pnas.1719903115, 2018.
- 786 Metcalfe, D. B., Hermans, T. D. G., Ahlstrand, J., Becker, M., Berggren, M., Björk, R. G., Björkman, M.
- P., Blok, D., Chaudhary, N., Chisholm, C., Classen, A. T., Hasselquist, N. J., Jonsson, M., Kristensen, J.
- A., Kumordzi, B. B., Lee, H., Mayor, J. R., Prevéy, J., Pantazatou, K., Rousk, J., Sponseller, R. A.,
- 789 Sundqvist, M. K., Tang, J., Uddling, J., Wallin, G., Zhang, W., Ahlström, A., Tenenbaum, D. E., and
- 790 Abdi, A. M.: Patchy field sampling biases understanding of climate change impacts across the Arctic,
- 791 Nature Ecology and Evolution, 2, 1443–1448, https://doi.org/10.1038/s41559-018-0612-5, 2018.
- 792 Noor, K., Marttila, H., Welker, J. M., Mustonen, K.-R., Kløve, B., and Ala-aho, P.: Snow sampling
- 793 strategy can bias estimation of meltwater fractions in isotope hydrograph separation, Journal of
- 794 Hydrology, 627, 130429, https://doi.org/10.1016/j.jhydrol.2023.130429, 2023.
- Osuch, M., Wawrzyniak, T., and Majerska, M.: Changes in hydrological regime in High Arctic non-
- 796 glaciated catchment in 1979–2020 using a multimodel approach, Advances in Climate Change
- 797 Research, 13, 517–530, https://doi.org/10.1016/j.accre.2022.05.001, 2022.
- 798 Pearson, R. G., Phillips, S. J., Loranty, M. M., Beck, P. S. A., Damoulas, T., Knight, S. J., and Goetz, S. J.:
- 799 Shifts in Arctic vegetation and associated feedbacks under climate change, Nature Climate Change,
- 800 3, 673–677, https://doi.org/10.1038/nclimate1858, 2013.
- Pedron, S. A., Jespersen, R. G., Xu, X., Khazindar, Y., Welker, J. M., and Czimczik, C. I.: More Snow
- Accelerates Legacy Carbon Emissions From Arctic Permafrost, AGU Advances, 4, e2023AV000942,
- 803 https://doi.org/10.1029/2023AV000942, 2023.
- Prokushkin, A. S., Pokrovsky, O. S., Shirokova, L. S., Korets, M. A., Viers, J., Prokushkin, S. G., Amon, R.
- 805 M. W., Guggenberger, G., and McDowell, W. H.: Sources and the flux pattern of dissolved carbon in
- rivers of the Yenisey basin draining the Central Siberian Plateau, Environmental Research Letters, 6,
- 807 45212–45226, https://doi.org/10.1088/1748-9326/6/4/045212, 2011.
- Pulliainen, J., Luojus, K., Derksen, C., Mudryk, L., Lemmetyinen, J., Salminen, M., Ikonen, J., Takala,
- 809 M., Cohen, J., Smolander, T., and Norberg, J.: Patterns and trends of Northern Hemisphere snow

- 810 mass from 1980 to 2018, Nature 2020 581:7808, 581, 294–298, https://doi.org/10.1038/s41586-
- 811 020-2258-0, 2020.
- 812 Rantanen, M., Karpechko, A. Y., Lipponen, A., Nordling, K., Hyvärinen, O., Ruosteenoja, K., Vihma, T.,
- and Laaksonen, A.: The Arctic has warmed nearly four times faster than the globe since 1979,
- 814 Commun Earth Environ, 3, 1–10, https://doi.org/10.1038/s43247-022-00498-3, 2022.
- 815 Räsänen, A., Manninen, T., Korkiakoski, M., Lohila, A., and Virtanen, T.: Predicting catchment-scale
- 816 methane fluxes with multi-source remote sensing, Landscape Ecology, 36, 1177–1195,
- 817 https://doi.org/10.1007/S10980-021-01194-X/FIGURES/4, 2021.
- 818 Rosset, T., Gandois, L., Le Roux, G., Teisserenc, R., Durantez Jimenez, P., Camboulive, T., and Binet,
- 8.19 S.: Peatland Contribution to Stream Organic Carbon Exports From a Montane Watershed, Journal of
- 820 Geophysical Research: Biogeosciences, 124, 3448–3464, https://doi.org/10.1029/2019JG005142,
- 821 2019.
- 822 Ruckhaus, M., Seybold, E. C., Underwood, K. L., Stewart, B., Kincaid, D. W., Shanley, J. B., Li, L., and
- Perdrial, J. N.: Disentangling the responses of dissolved organic carbon and nitrogen concentrations
- to overlapping drivers in a northeastern United States forested watershed, Frontiers in Water, 5,
- 825 2023.
- 826 Sallinen, A., Akanegbu, J., Marttila, H., and Tahvanainen, T.: Recent and future hydrological trends of
- aapa mires across the boreal climate gradient, Journal of Hydrology, 617, 129022,
- 828 https://doi.org/10.1016/j.jhydrol.2022.129022, 2023.
- 829 Shatilla, N. J. and Carey, S. K.: Assessing inter-annual and seasonal patterns of DOC and DOM quality
- across a complex alpine watershed underlain by discontinuous permafrost in Yukon, Canada,
- 831 Hydrology and Earth System Sciences, 23, 3571–3591, https://doi.org/10.5194/hess-23-3571-2019,
- 832 2019.
- 833 Shatilla, N. J., Tang, W., and Carey, S. K.: Multi-year high-frequency sampling provides new runoff
- and biogeochemical insights in a discontinuous permafrost watershed, Hydrological Processes, 37,
- 835 e14898, https://doi.org/10.1002/hyp.14898, 2023.
- 836 Shogren, A. J., Zarnetske, J. P., Abbott, B. W., Iannucci, F., and Bowden, W. B.: We cannot shrug off
- the shoulder seasons: Addressing knowledge and data gaps in an Arctic headwater, Environmental
- 838 Research Letters, 15, 104027, https://doi.org/10.1088/1748-9326/ab9d3c, 2020.
- Shogren, A. J., Zarnetske, J. P., Abbott, B. W., Iannucci, F., Medvedeff, A., Cairns, S., Duda, M. J., and
- 840 Bowden, W. B.: Arctic concentration—discharge relationships for dissolved organic carbon and nitrate
- vary with landscape and season, Limnology and Oceanography, 66, S197–S215,
- 842 https://doi.org/10.1002/lno.11682, 2021.
- 843 Speetjens, N. J., Tanski, G., Martin, V., Wagner, J., Richter, A., Hugelius, G., Boucher, C., Lodi, R.,
- 844 Knoblauch, C., Koch, B. P., Wünsch, U., Lantuit, H., and Vonk, J. E.: Dissolved organic matter
- characterization in soils and streams in a small coastal low-Arctic catchment, Biogeosciences, 19,
- 846 3073–3097, https://doi.org/10.5194/bg-19-3073-2022, 2022.
- Tan, A., Adam, J. C., and Lettenmaier, D. P.: Change in spring snowmelt timing in Eurasian Arctic
- rivers, Journal of Geophysical Research: Atmospheres, 116, D03101,
- 849 https://doi.org/10.1029/2010JD014337, 2011.

- 850 Tank, S. E., Striegl, R. G., McClelland, J. W., and Kokelj, S. V.: Multi-decadal increases in dissolved
- 851 organic carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic Ocean,
- 852 Environmental Research Letters, 11, 054015, https://doi.org/10.1088/1748-9326/11/5/054015,
- 853 2016.
- 854 Tiefenbacher, A., Weigelhofer, G., Klik, A., Mabit, L., Santner, J., Wenzel, W., and Strauss, P.:
- Antecedent soil moisture and rain intensity control pathways and quality of organic carbon exports
- 856 from arable land, CATENA, 202, 105297, https://doi.org/10.1016/j.catena.2021.105297, 2021.
- 857 Vaughan, M. C. H., Bowden, W. B., Shanley, J. B., Vermilyea, A., Sleeper, R., Gold, A. J., Pradhanang,
- 858 S. M., Inamdar, S. P., Levia, D. F., Andres, A. S., Birgand, F., and Schroth, A. W.: High-frequency
- 859 dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and
- loading in relation to land cover and seasonality, Water Resources Research, 53, 5345–5363,
- 861 https://doi.org/10.1002/2017WR020491, 2017.
- Vihma, T., Screen, J., Tjernström, M., Newton, B., Zhang, X., Popova, V., Deser, C., Holland, M., and
- 863 Prowse, T.: The atmospheric role in the Arctic water cycle: A review on processes, past and future
- changes, and their impacts, Journal of Geophysical Research: Biogeosciences, 121, 586–620,
- 865 https://doi.org/10.1002/2015JG003132, 2016.
- 866 Ward, A. S., Wondzell, S. M., Schmadel, N. M., and Herzog, S. P.: Climate Change Causes River
- Network Contraction and Disconnection in the H.J. Andrews Experimental Forest, Oregon, USA,
- 868 Frontiers in Water, 2, 2020.
- Williams, G. P.: Sediment concentration versus water discharge during single hydrologic events in
- 870 rivers, Journal of Hydrology, 111, 89–106, https://doi.org/10.1016/0022-1694(89)90254-0, 1989.
- de Wit, H. A., Valinia, S., Weyhenmeyer, G. A., Futter, M. N., Kortelainen, P., Austnes, K., Hessen, D.
- 872 O., Räike, A., Laudon, H., and Vuorenmaa, J.: Current Browning of Surface Waters Will Be Further
- Promoted by Wetter Climate, Environ. Sci. Technol. Lett., 3, 430–435,
- 874 https://doi.org/10.1021/acs.estlett.6b00396, 2016.
- Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., and Raymond, P. A.: Generality of Hydrologic
- 876 Transport Limitation of Watershed Organic Carbon Flux Across Ecoregions of the United States,
- 877 Geophysical Research Letters, 45, 11,702-11,711, https://doi.org/10.1029/2018GL080005, 2018.