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Seasonal and interannual Dissolved Organic Carbon transport process dynamics in a subarctic headwater catchment revealed by high-resolution measurements.

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Abstract

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 assess transport processes multiple methods 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 displays a strong seasonal trend, indicating increasing transport limitation each month after snowmelt begins; (b) the hysteresis index decreases post-snowmelt, signifying the influence of distal sources and DOC mobilization through slower pathways; and (c) interannual variations in these metrics are generally low, often smaller than month-to-month 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 seasonal variations is vital for evaluating how the carbon cycle will change in the future in Arctic ecosystems.

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

1. Introduction

The dynamics of Dissolved Organic Carbon (DOC) in Arctic catchments are undergoing profound transformations due to the impacts of climate change, recovery from acidification, 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 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 transport mechanisms (Liu et al., 2022). Climate change-induced alterations are occurring in permafrost extent (Koch et al., 2022), snowpack water storage (Bokhorst et al., 2016; Pulliainen et al., 2020), snowpack duration (Bowering et al., 2023), snowmelt timing (Tan et al., 2011), and hydrological seasonality (Osuch et al., 2022), which have been significantly 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 carbon cycles that are both climatically sensitive (Bintanja and Andry, 2017; Bruhwiler et al., 2021; Mcguire et al., 2009; Vihma et al., 2016).

DOC transport processes in the Arctic exhibit pronounced seasonality and are highly susceptible to change (Bowering et al., 2023; Csank et al., 2019; Shatilla and 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). 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., 2011; Finlay et al., 2006; Prokushkin et al., 2011). However, in the Arctic, climate change is reducing snow cover duration and increasing the fraction of precipitation in the liquid phase (Bintanja and Andry, 2017). Consequently, storm events are emerging as increasingly important mechanisms for the export of DOC from terrestrial catchments to streams (Day and Hodges, 2018; Speetjens et al., 2022). 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 DOC dynamics in the Arctic region (Bowering et al., 2020; Pearson et al., 2013). Additionally, while the significance of shoulder seasons (defined in the Arctic as the transitional period between the end of plant senescence and the freezing of the headwaters, and after the onset of thaw till the end of snowmelt) for DOC export has

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

been acknowledged in recent years, their characterization remains limited. Therefore, there is a pressing need for more extensive documentation to elucidate the influence of shifting climate on DOC dynamics in the Arctic (Shogren et al., 2020).

Headwater catchments play a crucial role in the transport of DOC into streams (Fork et al., 2020; Lambert et al., 2014). These catchments constitute approximately 90% of the total global stream length and serve as the primary connection for carbon transport between terrestrial landscapes and oceans (Argerich et al., 2016; Li et al., 2021). Allochthonous inputs into the stream, driven by rain and snowmelt events, dominate the dynamics of headwater 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 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, the seasonal dynamics of carbon transfer processes in headwater wetlands differ significantly depending on the season. During snowmelt, rapid superficial pathways are observed, which later evolve into more complex pathways in the landscape during the summer and autumn (Croghan et al., 2023; Laudon et al., 2011). Additionally, headwater 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 al., 2020). The increasing hydrological stochasticity in Arctic catchments (e.g. occurrence and magnitude of extremes) highlight the need to better understand inter-annual variability 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 essential to better understand their functioning and response to environmental changes, especially in high latitude conditions (Bruhwiler et al., 2021; Marttila et al., 2022, 2021).

To comprehensively investigate the transport processes of DOC across seasons, it is essential to employ high-resolution, long-term monitoring approaches (Shogren et al., 2020). This need is particularly pronounced in headwater environments, where the majority 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 the transport processes and characteristics associated with sudden episodic and unpredictable storm and snowmelt events, capturing the necessary resolutions for

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

improved process understanding (Blaen et al., 2016). Furthermore, higher-resolution data collection can facilitate the use of multiple analytical techniques, such as hysteresis analysis, 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 understanding of the impacts of climate change in Arctic regions (Metcalfe et al., 2018; Shogren et al., 2020). Additionally, high-frequency DOC measurements in the Arctic remain relatively rare, especially datasets that cover the shoulder seasons and encompass multi-year measurements for assessing inter-annual differences (Beel et al., 2021; Shogren et al., 2021). Hence, there is an urgent need to integrate high-frequency monitoring sites in subarctic, low Arctic, and high Arctic regions, particularly for evaluating the ongoing evolution of the Arctic carbon and water cycles (Laudon et al., 2017; Marttila et al., 2021; Pedron et al., 2023).

To address key knowledge gaps in Arctic headwater DOC transport, our study focused on a peatland-influenced headwater catchment located in subarctic, Northern Finland (68°N), with the overarching aim to identify the primary drivers of transport processes of DOC and explore their seasonal and interannual dynamics. We utilized a unique four-year high-resolution dataset of DOC, allowing us to conduct high-frequency analyses. To enhance understanding of DOC transport processes in the Arctic and their implications for future dynamics the following interlinked research questions were addressed:

1) How do the main drivers of DOC transport processes vary across different seasons?
2) To what extent do DOC transport processes and their drivers vary inter-annually?

2.0 Methods

2.1 Site Description

The research was conducted within the Lompolojänganoja catchment, also referred to as the Pallas catchment (Marttila et al., 2021), situated in a peatland-influenced headwater stream (Figure 1). This catchment is located in Northern Finland (68°02'N, 24°16'W) within the Pallas-Yllästunturi National Park. Encompassing a total area of 4.42 km^2, the Pallas catchment exhibits elevations ranging from 268 m to 375 m above sea level.

The stream location is strongly influenced by a peatland, which comprises fens, mires, paludified forest and floodplains. This peatland exerts significant control over the flow

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

dynamics within the catchment, contributing most of the flow at the headwater location (Marttila et al., 2021). Within the broader catchment area, coniferous forests account for 79% of the land classification, followed by mixed forests (9%) and peatbogs (8%).

The Pallas catchment is categorized as subarctic, characterized by long winters with substantial snowfall and short, rainy summers. Notably, despite its northern latitude, the catchment lacks a permafrost layer, making it one of the most northern research catchments without permafrost (Marttila et al., 2021). The mean annual rainfall in the catchment amounts to 521 mm, with 42% of that precipitation occurring as snowfall. Typically, snowmelt occurs towards the end of April or early May and concludes by late May 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).

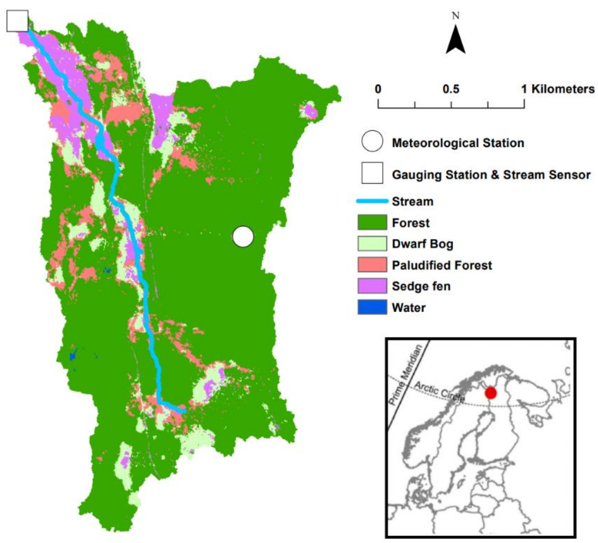


Figure 1 – Map of the study location (inset), catchment and measurement locations within the catchment. Classification of vegetation in the catchment was derived from (Räsänen et al., 2021)

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-

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

EXO3; Excitation 365 nm, Emission 480 nm) was deployed at the catchment outlet in the Lompolojänganoja 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 was further corrected for turbidity using the following equation:

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

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 anti-fouling 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).

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

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 an increase in flow, until there was no remaining snow cover at the Kenttärova site. The snow cover season referred to the period when snow cover was present and persisted until the subsequent snowmelt season. The snow free season referred to the period between the snowmelt and snow cover seasons. All analyses were performed using R in RStudio (version 2023.03.0).

To conduct event-based analysis, we extracted specific events from the dataset. Events 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; Vaughan et al., 2017). Baseflow was computed using a Lyne-Hollick baseflow filter 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 place during the snow-free period, and 11 events were observed within the snow cover period.

Concentration-Discharge (C-Q) analysis was performed to examine variations in transfer processes at seasonal scales. We calculated the slope (β) of the logarithmic relationship between DOC and streamflow (Q) for each year and each season of the study. The months of December to March were not included in the seasonal analysis as flow remained at baseflow during these months throughout the study. A positive slope ($\beta > 0$) suggests a transport-limited relationship, indicating that the concentration of DOC is primarily controlled by the transport processes. Conversely, a negative slope ($\beta < 0$) suggests a 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, indicating no significant change in DOC concentration with variations in streamflow. C-Q slopes have been widely employed to assess the extent of transport or source limitation in catchments (Godsey et al., 2009; Zarnetske et al., 2018).

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

Hysteresis analysis was conducted to gain insights into flow pathways and transport processes at event scale. The Modified Hysteresis Index (HI) was calculated following Lloyd et al., (2016b). Only single-peak events, where the flow returned to at or near baseflow, were selected for analysis. 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 km^2) 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). Differences in the linear regression relationships signify variations in transport and source 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 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 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 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

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

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.

3.0 Results

3.1 Time Series

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

When considering the total annual cumulative DOC load averaged across the study (Fig. 2e; Table 1), the ~6 week snowmelt period contributed around 33.4% of the total annual DOC

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

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 ± Standard Deviation.

Measurement	Snow Cover	Snow Melt	Snow Free
Flow (L s-^{1} km^{2})	4.89 ± 4.06	34.38 ± 35.77	12.05 ± 10.90
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	4.62 ± 5.26	1.71 ± 1.98
Air Temperature (°C)	-6.74 ± 6.03	3.62 ± 5.37	9.51 ± 6.08
Water Temperature (°C)	0.18 ± 0.14	1.76 ± 3.14	9.31 ± 4.31
Turbidity (NTU)	0.91 ± 0.62	1.37 ± 0.88	0.77 ± 0.52

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

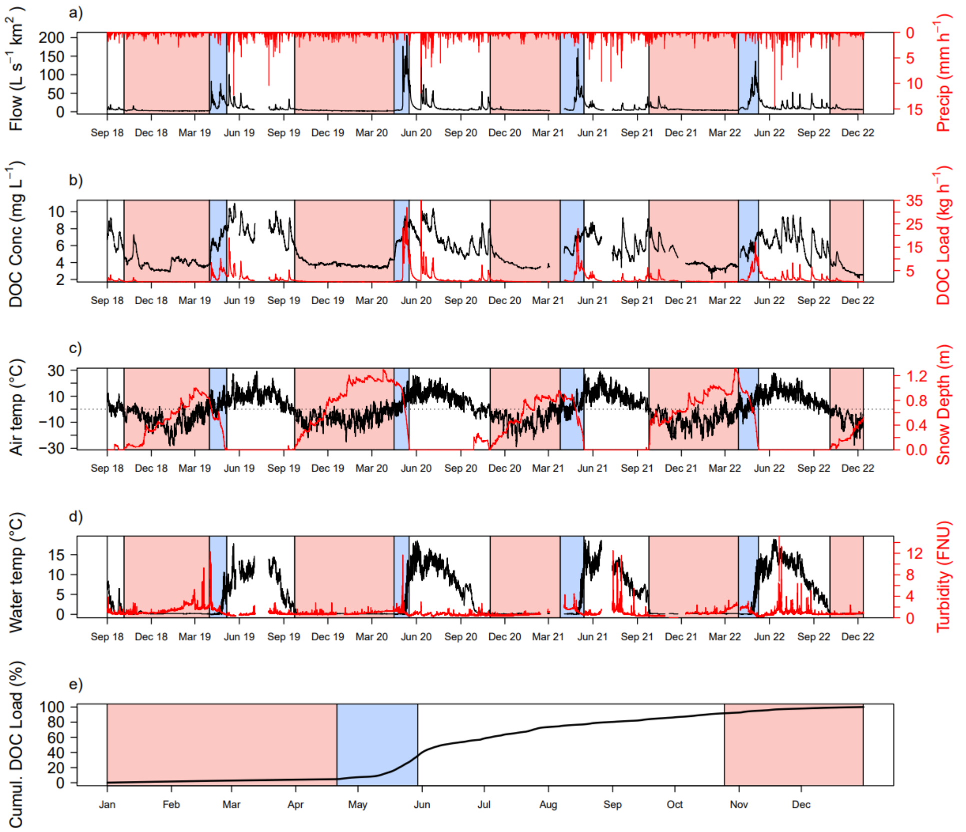


Figure 2 – Time series depicting: a) Flow (black) and Precipitation (red), b) DOC concentration (black) and DOC load (red), c) Air temperature (black) and snow depth (red), d) Water temperature (black) and Turbidity (red), and e) Average cumulative DOC load for the study period. The background shading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

3.2 Concentration-discharge (C-Q) relationships

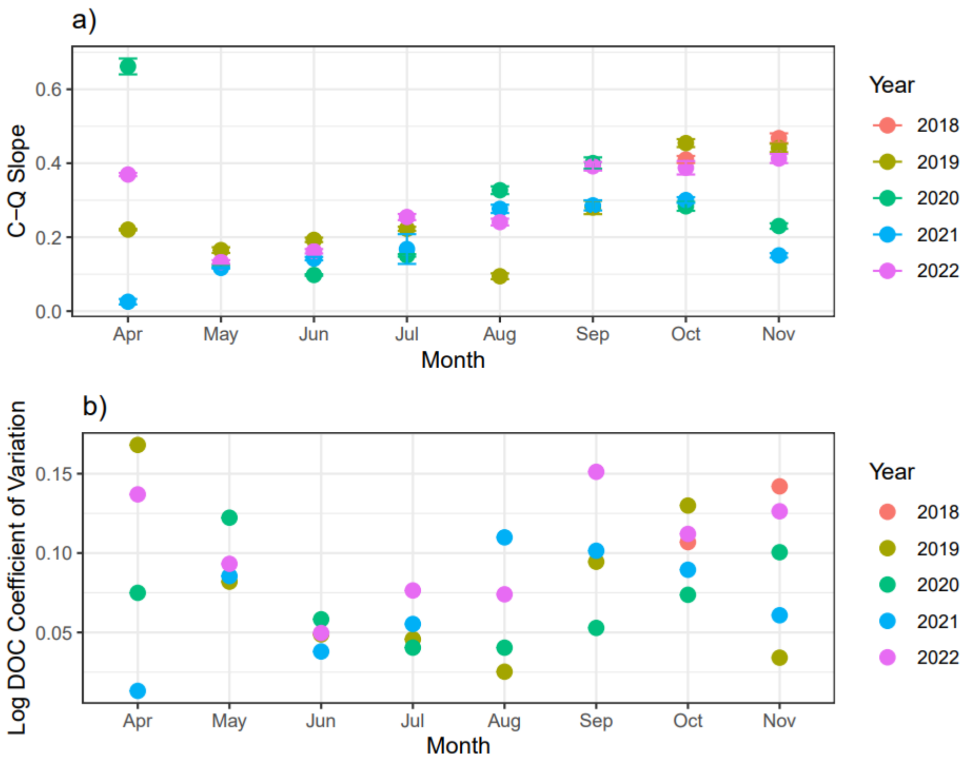
The analysis of the C-Q relationship revealed consistent positive slopes across all months and years, indicating transport limitation (Fig. 3a). A pronounced seasonal trend in slope was observed throughout the study period. From May to November, the slope exhibited a consistent increase. In April, substantial 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

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

months. Notably, the variation between years was relatively small and generally smaller than the month-to-month differences. The coefficient of variance data shows strong seasonal and between years differences in variation of the DOC data (Fig. 3b). The largest 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 increasing again in the Autumn months.

In contrast, when considering events only, the C-Q slope showed less pronounced seasonal variation (Fig. 4a). No significant differences were found between months ($F = 0.77$, $P > 0.05$) or seasons ($F = 1.54$, $P > 0.05$), although the slope during snow cover exhibited slightly higher values compared to other months. Notably, non-linear relationships emerged between the C-Q slope and 7-day antecedent precipitation for flow events (Fig. 4b). During the snow-free season, the slope was significantly negatively correlated with antecedent precipitation up to approximately 20 mm ($R^2 = 0.26$, $P < 0.001$), beyond which the slope relationship plateaued around 0 despite increasing antecedent precipitation. A similar significant relationship was observed during the snow cover season ($R^2 = 0.57$, $P < 0.01$). However, a no significant relationship was observed during the snowmelt season ($R^2 = 0.00$, $P > 0.05$). Interestingly, the C-Q slope consistently exhibited higher values during the snow cover season compared to the snow-free season.

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023



<u>Figure 3 –</u> a) All flow C-Q Slope Analysis. Each individual dot represents the slope of the C-Q relationship for the given month. B) All Log DOC coefficient of variation. Each individual dot represents the coefficient of variation for Log DOC for the given month. The year of the sample is shown by the colour of the dot.

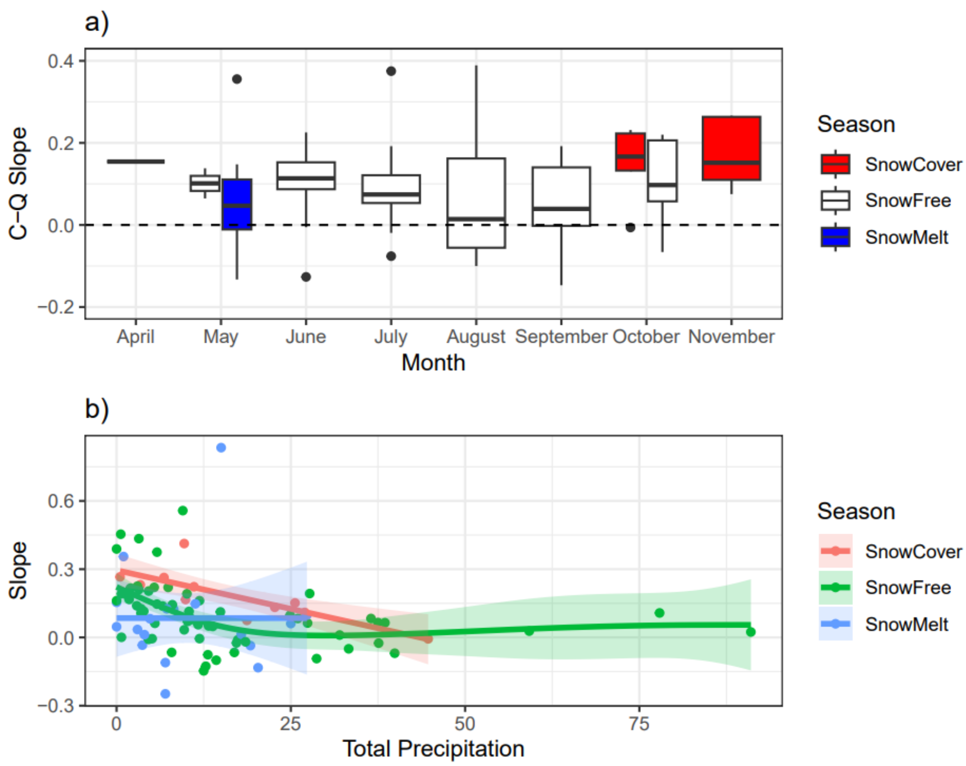


Figure 4 – C-Q slope analysis for individual events. A) Boxplot of C-Q slope for events by month, b) Relationship of slope of C-Q relationship with 7-day antecedent precipitation. Shading shows the standard error. Dot colours show season of event, and the line shows the fitted General Additive Model.

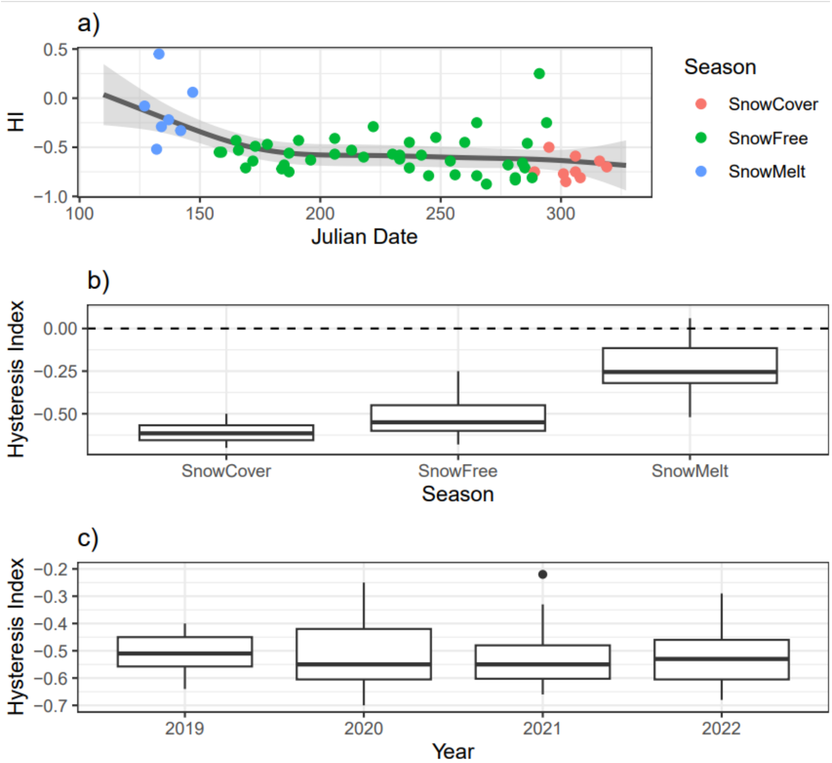
Hysteresis patterns

In the Hysteresis analysis, the HI exhibited significant (R^2 = 0.28, P < 0.001) and distinct seasonal patterns (Fig. 5a). During the snowmelt season, HI values were generally highest, ranging from weakly 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 (T = 5.15, P < 0.001), and the snowmelt season and snow cover season (T = 5.46, P < 0.01; Fig.

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

5b), indicating distinct hysteresis patterns during different periods. However, no significant difference was observed between the snow cover season and the snow-free season ($T = 1.76$, $P > 0.05$), suggesting similar hysteresis behaviour during these periods. Furthermore, there were no significant differences in HI between different years of the study ($F = 0.51$, $P > 0.05$; 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 <u>DOC load and event water yields relationships</u>

The analysis of event yield revealed significant inter-annual variations in the relationship between DOC load yield and Event Water Yield (Fig. 6a; $F = 7.95$, $P < 0.0001$). Specifically, the regressions for 2018 and 2019 was significantly steeper than 2020 (2018 – 2020: $T = 3.04$, $P < 0.05$ and 2019 – 2020: $T = 3.24$, $P < 0.05$) and 2022 (2018 – 2022: $T = 4.10$, $P < 0.01$;

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

2019 – 2022: T = 5.19, P < 0.0001), indicating differences in the transport and source dynamics between these years. However, no significant differences were observed between the seasons during the study (F = 0.27, P > 0.05; Fig. 6b).

Across all years and seasons, the relationship between DOC load yield and Event Water Yield remained strongly linear (all P < 0.001; R^2 = 0.91 - 0.98). This suggests a consistent and predictable relationship between the amount of dissolved organic carbon 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 (F = 1.07; P > 0.05).

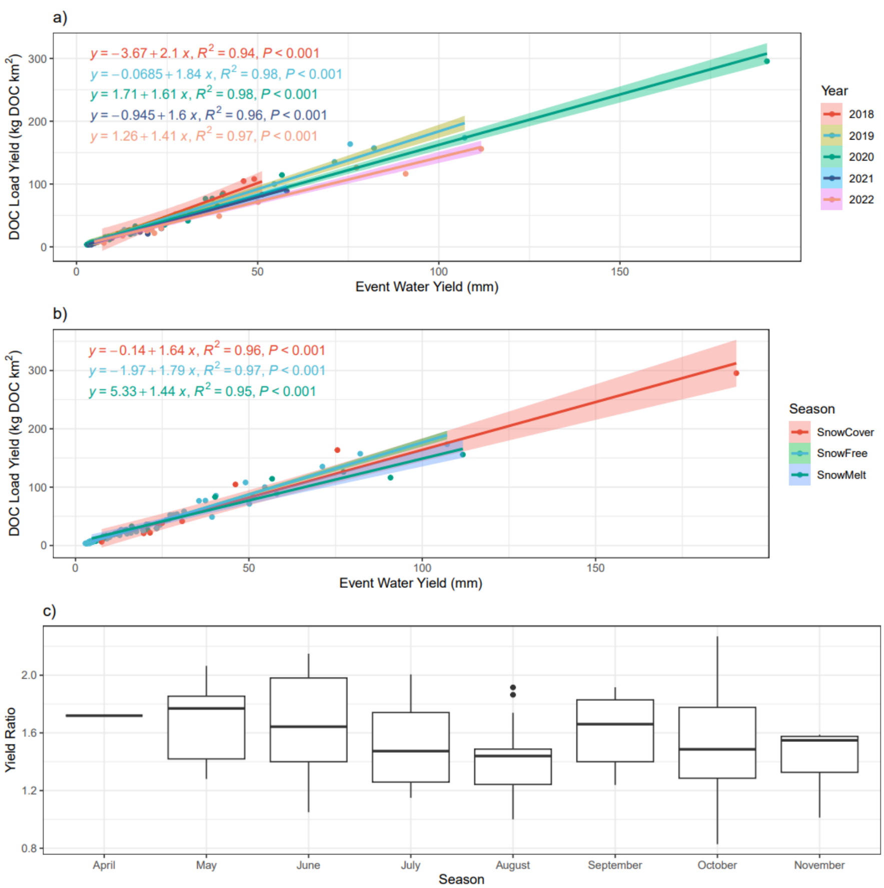


Figure 6 – Event yield analysis figures showing a) Linear regression of DOC load yield vs Event Water Yield separated by year, b) Linear regression of DOC load yield vs Event Water Yield separated by season, c) Boxplot of yield ratio for different months in study.

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

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 34.82% and 32.55% of the variance, respectively.

Table 2 – 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) Snow Melt							
	Predictors					**Model**	
Target	MaxDis	AvgW Temp	AvgA Temp	AntPre	EventPre	%Var	Res Mean
MaxDOC	**3.18**	2.80	2.70	2.15	1.06	19.81	0.61
DOC Change						NS	
Slope	**0.227**	0.14	0.15	0.07	0.04	10.52	0.04
Yield Ratio						NS	

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

b) Snow Free							
	Predictors					**Model**	
Target	MaxDis	AvgW Temp	AvgA Temp	AntPre	EventPre	%Var	Res Mean
MaxDOC	**50.19**	17.45	15.12	21.51	30.21	55.2	1.04
DOC Change	6712.51	5572.31	5767.61	**9270.8**	6113.33	17.68	523.9
Slope						NS	
Yield Ratio	1.06	0.95	0.92	**1.17**	0.96	11.67	0.08
c) Snow Cover							
	Predictors					**Model**	
Target	MaxDis	AvgW Temp	AvgA Temp	AntPre	EventPre	%Var	Res Mean
MaxDOC	**1069.83**	1035.79	885.8	585.89	531.53	34.82	285.6
DOC Change						NS	
Slope	0.01	**0.02**	0.01	0.01	**0.02**	32.55	0.01
Yield Ratio						NS	

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). During the snowmelt, approximately 60% of the stream water is comprised of event water, i.e., the melting snowpack (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).

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

In contrast, the relationship between snowmelt DOC load yield and event water yield (Fig. 6b) did not exhibit significant variation compared to other seasons. This 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 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 during the snowmelt season. This was possibly because of an accumulation of DOC on the top soil surface during winter (Billett et al., 2006; Dyson et al., 2011). In Pallas, soil frost is relatively minimal in the peatlands and soil temperature remains above zero during early 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 annually (Muhic et al., 2023) - firstly during the snow melt and secondly during the late summer. This also primes conditions for DOC transport from the soil column during these periods, supporting our observations from the stream.

During the snow-free season, the C-Q slopes became consistently more transport-limited as the season progressed (Fig. 3a), likely due to increased source availability as the catchment gradually wetted up, activating pathways and connectivity (Birkel et al., 2017; Gómez-Gener et al., 2021). Additionally, enhanced microbial activity and increased vegetation breakdown throughout the growing season could provide more abundant sources of DOC (Campbell et al., 2022). This interpretation is partially supported by the HI, which consistently revealed strong anti-clockwise hysteresis, indicative of likely distal sources and slow DOC transport (Ducharme et al., 2021). However, the HI did not show significant seasonal variation across the snow-free season. Notably, a steeper linear relationship between DOC yield and event yield was observed during the snow-free season 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 consistently influenced DOC dynamics in all seasons, antecedent precipitation emerged as 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

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

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 decay of organic matter dominating 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

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). While there were some differences in C-Q slopes between years, the month-to-month variation outweighed the year-to-year variation, suggesting a remarkable 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 (Vaughan et al., 2017; Zarnetske et al., 2018). Similarly, the HI values showed no discernible differences on an annual basis, indicating flow path stability in this system (Lloyd

https://doi.org/10.5194/egusphere-2023-1986
Preprint. Discussion started: 6 September 2023

et al., 2016b). Source activation and transport processes have a strong seasonal pattern; however, the differences between years may not have been pronounced enough to drive substantial changes, underscoring the need for longer-term data series for a comprehensive understanding.

In contrast, the yield analysis revealed variations between years. Specifically, we observed steeper regressions for 2018 and 2019 compared to 2020 and 2022, indicating a higher transport of DOC per unit of water during these years. Thus, though source activation processes do not appear to be changing year on year, the DOC yield does, which highlights the need to understand how changes in water source contribution drive changes in both processes and yield. Previous long-term studies have suggested that warmer years lead to 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 layer (Bowering et al., 2023, 2020). 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, 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

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 improving DOC storage and transport process 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 water sources and paths shift.

Our findings emphasize the vulnerability of DOC transport processes to change with snow and snowmelt season in response to climate change. Our study highlights the importance of long-term monitoring to assess the long-term impacts on DOC transport. To further enhance our understanding, future research should focus on establishing causal relationships between transport metrics and indicators of sources and transport processes, integrating high-resolution stable water isotope monitoring and spatially distributed hydrological modelling with *in-situ* DOC monitoring. This work contributes to advancing our knowledge of DOC transport processes in Arctic ecosystems, providing valuable information for informed decision-making and effective management of these fragile environments in the face of climate change.

Data Availability

Data supporting this study are available from the corresponding author upon request.

Author Contribution

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.

Competing Interests

The authors declare that they have no conflict of interest.

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