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Key Points:

- In both catchments, high-flow conditions dominated annual dissolved organic carbon (DOC) and nitrate (NO_3^-) yields
- Catchments showed distinct DOC and NO_3^- transport behaviors, particularly during storms, driven by differences in landscape characteristics
- More frequent or intense storms are likely to significantly increase lateral fluxes of DOC and NO_3^- from Arctic landscapes to rivers

Supporting Information:

Supporting Information may be found in the online version of this article.

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Landscape and Storm Characteristics Influence DOC and Nitrate Mobility and Riverine Export Magnitude in Two Arctic Catchments

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Abstract Intensifying Arctic hydrological cycles and permafrost thaw alter the magnitude and timing of lateral solute fluxes to rivers, yet interactions among hydrological, biogeochemical, and landscape controls on carbon and nutrient export remain unclear. We calculated yields of dissolved organic carbon (DOC) and nitrate (NO_3^-) and storm hysteresis (HI) and flushing indices (FI) across six thaw seasons of high-frequency monitoring to examine solute export dynamics across timescales (daily, storm-event, monthly, annual) and flow conditions in two headwater catchments (River-dominated tundra vs. Lake-influenced tundra). High-flow conditions comprising less than 40% of the study period dominated annual thaw-season solute yields in both catchments, accounting for 75%–80% of annual thaw-season DOC and 55%–65% of NO_3^- yields. Storm-events reflected abundant DOC sources (+FI) and limited NO_3^- supply (−FI) in catchment soils. In the River-dominated catchment, storm HI and solute yields were related to storm intensity (as storm rising limb duration and peak storm discharge), while responses in the Lake-influenced catchment were more variable. Flow-weighted concentrations at daily and monthly timescales revealed patterns not detectable during individual storms, including a late-season increase in DOC in the Lake-influenced catchment that may indicate a seasonal shift in DOC source. Overall, our analysis suggests that catchment storage components such as in-network lakes introduce variability in solute export behaviors and may decouple concentration-discharge relationships at high flows. This study provides a mechanistic framework to connect disparate temporal scales of hydrochemical observation and offers a clearer understanding of catchment-specific processes that regulate the timing and magnitude of solute export in Arctic headwaters.

Plain Language Summary Arctic warming and permafrost thaw are expected to change how and when carbon and nutrients move from the landscape to rivers, though the amount, timing, and landscape properties controlling these fluxes remain unclear. In this study, we used 6 years of high-frequency measurements to monitor dissolved organic carbon (DOC) and nitrate (NO_3^-) concentrations in two Arctic headwaters: one catchment with river-dominated headwaters (hereafter, River-dominated catchment) and one catchment with lake-influenced headwaters (hereafter, Lake-influenced catchment). We examined DOC and NO_3^- yields and export patterns across flow conditions (high to low flows) and across timescales (daily, storm-event, monthly, annual). Overall, we found that high-flow conditions dominate annual thaw-season DOC yields (75%–80%) and NO_3^- yields (55%–65%) in both catchments, but that lakes may cause variability in how and when solutes are transported from the landscape to the river. Throughout the 6-year period, we also observed an increase in flow-weighted concentrations of DOC in the Lake-influenced catchment from June to August that indicates a seasonally activated DOC source. Our findings show that landscape features such as lakes strongly influence how Arctic rivers export carbon and nutrients, and emphasize the value of long-term, high-resolution hydrochemical monitoring to document changes in riverine exports as Arctic ecosystems rapidly change.

1. Introduction

Rapid warming and intensifying disturbance regimes in the permafrost zone alter carbon and nutrient cycles by thawing massive stocks of permafrost carbon and nutrients and changing the structural and functional landscape properties that control terrestrial-aquatic connectivity (Abbott et al., 2015; Schuur et al., 2015; Tank et al., 2020). For example, high-latitude warming and large-scale permafrost degradation have been linked to increased depth

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of thaw (Faucherre et al., 2018; Yi et al., 2015) and deepening of subsurface flow paths (Bense et al., 2009; S. G. Evans et al., 2020), changes in terrestrial vegetation community composition (Heijmans et al., 2022; Standen & Baltzer, 2021) and circumpolar changes in surface-water solute fluxes (Frey & McClelland, 2009; Kendrick et al., 2018; McClelland et al., 2007; Tank et al., 2023).

As hydrological cycles intensify and precipitation increases in the Arctic (Bintanja, 2018), the complex interactions among physical, hydrological and biogeochemical processes that regulate the availability of carbon and nutrients in the landscape make it difficult to predict the magnitude and drivers of lateral solute flux to riverine ecosystems. Shallow flow paths activated during snowmelt and rainfall route water through organic-rich surface soils and promote DOC export to streams (Lafrenière & Lamoureux, 2019). As permafrost thaws and the active layer thickens, water may increasingly interact with deeper mineral soils where DOC can be sorbed or mineralized, and where access to deeper subsurface sources may alter the availability of inorganic nutrients (Harms et al., 2016). Landscape features such as lakes and water tracks may further modify these responses by altering water storage, residence times, and the connectivity between terrestrial source areas and stream networks (Covino et al., 2021; Harms & Ludwig, 2016; Kalinin et al., 2016). Therefore, our understanding of how terrestrial-aquatic linkages are changing in a warmer and wetter Arctic remains a major source of uncertainty in predicting the fate of carbon and nutrients in the permafrost zone (Kelley et al., 2025; Zolkos et al., 2022).

Flagship efforts to monitor circumpolar changes in major solute fluxes across the six largest Arctic rivers through the Arctic Great Rivers Observatory (Arctic-GRO) have documented widespread divergence in river chemistry trends over the past two decades (Tank et al., 2023). Prior studies using long-term, low-frequency (i.e., every 2 months) concentration-discharge ($C-Q$) monitoring found a decline in nitrate (NO_3^-) flux and no overall change in DOC flux across the major Arctic river catchments to the Arctic Ocean (Tank et al., 2023). These trends have been broadly attributed to the effects of long-term changes in active layer dynamics and permafrost thaw, specifically deepening subsurface flow paths that increase mineral weathering while promoting organic matter adsorption to thawed mineral soils. While these decadal $C-Q$ relationships serve as critical benchmarks for pan-Arctic change in riverine solute fluxes, their low temporal resolution at extremely large scales of observation (i.e., catchments draining $>100,000 \text{ km}^2$) obscures fine-scale processes and landscape patterns responsible for the large-scale behavior of these catchments (Shogren et al., 2019). Therefore, constraining landscape drivers of lateral solute flux, as well as regional and pan-Arctic biogeochemical models to predict how these fluxes are expected to change under future climate change scenarios such as widespread permafrost thaw requires $C-Q$ observations across a range of spatial and temporal scales (Tank et al., 2023).

To adequately capture carbon and nutrient dynamics in Arctic rivers at finer spatial and temporal scales requires consideration of the unique characteristics of the Arctic environment. Runoff in Arctic headwater catchments varies seasonally, with a brief thaw season in which water flows openly in streams and rivers before re-freezing during the winter months. About 30%–40% of annual precipitation in the Alaskan Arctic accumulates as snow, which is released to surface waters over a short duration during spring snowmelt at the start of the thaw season. Snowmelt can dominate annual riverine solute loads, accounting for more than a third or more of total annual dissolved organic carbon (DOC) exports (Bring et al., 2016; Kane et al., 2008; Townsend-Small et al., 2011). Rainfall comprises the remainder of annual precipitation and runoff, and storm events serve as “hot-moments” of runoff generation and solute export between late May–September in northern Alaska (Fabre et al., 2019; Lewis et al., 2012; McNamara et al., 2008). Analyzing solute export regimes of permafrost catchments during high-flow events reveals the processes controlling carbon and nutrient balance in changing ecosystems (Battin et al., 2008). However, documenting the spatial and temporal variability in processes controlling runoff and solute abundance in permafrost landscapes presents major logistical and analytical challenges, from very remote site locations to highly destructive conditions for instrumentation. As a result, few studies in Arctic regions have captured changes in riverine solute flux at adequate frequency to understand catchment-specific flux responses to flow changes across the thaw season and over multiple years (e.g., Shogren et al., 2021, 2024).

Recent advancements in situ sensor technology that enable high-frequency, sub-hourly measurements of hydrological and biogeochemical parameters have significantly expanded our ability to (a) characterize $C-Q$ relationships across catchments at finer time scales and for long periods, (b) express important variability in both long-term $C-Q$ trends and episodic events such as storms, and (c) synthesize a broad suite of metrics to interpret event-scale behaviors (Burns et al., 2019; Ruhala & Zarnetske, 2017). High-frequency continuous monitoring of DOC and NO_3^- often reveals distinct, non-linear behavior between solute concentration and discharge during

storm events (Creed et al., 2015; Godsey et al., 2009). Flushing and hysteresis indices (FI and HI, respectively) are common metrics that together indicate whether solute concentrations are being enriched or diluted during storm events, and how these changes in concentration throughout the storm hydrograph may relate to solute abundance and transport dynamics within the catchment (Lloyd et al., 2016). Previously, HI and FI indices applied across three distinct Arctic headwater catchments revealed strong landscape and seasonal controls on storm-event DOC and NO_3^- flux (Shogren et al., 2021). However, these metrics alone characterize only a limited portion of the annual hydrograph (only storms) and cannot capture important changes in biogeochemical dynamics that occur during median or low-flow conditions (Moatar et al., 2017).

Landscape heterogeneity and rapid seasonal changes in hydrological connectivity can confer variability in processes that regulate C - Q relationships throughout space and time within the permafrost zone (Bring et al., 2016; Tetzlaff et al., 2015; Townsend-Small et al., 2011). We collected high-frequency measurements of DOC, NO_3^- , and discharge every 15 min from early June to early September across six years (2017–2019 and 2021–2023) at the outlet of two Arctic Alaskan catchments with either lake-influenced headwaters or River-dominated headwaters (hereafter, Lake-influenced catchment and River-dominated catchment). Our research objectives were: (a) to explore how catchment characteristics (e.g., lake presence) influence the coupled exports of water, NO_3^- , and DOC under different flow conditions, and (b) to determine how our interpretations of catchment export patterns and C - Q relationships change across storm-event, daily, monthly, and annual timescales.

1.1. Conceptual Framework

We quantified solute yield (i.e., load normalized to catchment area) and flow-weighted concentrations (i.e., solute yield normalized to water yield) to compare DOC and NO_3^- export magnitudes between catchments, across flow conditions, and across timescales. We compare patterns in daily flow-weighted solute concentration across flow conditions to storm event solute transport patterns (FI and HI), which provide complementary but unique information about solute source dynamics during extended periods of connectivity within the catchment (Lloyd et al., 2016). FI describes the overall tendency of solute concentrations to increase (+FI) or decrease (−FI) with rising discharge, thereby distinguishing between source enrichment versus dilution behaviors during storms. HI reflects the timing of solute source mobilization relative to peak discharge, where clockwise hysteresis (+HI) indicates rapid source mobilization, while anticlockwise hysteresis (−HI) reflects slower source mobilization and a lag in the response of concentration relative to changing discharge (Lloyd et al., 2016).

Figure 1 outlines (a) the difference between the daily (Figure 1a) and storm-event (Figure 1b) discharge integration used to characterize daily flow-class, yields, and flow-weighted concentration, and storm-event HI and FI, (b) possible outcomes of daily solute export patterns across flow conditions (Figure 1c) versus storm event solute transport patterns (Figure 1d), and (c) their relationship to general catchment function (Figure 1e). Taken together, the behaviors of solute yield and flow-weighted concentration across flows provide context about solute abundance and catchment source connectivity, where an increase in yield matched by an increase in flow-weighted concentration can indicate abundant, mobile solute sources (Figures 1c and 1e, scenario X). Alternatively, an increase in yield paired with a decrease in flow-weighted concentration may indicate limited or depletable solute sources (Figures 1c and 1e, scenario Z), while no change in flow-weighted concentration may indicate diverse flow paths or seasonally activated sources (Figures 1c and 1e, scenario Y).

We hypothesize that the River-dominated catchment will exhibit strong coupling between flow and solute export, evidenced by consistent DOC enrichment and NO_3^- dilution across flow conditions and storm events. In contrast, we predict that the Lake-influenced catchment will show weaker coupling between flow and solute export due to the buffering effect of in-network lakes. We predict that this will result in smaller differences in solute concentrations across flow conditions and greater seasonal and event-scale variability in DOC and NO_3^- hysteresis, as lakes obscure seasonal shifts in solute availability and catchment connectivity.

2. Materials and Methods

2.1. Study Sites

We conducted our study in two clear-water Arctic catchments that have been the subject of extensive research as part of the Arctic Long-Term Ecological Research project on the North Slope of Alaska (Figure 2). Both catchments are underlain by continuous permafrost and therefore, subsurface flow is limited to a shallow active

Partitioning Annual Hydrograph by Daily and Storm event timescales:

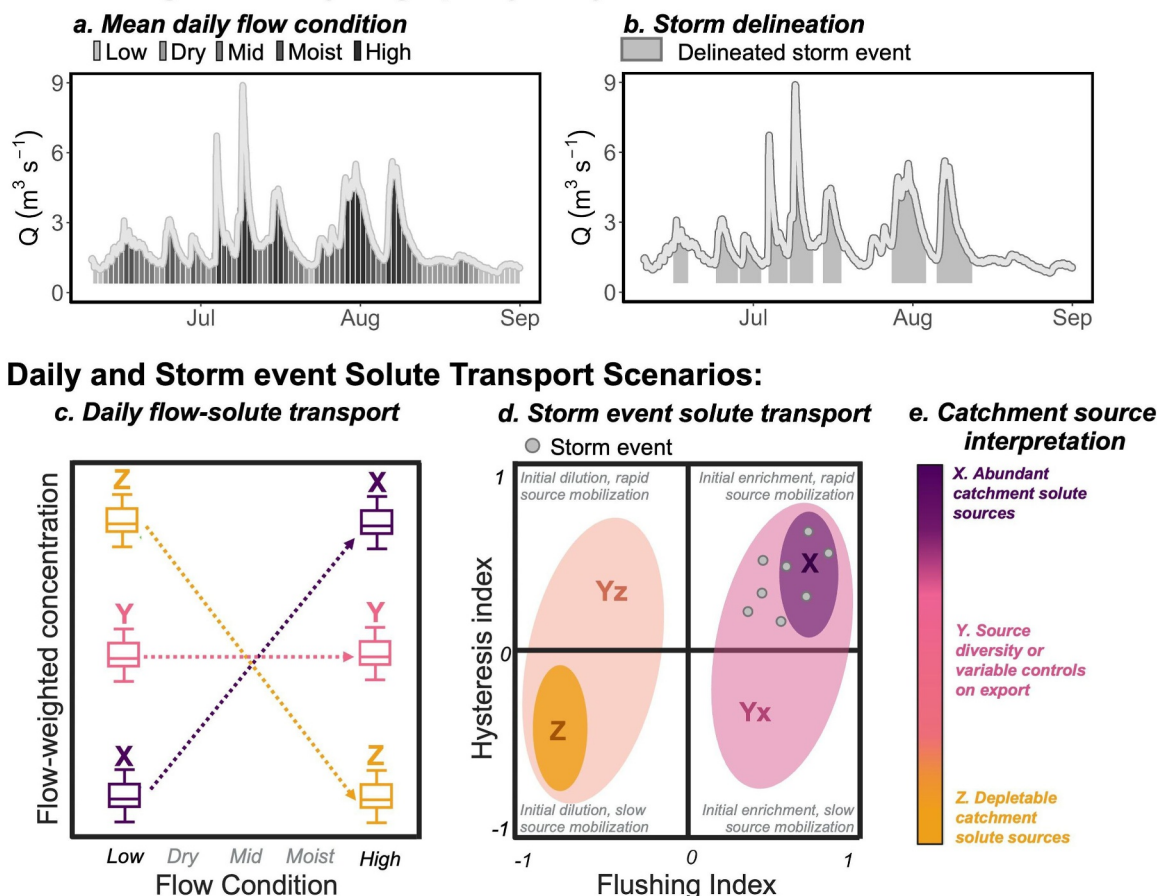


Figure 1. The top row depicts the discharge integration period for daily (a) versus storm event (b) timescales during the 2022 thaw season in the River-dominated catchment. For daily timescales (a), each bar and point represents one 24-hr period, while shade indicates flow condition designated according to mean daily discharge (see methods). We calculated dissolved organic carbon (DOC) and NO_3^- yield and flow-weighted concentration for each day. For storm events (b), the shaded regions of the hydrograph indicate storm-flow periods. We calculated DOC and NO_3^- yield, hysteresis, and flushing indices (FI) for each individual storm. The bottom row depicts possible outcomes of flow-solute transport relationships for daily (c) and storm event (d) timescales, as well as a simplified interpretation of catchment solute source behavior for each scenario (e). For daily timescales (c), flow-weighted solute concentrations are grouped by flow condition. Boxplot color and letter indicate possible outcomes for the relationship between flow-weighted solute concentrations and flow condition, given our expectation that DOC and NO_3^- yields will increase with flow. For storm event timescales (d), each point represents the one storm event from (b). Shaded ellipses and letters represent possible ranges of storm hysteresis index and FI, which are expected to vary by solute and catchment. In both (c) and (d), color gradient and letter correspond with a possible interpretation of daily or storm event catchment solute source behavior in (e).

layer that gradually thaws throughout the annual thaw season from mid-May to mid-September (Romanowicz & Kling, 2022). Silty soils cover most of this region of the North Slope, and the average active layer thickness is about 50 cm (Luo et al., 2016; Nicolsky et al., 2017; Yi et al., 2018). Locally, the soil organic layer ranges from ~10 to 20 cm in thickness, with hydraulic conductivity between 10 and 100 times greater than the underlying mineral soil (Harms & Ludwig, 2016; Hinzman et al., 1991; Whittinghill & Hobbie, 2011). The study catchments are located immediately adjacent to each other and therefore enable paired catchment comparisons, with the presence of lakes being the most significant difference between the two.

The Upper Kupaaruk River catchment (River-dominated catchment) is a 4th order meandering stream at the location of our outlet monitoring station, underlain by glacial deposits from the Sagavanirktok River glaciation in the middle-Pleistocene (Hamilton, 2003). Soil organic horizons overlying parent material from the Sagavanirktok glaciation in the River-dominated catchment contain carbon stocks of the order of 27.5 mtC m^{-2} and nitrogen stocks of the order of 0.716 mtN m^{-2} (Whittinghill & Hobbie, 2011). This catchment drains stream-dominated headwaters, with only about 0.3% of the total catchment area covered by lakes. The catchment is also flanked by hillslopes that compose a complex network of water tracks, which have been shown to strongly retain inorganic

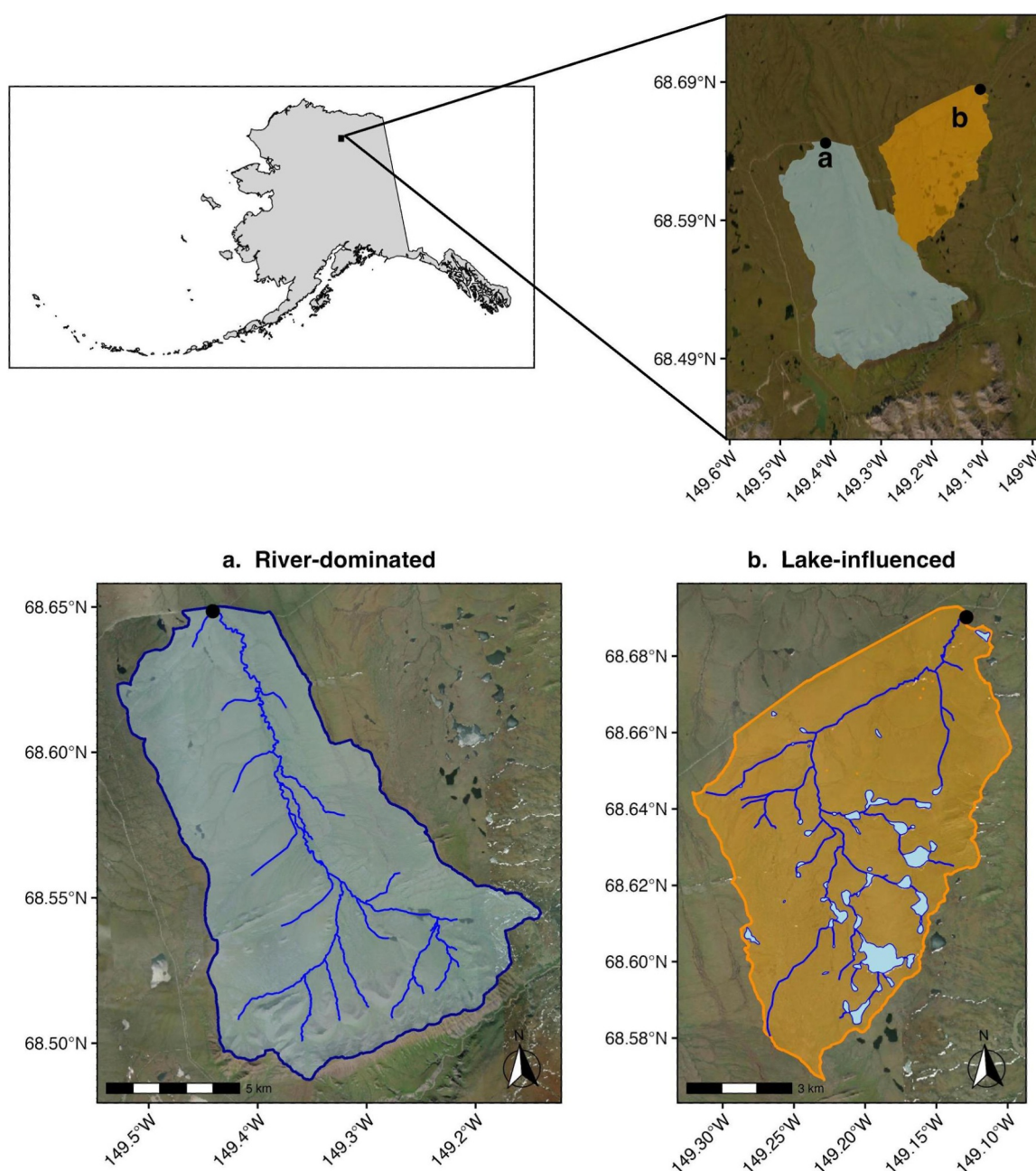


Figure 2. Top panel: Map of the state of Alaska, USA (left), proximity of study catchments on the North Slope (right). Bottom panel: Map of the River-dominated catchment (a) and Lake-influenced catchment (b). Black circles denote the sensor location at the outlet of each catchment. Light blue polygons in the Lake-influenced catchment are in-network lakes.

phosphorus and weakly retain, or export, inorganic nitrogen (Harms et al., 2019; Harms & Ludwig, 2016; McNamara et al., 2008).

The Oksrukuyik Creek headwater catchment (Lake-influenced catchment) is a low-gradient, 3rd order meandering stream that drains a large network of lake chains that comprise 3.6% of the catchment area, particularly in the headwater tributaries. Glacial deposits are attributed to the Itkillik I glaciation (late Pleistocene) of the central Brooks Range glacial succession (Hamilton, 2003). Organic horizon carbon and nitrogen stocks in soils overlying parent material from the Itkillik I glaciation have been estimated to contain about 18.5 mtC m^{-2} and 0.626 mtN m^{-2} , respectively (Whittinghill & Hobbie, 2011). Both River-dominated and Lake-influenced

catchments drain wet acidic tundra consisting largely of tussock tundra, dwarf willows and birch, mosses, heath, and sedges (Shaver et al., 2014). However, the Lake-influenced catchment (mean gradient = 3.3°) is less steep than the River-dominated catchment (mean gradient = 7.1°), which is conducive to the formation of wet-sedge meadows and bogs throughout the catchment (Harvey et al., 1998). Further catchment landscape, nutrient and flow characteristics are summarized in Table 1.

2.2. In Situ Data Collection

From mid-June to late-August of 2017–2019 and 2021–2023, we monitored discharge, DOC, and NO_3^- concentrations at the outlets of the two headwater catchments. Data from 2020 were omitted from this analysis because of limited monitoring capacity during the COVID-19 pandemic. We deployed pressure transducers (Onset HOBO U20 Water Level Data Loggers, Bourne, Massachusetts, USA) at each catchment outlet to monitor stream depth (stage) at 10-min intervals. We calculated discharge using discharge-stage rating curves established from long-term monitoring by the Arctic Long Term Ecological Research (LTER) at each of our monitoring sites, as well as weekly field measurements conducted by the Arctic LTER during each field season using a SonTek FlowTracker acoustic Doppler velocimeter (YSI Inc., Yellow Springs, Ohio, USA) (Arp et al., 2017). The early freshet period at the beginning of the thaw season was excluded from analysis in all years, as accurate discharge measurement was not possible due to channel ice and bank overflow conditions. Therefore, the available discharge data reflect predominantly rainfall-driven discharge dynamics during the thaw season. Hydrographs and hyetographs for each monitoring year 2017–2019 and 2021–2023 are provided in (Figures S2 and S3 in Supporting Information S1).

We measured DOC and NO_3^- concentrations at 15-min intervals using s::can UV-Visible spectrophotometers (Messtechnik GmbH, Vienna, Austria) co-located with our pressure transducers in each stream. The spectrophotometers measure light absorbance wavelengths 220–750 nm, and absorbance spectra were normalized by optical path length (35 mm at both catchments). An attached rotating brush cleaned the spectrophotometer lenses 1 minute prior to each absorbance measurement.

For catchment-specific calibration of absorbance spectra, we collected weekly grab samples at each sensor site to calibrate the s::can spectrophotometer measurements to the laboratory-measured DOC and NO_3^- concentrations. We syringe-filtered each grab sample through 47 mm 0.2 μm cellulose acetate filters (Sartorius 1110725N) into clear (NO_3^-) or amber (DOC) HDPE bottles, which were then either frozen (NO_3^-) or refrigerated (DOC) until analysis. We measured DOC concentrations on a Shimadzu TOC-L analyzer using the combustion catalytic oxidation method (method detection limit = 0.06 mg L^{-1} ; limit of quantification = 0.1 mg L^{-1}), and NO_3^- concentrations using a QuickChem Lachat analyzer (2017) or a Seal AA3 segmented flow analyzer (2018, 2019, 2021–2023; method detection limit = 0.0002 mg L^{-1} ; limit of quantification = 0.001 mg L^{-1}). Using methods outlined in Etheridge et al. (2014), we used partial least squares regression to establish catchment-specific relationships between spectrophotometer absorbance spectra and laboratory-measured NO_3^- and DOC concentrations for each year of record (Shogren et al., 2021, 2024; Figure S1 in Supporting Information S1). PLSR model validation metrics are provided in (Table S1 in Supporting Information S1).

2.3. Flow Duration Curve Analysis

We generated flow duration curves (FDCs) for both catchments from average daily observations of specific discharge throughout the six years of record (2017–2019 and 2021–2023) to: (a) compare differences in the magnitude and frequency of daily streamflow between catchments, and (b) classify flow measurements across the six years of observation into flow categories (Vogel & Fennessey, 1994). We partitioned the FDCs into five different flow classes: high flow conditions (0–10th percentile flows), moist conditions (10–40th percentile flows), mid-range conditions (40–60th percentile flows), dry conditions (60–90th percentile flows) and low-flow conditions (90–100th percentile flows) following US EPA (2007) (Speir et al., 2021). We also conducted a Mann-Whitney U-test of specific discharges at sequential 2% intervals of exceedance probability between the two catchments to detect differences in catchment flow characteristics.

2.4. Storm Event-Scale C-Q Analysis

We delineated storm events using the *baseflow* function from *hydrostat R* package, which divides the hydrograph into baseflow and direct runoff components using the Lyne-Hollick digital filter (Bond, 2019; R Core

Table 1
Study Catchment Flow and Solute Characteristics for the 2017–2019 and 2021–2023 Flow Seasons

	River-dominated					Lake-influenced						
	2017	2018	2019	2021	2022	2023	2017	2018	2019	2021	2022	2023
Mean Q (m ³ s ⁻¹)	3.28	4.66	4.07	2.12	2.13	3.73	3.46	2.65	2.53	0.89	1.46	1.92
Q_{50} (m ³ s ⁻¹)	2.76	3.47	3.12	1.32	1.77	2.14	2.89	1.49	1.36	0.54	0.83	1.30
Mean flow-weighted DOC (mg L ⁻¹)	3.47	5.50	4.14	4.75	3.75	4.03	5.77	4.65	3.85	4.98	4.85	5.71
Mean flow-weighted NO ₃ ⁻ (mg L ⁻¹)	0.27	0.13	0.28	0.52	0.35	0.27	0.16	0.11	0.16	0.26	0.10	0.11
Mean daily DOC yield (kg km ⁻² d ⁻¹)	12.2	26.8	16.2	10.6	5.60	9.08	26.7	12.9	18.6	6.30	9.65	14.1
Mean daily NO ₃ ⁻ yield (kg km ⁻² d ⁻¹)	0.50	0.50	0.79	0.71	0.42	0.46	0.63	0.25	0.37	0.15	0.16	0.16
# Storm events	8	6	7	4	9	7	6	6	3	5	7	6
Mean storm DOC yield (kg km ⁻²)	78.8	231.9	106.7	97.9	33.1	48.8	153.9	46.4	73.9	63.3	60.3	54.1
Mean storm NO ₃ ⁻ yield (kg km ⁻²)	3.04	3.77	4.48	4.68	1.99	2.18	5.05	0.64	1.65	0.37	0.96	0.63
Catchment Area (km ²)	99.6	99.6	99.6	99.6	134.5	134.5	72.7	72.7	72.7	72.7	72.7	72.7
Monitoring Location	68.63803, -149.39285	68.63803, -149.39285	68.63803, -149.39285	68.63803, -149.39285	68.64313, -149.40315	68.64313, -149.40315	68.68617, -149.09844	68.68617, -149.09844	68.68617, -149.09844	68.68617, -149.09844	68.68617, -149.09844	68.68617, -149.09844
Monitoring Dates	Jun 5–Sep 1	Jun 27–Sep 1	Jun 16–Aug 10	Jun 24–Aug 27	Jun 9–Sep 3	Jun 17–Sep 4	Jun 5–Aug 14	Jul 4–Sep 3	Jun 17–Sep 1	Jun 21–Sep 1	Jun 8–Aug 30	Jun 17–Sep 4

Note. Data from 2020 was omitted due to limited monitoring capacity during the COVID-19 pandemic.

Note. Data from 2020 was omitted due to limited monitoring capacity during the COVID-19 pandemic.

Team, 2024). We defined a storm event as any hydrologic response to precipitation that produced at least a 20% increase in discharge from storm onset to peak discharge. This threshold was chosen to capture a broad range of storm magnitudes while excluding minor fluctuations in discharge unrelated to precipitation, and is consistent with prior studies of event-scale solute dynamics in Arctic streams that implemented relative thresholds to delineate storm events (Shogren et al., 2021). We defined the time of storm end as the point on the storm hydrograph falling limb at which discharge returns to antecedent or inter-event conditions. When prolonged high-flow events exhibited multiple peaks, we treated each subsequent rise in discharge as a separate event to capture distinct biogeochemical behaviors in response to changing flow. We identified 50 total events in the River-dominated catchment and 40 total events in the Lake-influenced catchment over the six-year period. However, we omitted 11 events from the River-dominated catchment and 10 events from the Lake-influenced catchment from C - Q analysis because of incomplete or unavailable corresponding DOC and NO_3^- concentration data during major floods (e.g., 8–11 July 2023) or periods when sensors were temporarily removed from the water for maintenance. We used hourly precipitation data monitored nearby by the Toolik Field Station Environmental Data Center (EDC) to manually confirm that each event occurred in response to precipitation (Environmental Data Center Team, 2024).

To explore export patterns of DOC and NO_3^- in the River-dominated and Lake-influenced catchments, we calculated HI and FI for each storm event. HI and FI are valuable tools to identify non-linear and hysteretic relationships between solute concentration and discharge during high flow events (Evans & Davies, 1998; Rose et al., 2018; Vaughan et al., 2017). When concentration is higher on the rising limb of the storm than on the falling limb, the C - Q relationship forms a clockwise loop. Conversely, when the concentration is higher on the falling limb of the storm than on the rising limb, the C - Q relationship forms an anticlockwise loop. We calculated HI according to methods introduced by Lloyd et al. (2016). We first normalized all discharge (Q) and concentration (C) values:

$$Q_{\text{norm},i} = \frac{Q_i - Q_{\min}}{Q_{\max} - Q_{\min}}$$

$$C_{\text{norm},i} = \frac{C_i - C_{\min}}{C_{\max} - C_{\min}}$$

Where Q and C are the discharge and concentration measurements at timestep i , $Q_{\min}$ and $C_{\min}$ are the minimum discharge and concentration observed during the storm, and $Q_{\max}$ and $C_{\max}$ are the maximum discharge and concentration observed during the storm. We then linearly interpolated $C_{\text{norm},i}$ by 2% intervals of $Q_{\text{norm},i}$ for the rising and falling limbs of the storm. We calculated HI at each 2% interval of $Q_{\text{norm},i}$ as

$$\text{HI}_j = C_{\text{rising},j} - C_{\text{falling},j}$$

Where $C_{\text{rising},j}$ and $C_{\text{falling},j}$ are the concentrations at 2% interpolation interval j on the rising and falling limbs of the storm, respectively. An overall storm HI was calculated as the mean of all HI_j values. HI summarizes information about the direction of rotation of C - Q hysteresis and can indicate solute source proximity (Rose et al., 2018). Clockwise hysteresis (expressed as $\text{HI} > 0$) suggests that solutes are quickly mobilized into the catchment, while anticlockwise hysteresis (expressed as $\text{HI} < 0$) suggests that solutes have longer or slower transport times (e.g., deeper subsurface soils) (Rose et al., 2018).

Flushing index (FI) is defined as the slope of the rising limb of the C - Q relationship and was calculated using the following equation (Butturini et al., 2008; Vaughan et al., 2017):

$$\text{FI} = C_{\text{Qpeak,norm}} - C_{\text{initial,norm}}$$

Where $C_{\text{Qpeak,norm}}$ and $C_{\text{initial,norm}}$ are the normalized concentrations at peak storm discharge and at the beginning of the storm, respectively. FI provides information about whether solute concentrations increase ($\text{FI} > 0$) or are diluted ($\text{FI} < 0$) as discharge rises. For example, $\text{FI} = 1$ indicates synchronized flushing in which peak storm concentration coincides exactly with peak storm Q , while $\text{FI} = -1$ indicates synchronized dilution in which minimum storm concentration coincides exactly with peak Q . We compared HI and FI behaviors between

catchments using non-parametric Wilcoxon rank-sum test to detect differences in median, and Levene's test to assess equality of variances.

2.5. Solute Yields Across Timescales

We calculated daily and storm event DOC and NO_3^- yields to explore patterns in solute export across timescales. We integrated DOC and NO_3^- loads over total discharge for each day and then for each storm to determine the daily and storm event export mass. Runoff volume was estimated by integrating discharge for each day and storm event throughout the 6-year period. We calculated water yield and solute yield by normalizing runoff and solute loads to catchment area (mm and kg km^{-2} , respectively) and implemented the non-parametric Wilcoxon rank-sum test to detect overall differences in median daily export trends between catchments (Vaughan et al., 2017). We also grouped solute yields by month (June, July, or August) and implemented the non-parametric Kruskal-Wallis test to assess the effect of seasonal change on catchment solute yields. When a significant effect was detected, we used Dunn's post hoc test with Bonferroni correction to make pairwise comparisons between months.

To control for the effect of runoff volume on solute yield magnitude, we calculated daily flow-weighted concentration (mg L^{-1}) by taking the ratio of solute yield to water yield (Vaughan et al., 2017). We repeated the above statistics to test for significant differences in median flow-weighted concentration between catchments and across months.

2.6. Solute Yields Across Flow-Conditions

We also categorized daily discharge measurements according to flow percentile (as described in FDC method) and explored trends of DOC and NO_3^- yield across flow conditions. For annual timescales, we summarized the influence of flow conditions on cumulative annual exports by calculating the proportion of total annual solute yields contributed by each flow class for each year. For monthly timescales, we calculated median daily DOC and NO_3^- yields, as well as median flow-weighted DOC and NO_3^- concentrations, for each flow condition during June, July, and August. We used Kruskal-Wallis and, when applicable, Dunn's post hoc tests with a Bonferroni correction to capture changes in solute export behaviors across flow conditions and timescales.

3. Results

3.1. Water Yield Dynamics Across Timescales

Flow duration curve analysis revealed distinct flow trends between River-dominated and Lake-influenced catchments across the 6-year period. The River-dominated catchment exhibited generally larger specific discharge than the Lake-influenced catchment, and we detected a significant difference between catchment specific discharge across all flows except during the highest 0–6th percentile flows over the 6-year period (Mann-Whitney $p > 0.05$; Figure S4 in Supporting Information S1).

The catchments also showed distinct trends in water yield across timescales. The River-dominated catchment exhibited generally larger median water yields across annual, monthly, and daily timescales than the Lake-influenced catchment, though statistical significance differed by year and month (Figure 3). Notably, there was no significant difference in median catchment water yield during storm events (Wilcoxon $p = 0.53$; Figure 3b). The largest proportion of annual water yield was exported during moist flow conditions in both the River-dominated (43.4%) and Lake-influenced (40.3%) catchments, though catchment water yield differed significantly during mid-range and dry flow conditions (Wilcoxon $p < 0.01$; Figure S5 in Supporting Information S1).

3.2. Daily Solute Dynamics Across Flow Conditions and Timescales

3.2.1. DOC

High and moist flow conditions (0–40th percentile flows) consistently dominated total annual DOC yields, accounting for an average of 77% of DOC exports in the River-dominated catchment and 80% in the Lake-influenced catchment throughout the six-year period (Figure S5 in Supporting Information S1). These DOC exports are disproportionately large relative to total annual water exported during high and moist flow conditions, which ranged from 70% to 76% in the River-dominated and Lake-influenced catchments, respectively. Mid-range

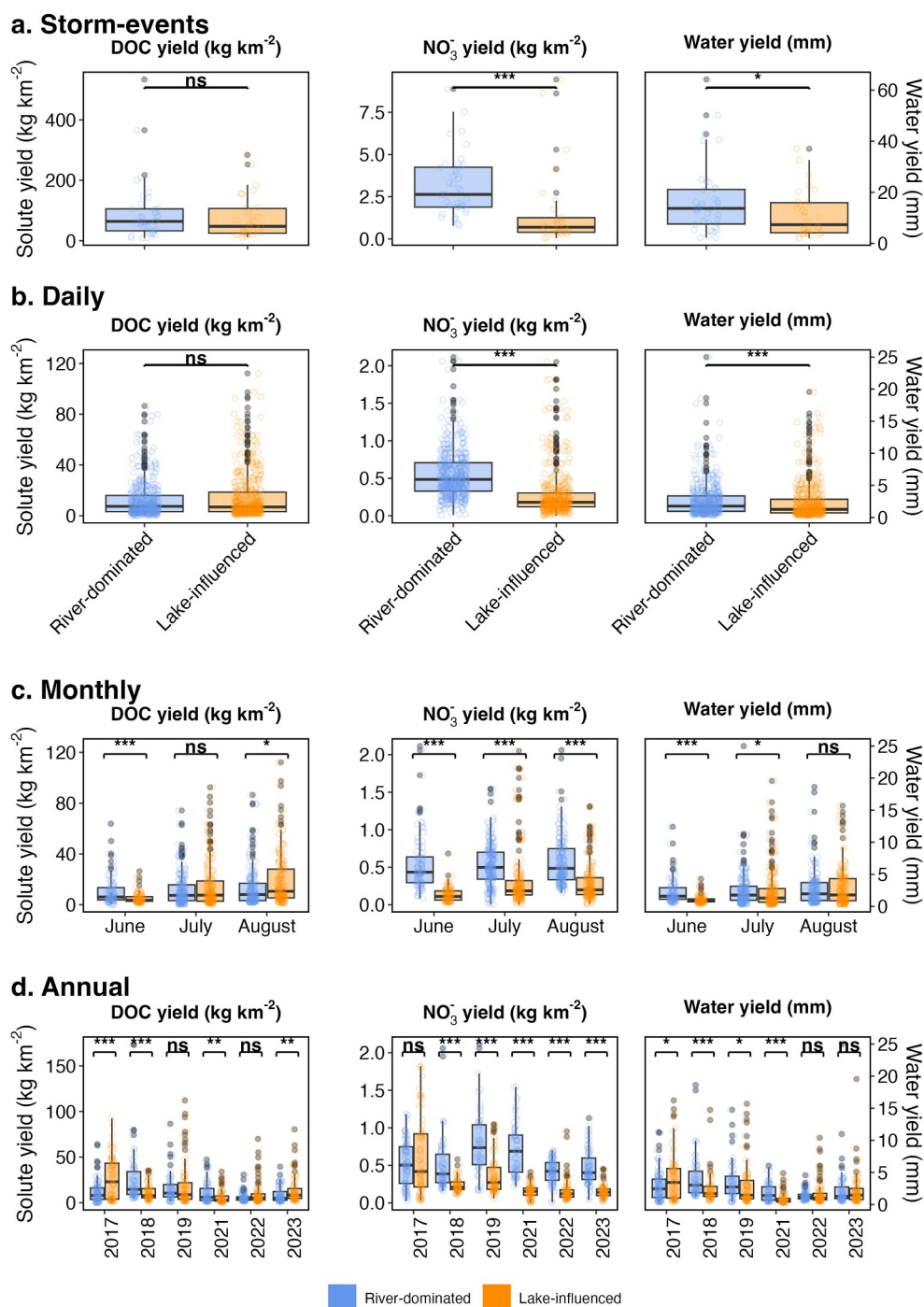


Figure 3. Boxplots depicting the interquartile range and median dissolved organic carbon (kg km^{-2}), NO_3^- (kg km^{-2}), and water yields (mm) across timescales for the River-dominated (blue) and Lake-influenced catchments (orange). Panel (a) presents all storm-event yields throughout the 6-year period for each catchment, and panel (b) presents all daily yields throughout the 6-year period for each catchment. Panel (c) presents all daily yields grouped by months, and panel (d) presents all daily yields grouped by years. Significance outcomes from Wilcoxon rank-sum tests are provided above brackets in each plot (ns indicated $p > 0.05$, * indicated $p < 0.05$, ** indicates $p < 0.01$, *** indicates $p < 0.001$).

to low flow conditions (40th–100th percentile flows) accounted for an average of 23% of total annual DOC exports in the River-dominated catchment and 20% of exports in the Lake-influenced catchment (Figure S5 in Supporting Information S1). The Lake-influenced catchment had larger mean daily yields of DOC

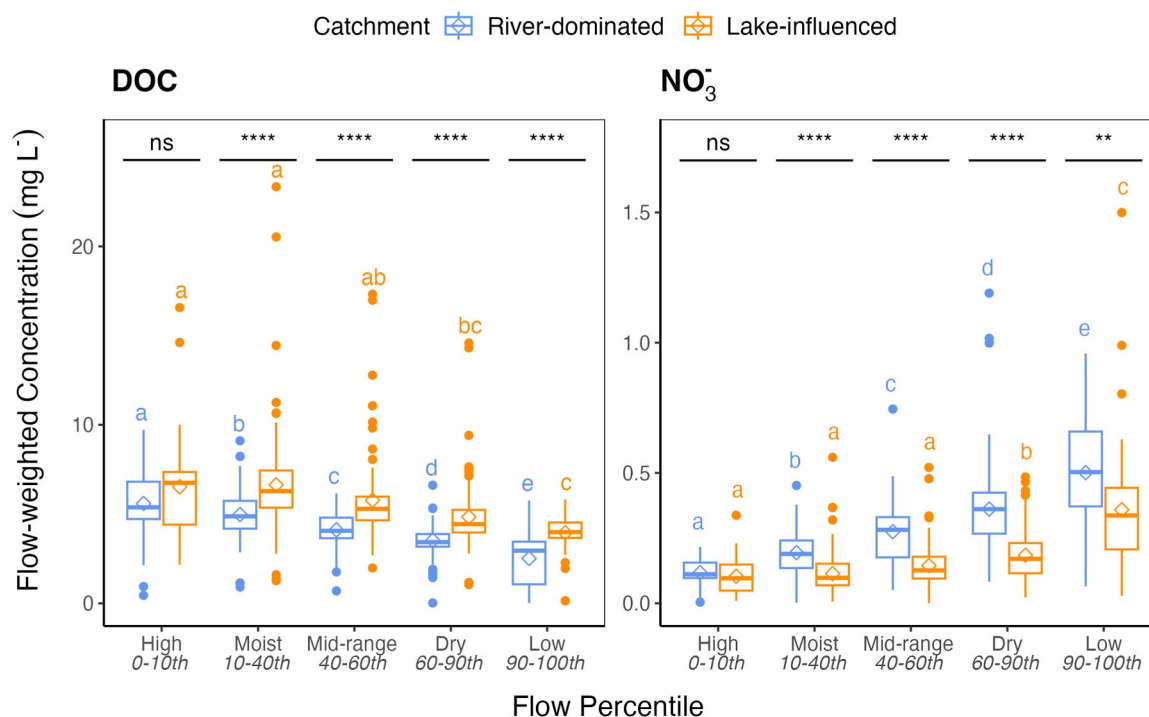


Figure 4. Boxplots depict the distribution of 6-years of daily flow-weighted dissolved organic carbon (left) and NO₃⁻ (right) concentrations for each flow condition in the River-dominated (blue) and Lake-influenced (orange) catchments. Diamonds within boxplots indicate mean flow-weighted concentration for each flow condition within each catchment. Asterisks denote significance outcomes from Wilcoxon rank-sum tests between catchments at each flow condition (* indicates $p < 0.05$, **** indicates $p < 0.001$, ns indicates $p > 0.05$). Letters indicate within-catchment significance outcomes from Dunn's post hoc test after testing for the effect of flow condition on flow-weighted concentrations in the River-dominated (blue letters) and Lake-influenced (orange letters) catchments.

(14.7 kg m⁻² d⁻¹) than the River-dominated catchment (12.8 kg m⁻² d⁻¹), with the largest mean daily yields occurring in August (18.9 kg m⁻² d⁻¹) and the smallest occurring in June (5.15 kg m⁻² d⁻¹). Mean daily DOC yields increased across months in the River-dominated catchment, with June exhibiting the smallest daily DOC yields (10.4 kg m⁻² d⁻¹) and August exhibiting the largest daily yields (15.3 kg m⁻² d⁻¹; Figures 3b and 3c).

Daily DOC yields were strongly driven by water yield in both River-dominated ($R^2 = 0.86$) and Lake-influenced catchments ($R^2 = 0.73$). To control for variability in runoff, we compared flow-weighted concentration between catchments and flow conditions by calculating the ratio of daily solute yields to water yields (i.e., flow-weighted concentration). We found a significant effect of both catchments (i.e., River-dominated vs. Lake-influenced; Wilcox $p < 0.01$) and flow conditions (Kruskal $p < 0.01$) on DOC flow-weighted concentrations (Figure 4). Pairwise comparisons using Dunn's test revealed significant differences in median flow-weighted DOC concentration between catchments across all flow conditions except for high flows (Kruskal $p < 0.01$), with Lake-influenced exhibiting larger overall median flow-weighted DOC concentrations than River-dominated (Figure 4). Within catchments, we found that median flow-weighted DOC significantly decreased from high to low flow conditions in the River-dominated catchment, while remaining comparatively stable in the Lake-influenced catchment across flow conditions (Figure 4). This consistency across flows in the Lake-influenced catchment may be partially explained by statistically significant seasonal changes in median flow-weighted DOC concentrations at dry and low-flow conditions (Kruskal $p < 0.01$), which were shown to increase across June, July and August (Figure 5). In contrast, grouping River-dominated flow-weighted DOC concentration by month revealed no statistically significant changes in median monthly flow-weighted DOC concentration (Kruskal $p = 0.51$; Figure 5).

3.2.2. NO₃⁻

High and moist flow conditions also dominated total annual NO₃⁻ yields, comprising an average of 54% of NO₃⁻ exports in the River-dominated catchment and 66% in the Lake-influenced catchment throughout the 6-year period (Figure S5 in Supporting Information S1). NO₃⁻ exports under mid-range, dry and low flow conditions

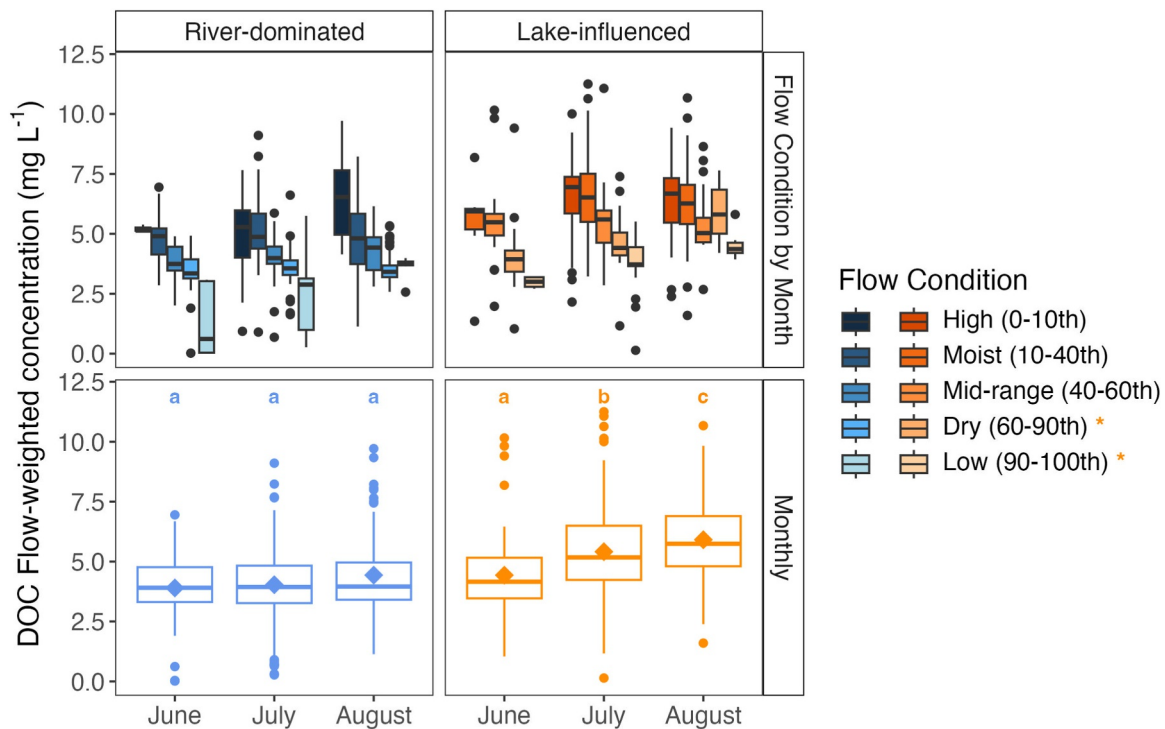


Figure 5. Boxplots depict the distribution of 6-years of daily flow-weighted dissolved organic carbon (DOC) concentration across flow conditions (top row) grouped by month (June, July or August) for the River-dominated (blue, left column) and Lake-influenced (orange, right column) catchments. The bottom row depicts the overall distribution of flow-weighted DOC concentration across months. Filled diamonds within box plots represent the mean monthly DOC flow-weighted concentration. Asterisks in legend represent flow conditions at which flow-weighted DOC concentrations significantly changed across all 3 months in either the River-dominated (blue) or Lake-influenced (orange) catchments.

were smaller in magnitude than high and moist flows, but were disproportionately large relative to total annual water exports under these flow conditions in both catchments.

We also found notable differences in overall NO_3^- yields between catchments. Mean daily NO_3^- yields across the 6-year period in the River-dominated catchment ($0.54 \text{ kg m}^{-2} \text{ d}^{-1}$) were nearly double those of the Lake-influenced catchment ($0.28 \text{ kg m}^{-2} \text{ d}^{-1}$). While we did not observe strong seasonal changes in mean daily NO_3^- yields in the River-dominated catchment, mean daily NO_3^- yields were lowest in July ($0.53 \text{ kg m}^{-2} \text{ d}^{-1}$) and peaked in August ($0.57 \text{ kg m}^{-2} \text{ d}^{-1}$). For the Lake-influenced catchment, yields were lowest in June ($0.14 \text{ kg m}^{-2} \text{ d}^{-1}$) and largest in July ($0.33 \text{ kg m}^{-2} \text{ d}^{-1}$; Figures 3b and 3c).

Water yields explained only 43% and 50% of the variance in daily NO_3^- yields in the River-dominated and Lake-influenced catchments, respectively. Median NO_3^- to water yield ratios (i.e., flow-weighted concentrations) were significantly different between catchments across all flow conditions, with River-dominated catchments having higher overall flow-weighted concentrations than the Lake-influenced catchments (Kruskal $p < 0.001$; Figure 4). In the River-dominated catchment, median flow-weighted NO_3^- concentrations generally increased from high to low flows, though there was no change in median flow-weighted NO_3^- yield between dry and low flows (Kruskal $p = 0.09$). Median flow-weighted NO_3^- concentrations remained stable across high to dry flows before increasing under low flow conditions (Figure 4). The Lake-influenced catchment exhibited significant monthly changes in overall median flow-weighted NO_3^- concentrations (Kruskal $p < 0.0001$), which were largest in July (Figure S7 in Supporting Information S1). We found that this seasonal increase is likely due to statistically significant changes in flow-weighted NO_3^- concentrations at mid-range (Kruskal $p < 0.01$) and dry flows (Kruskal $p < 0.01$), which increased between June and July (Figure S7 in Supporting Information S1). In contrast, the River-dominated catchment did not show any significant seasonal changes in overall monthly median flow-weighted NO_3^- yields (Kruskal $p = 0.89$; Figure S7 in Supporting Information S1).

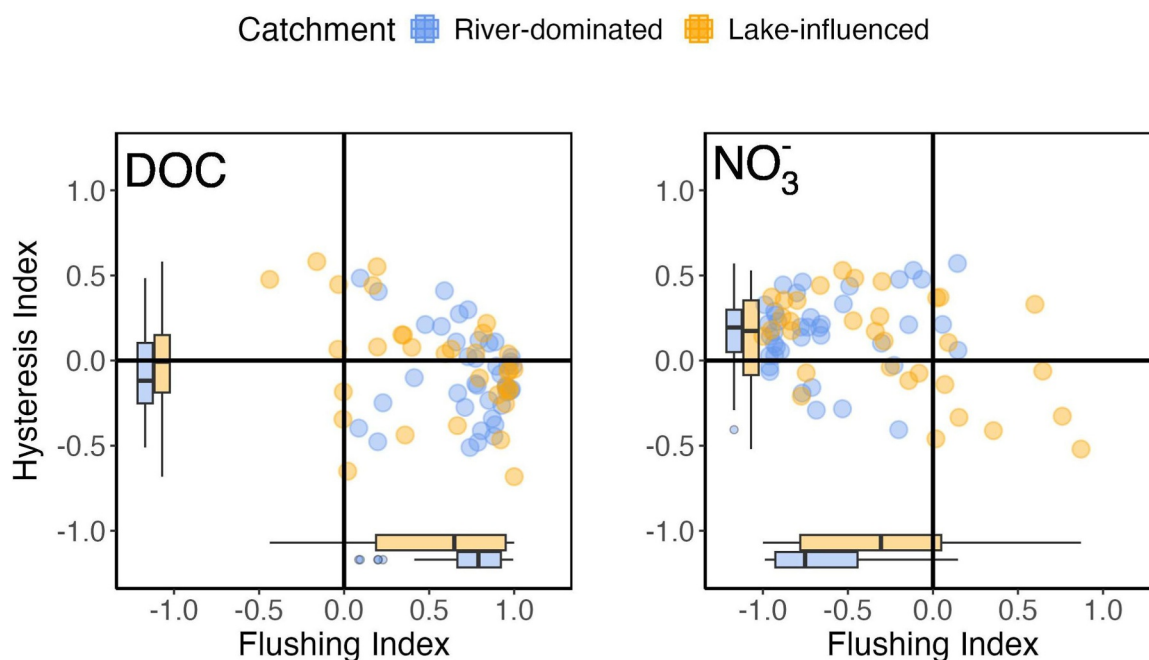


Figure 6. Storm-event hysteresis index (HI) versus flushing index trends for dissolved organic carbon (left) and NO_3^- (right) in the River-dominated (blue) and Lake-influenced (orange) catchments. Boxplots depict the distribution and median HI (y-axis) and flushing index (x-axis) behaviors for each catchment and solute.

3.3. Storm Solute Dynamics

3.3.1. DOC Yields During Storm Events

We analyzed 39 total storms in the River-dominated catchment and 30 in the lake-influenced catchment throughout the 2017–2019 and 2021–2023 thaw seasons (storm characteristics are summarized in Table S2 in Supporting Information S1). While we were unable to capture every storm event within the 6-year period, we found that storm events contributed on average $59.1 \pm 12.6\%$ and $37.9 \pm 19.9\%$ of total annual DOC yields in the River-dominated and Lake-influenced catchments, respectively. Between catchments, peak storm discharge was generally larger and explained a greater proportion of the variance in storm DOC yields in the River-dominated catchment (median peak storm $Q = 7.09 \text{ m}^3 \text{ s}^{-1}$; $R^2 = 0.778$) than in the Lake-influenced catchment (median peak storm $Q = 5.01 \text{ m}^3 \text{ s}^{-1}$, $R^2 = 0.559$). However, we did not find a significant difference in median storm DOC yields (Wilcox $p = 0.4$) between catchments (River-dominated median storm DOC yield = 64.1 kg km^{-2} ; Lake-influenced median storm DOC yield = 47.5 kg km^{-2} ; Figure 3a).

3.3.2. NO_3^- Yields During Storm Events

Storm events accounted for $49.8 \pm 11.2\%$ of total annual NO_3^- yields in the River-dominated catchment and $30.9 \pm 20.3\%$ in the Lake-influenced catchment. Median storm NO_3^- yields were nearly four times greater in the River-dominated catchment (median storm NO_3^- yield = 2.63 kg km^{-2}) than in the lake-influenced catchment (median storm NO_3^- yield = 0.695 kg km^{-2} ; Figure 3a). In contrast to DOC yields, peak storm discharge explained only 59.9% and 23.9% of the variance in storm NO_3^- yields in River-dominated and Lake-influenced catchments, respectively (Figure S6 in Supporting Information S1).

3.3.3. Hysteresis and Flushing Behaviors

Storms in both catchments exhibited frequent clockwise and anticlockwise DOC hysteresis patterns, with median DOC HI near zero and no significant difference in median (Wilcox $p = 0.36$) or variance (Levene's $p = 0.53$) between catchments (Figure 6a). Both catchments showed clockwise typical NO_3^- hysteresis patterns during storm events, with positive median NO_3^- HI though no significant difference in median (Wilcox $p = 0.562$) or variance (Levene's $p = 0.35$) between catchments (Figure 6b).

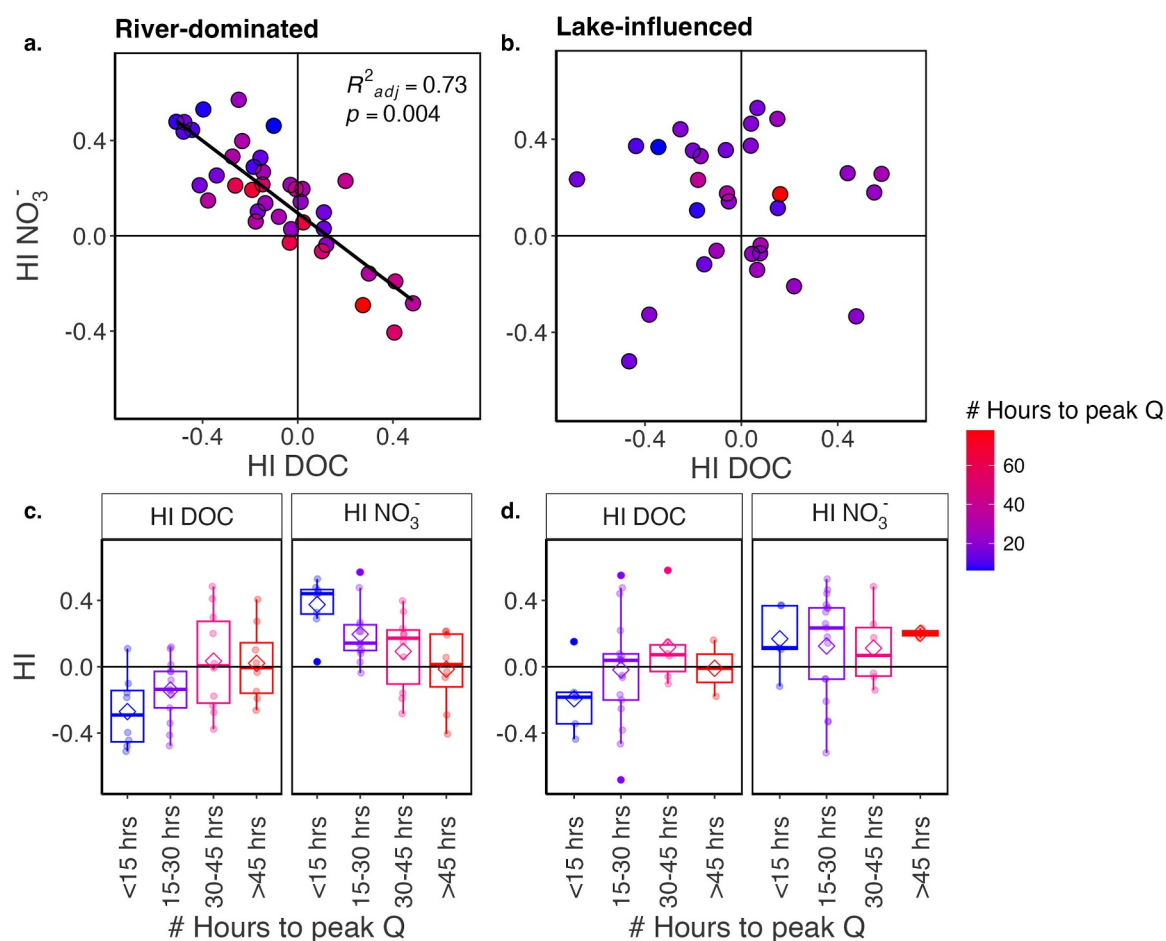


Figure 7. Storm-event dissolved organic carbon (DOC) versus NO_3^- hysteresis index behaviors for the River-dominated catchment (a) and Lake-influenced catchment (b). Points are shaded according to the length of time in hours from storm start to peak discharge (i.e., storm flashiness), with blue points indicating storms with rapid increase to peak storm discharge and red indicating storms with longer, gradual increase to peak storm discharge. Boxplots are provided to illustrate the distribution of DOC and NO_3^- hysteresis behaviors during storms binned by length of time in hours from storm start to peak discharge in the River-dominated catchment (c) and Lake-influenced catchment (d).

Plotting storm HI versus storm flushing index revealed consistent enriching behaviors (positive FI) for DOC and consistent diluting behaviors (negative FI) for NO_3^- within both catchments (Figure 6). Median DOC and NO_3^- FI during storms in the River-dominated catchment were larger in magnitude than in the Lake-influenced catchment, and there was a significant difference in NO_3^- FI between catchments (Wilcox $p = 0.005$). We found that variance in both NO_3^- and DOC FI differed significantly between catchments, with the Lake-influenced catchment exhibiting higher variance in both NO_3^- (Levene's $p < 0.01$) and DOC FI (Levene's $p < 0.001$). We did not find a significant effect of month on DOC or NO_3^- FI in either catchment (Kruskal $p > 0.05$).

Storms in the River-dominated catchment showed a significant negative linear relationship between HI DOC and HI NO_3^- ($p < 0.001$), while Lake-influenced exhibited no relationship ($p = 0.99$) (Figure 7). Using multiple regression, we tested the effects of several different storm characteristics on the linear model, including storm duration, number of hours to peak discharge (herein, storm flashiness), number of hours between storms, and peak storm discharge. We found that DOC HI and storm flashiness were each significant predictors of NO_3^- HI, together explaining 73% of the variance in NO_3^- HI (Figures 7a and 7c). During the flashiest storms, DOC exhibited anticlockwise rotation, while NO_3^- showed clockwise rotation in the River-dominated catchment (Figure 7c). We also identified a significant effect of month on DOC and NO_3^- HI in the River-dominated catchment (Kruskal $p < 0.01$), and found that median HI decreased in magnitude for both solutes in August

(median DOC and NO_3^- HI ~ 0 ; Figure S8 in Supporting Information S1). We did not find a significant effect of month on DOC or NO_3^- HI in the Lake-influenced catchment (Kruskal $p > 0.05$).

4. Discussion

We used high-frequency sensor data to interpret patterns in DOC and NO_3^- export regimes across flow intensities and timescales in distinct Arctic headwater catchments. In both catchments, high flows dominated cumulative annual DOC and NO_3^- yields, but we found meaningful variability in solute yield magnitude and flow-weighted concentrations across timescales that reflect fundamentally different controls on the abundance and activation of DOC and NO_3^- between River-dominated and Lake-influenced catchments.

In the River-dominated catchment, solute export behaviors were tightly coupled with changes in discharge across timescales (e.g., storm, daily, monthly, and annual), indicating that landscape connectivity is a prevailing control on the activation, mobilization, and transport of DOC and NO_3^- across flow conditions. The Lake-influenced catchment exhibited significant variability in storm C-Q responses and strong seasonal shifts in flow-weighted DOC concentrations, particularly at lower flows, suggesting that in-network lakes regulate solute abundance and mobility by altering hydrologic connectivity, water residence times, and opportunities for biogeochemical processing within the river network. Together, our results demonstrate the utility of high-frequency monitoring in capturing catchment-specific nuances in solute export patterns, and emphasize that accurate characterization of Arctic riverine fluxes must account for variability in flow and landscape characteristics.

4.1. Storm C-Q Reveals Highly Variable Controls on Storm DOC and NO_3^- Export Between Catchments

We used storm-event HI and FI to identify patterns in DOC and NO_3^- export during moments of high connectivity between the upland catchment area and river. Together, the HI and FI can reflect unique physical and hydrological characteristics that regulate solute abundance and source activation within the catchment. The river-dominated and lake-influenced catchments drain low-gradient wet acidic tundra that is characterized by peaty, organic-rich soils and a relatively shallow maximum active layer thickness that thaws during summer months and supports productive vegetation communities (Hinzman et al., 1991; McNamara et al., 2008; Whittinghill et al., 2014; Yi et al., 2018). Tundra soils exhibit strong nitrogen limitation of terrestrial primary productivity and low availability of inorganic N species due to high uptake rates by vegetation and soil microbes (Harms et al., 2016; Keuper et al., 2012). We observed consistent dilution of NO_3^- (-FI) and enrichment of DOC (+FI) in both catchments that reflect source limitation of NO_3^- transport to stream water, and mobilization of the large terrestrial DOC pool from soils to streams during storms. However, we identified meaningful differences between catchments in the patterns of flushing and hysteresis behaviors that suggest distinct catchment controls on solute export during storms. First, the River-dominated catchment exhibited higher overall typical DOC FI, lower overall typical NO_3^- FI, and significantly less variability in overall storm solute flushing behaviors than the Lake-influenced catchment. This suggests that concentrating patterns of DOC and diluting patterns of NO_3^- during storms in the River-dominated catchment exhibit greater coherence between changing solute concentrations and discharge than in the lake-influenced catchment. In other words, patterns of solute export during storms in the River-dominated catchment are more tightly coupled with discharge than the Lake-influenced catchment, likely because the absence of major water storage components promotes more direct hydrologic connectivity between terrestrial source areas and the stream network during storm events.

Second, both catchments exhibited a combination of clockwise (+HI) and anticlockwise (-HI) hysteresis in NO_3^- and DOC concentrations during storm events. High variability in hysteresis patterns indicates the presence of multiple source areas, seasonally evolving hydrologic pathways, and complex mixing dynamics that can challenge our interpretation of catchment-scale controls on solute generation and transport (D'Amario et al., 2021; Shogren et al., 2021; Wymore et al., 2019). By comparing within-catchment trends of solute hysteresis, we found that NO_3^- and DOC hysteresis behaviors in the River-dominated catchment reflected distinct catchment sources but similar mechanisms controlling solute transport. Storm rising limb duration strongly predicted variability in the relationship between NO_3^- and DOC hysteresis behaviors, suggesting that the activation and lateral connectivity of solute reservoirs in the catchment relies on event intensity. In our study, it is during storms with rapid rising limbs when the hydrochemical response is driven by localized direct runoff, NO_3^- sources are rapidly mobilized while subsurface soils and other catchment sources of DOC are least accessible. Conversely, during storms with slower rising limbs, the catchment becomes sufficiently saturated to deplete

terrestrial sources of NO_3^- and hydrologically activate available DOC sources as connectivity between terrestrial source areas and deeper soil horizons increases.

Solute sources in the River-dominated catchment were strongly regulated by hydrologic connectivity in the catchment, though we observed no clear relationships between DOC and NO_3^- hysteresis or storm characteristics within the Lake-influenced catchment. We expect that highly variable hysteresis and transport dynamics in the lake-influenced catchment reflect its complex network structure. In-network lakes can attenuate peak-flows from downstream systems, thereby decoupling hydrological and biogeochemical exports (Arp et al., 2006; Kalinin et al., 2016). In our study catchments, $C-Q$ relationships are also likely to be influenced by the timing of lake mixing, thermal stratification, and autochthonous DOC production during the flow season, which can impact water residence time and opportunities for biogeochemical transformation as water is transported through stream-lake connections (Cortés & MacIntyre, 2020; MacIntyre et al., 2006; Shogren et al., 2021). The biogeochemical response that we observed during storm events in the Lake-influenced catchment may therefore be buffered by lake dynamics that can sequester and transform solutes at timescales not captured within storm $C-Q$ metrics such as hysteresis and FI. This further reinforces the importance of understanding how catchment biogeochemical responses differ across timescales, flow conditions, and landscape types.

4.2. High Flows Dominate Solute Yields Across Timescales

Our storm-event $C-Q$ behaviors contribute to a growing body of literature that suggests that terrestrial DOC pools in the Arctic are abundant and can be mobilized via runoff and subsurface flows, while inorganic N sources are limited and insufficient to elevate ambient river concentrations during precipitation events (e.g., Ågren et al., 2007; Shogren et al., 2021; Townsend-Small et al., 2011). We also found notable variability in hysteresis patterns in both catchments that indicate that several different physicochemical and temporal variables interact to control the transport pathways of both DOC and NO_3^- during storms (e.g., catchment structure and storm characteristics). However, this variability in storm hydrographs and $C-Q$ behavior limits our ability to resolve key structural and functional differences between catchments that impart unique solute export behaviors, including solute export magnitude. However, by partitioning catchment FDCs into distinct flow conditions, we compared central trends in water and solute export dynamics across flows and timescales that are not well-characterized through the analysis of isolated storm-events.

By partitioning catchment FDCs into distinct flow conditions, we were able to compare central trends in water and solute export dynamics across flows and timescales that are not well-characterized through the analysis of isolated storm-events. High and moist flow conditions (0–40th percentile flows) accounted for greater than 75% of annual DOC exports and 55%–65% of annual NO_3^- exports in both catchments. Integrating solute yields during individual storm events showed that a single storm alone can export up to 8.5%–10% of total annual DOC yields, and 6%–8% of total annual NO_3^- yields in the Lake-influenced and River-dominated catchments, respectively. Our yield estimates are of similar magnitude to daily and monthly DOC and NO_3^- solute loads reported in prior studies in the region (e.g., McClelland et al., 2007) and align with findings from relevant studies across biomes, where 60%–99% of annual elemental fluxes have been found to occur at flows that exceed median discharge in temperate, semi-arid, and permafrost catchments (Meybeck & Moatar, 2012; Raymond & Saiers, 2010; Shogren et al., 2020; Speir et al., 2021). Additionally, previous studies of $C-Q$ dynamics in the River-dominated catchment during the Arctic “shoulder seasons” have reported cumulative storm solute yields that rival spring snowmelt DOC exports in magnitude, suggesting that our estimates may even underestimate the influence of storm-events on annual solute fluxes (Shogren et al., 2020).

While River-dominated and Lake-influenced catchments contributed similar proportions of total annual solute yield across flow conditions, catchments differed in export magnitude, particularly at high flows. By analyzing daily solute yields across flow conditions, we found that median daily DOC yields on high-flow days in the Lake-influenced catchment were 20% greater than those in the River-dominated catchment, though this dynamic was not conserved at storm-event timescales and we found no significant difference in storm DOC yields between catchments. While there are many potential causes of this behavior related to our ability to capture a wide range of storm events in each catchment, this discrepancy suggests that catchment storage capacity or processes occurring in the landscape may confound an interpretation of source availability at storm-event timescales. For example, storm solute yields in the River-dominated catchment were well-predicted by peak storm discharge in comparison to the Lake-influenced catchment, suggesting that runoff volume and the absence of major storage components

(e.g., lakes or wetlands) promote direct hydrological connectivity during prolonged storm-flow periods. In contrast, the lack of observable hysteresis, flushing, and solute yield patterns with specific storm characteristics in the Lake-influenced catchment suggests highly variable controls on storm-event fluxes, or perhaps a “threshold decoupling” of runoff and concentration when rich sources of DOC from densely vegetated riparian zones and interspersed wetland areas become overwhelmed or buffered during the storm hydrograph (Lottig et al., 2013; McNamara et al., 2008). While we may lose “resolution” or detectability of DOC source dynamics during prolonged storm-events, daily solute yields during high flows suggest that the Lake-influenced catchment exhibits large instantaneous fluxes of DOC at shorter timescales of high-flow.

4.3. Flow-Weighted Solute Concentrations Inform Functional Drivers of Catchment Solute Generation

Storm-events and high flow episodes can dampen important biogeochemical dynamics that may otherwise provide insight into solute generation processes that occur at lower flows (Moatar et al., 2013; Shogren et al., 2024). Expressing the overall change in solute export patterns across flow conditions as flow-weighted concentration (i.e., solute yield to water yield ratio) allowed us to consider hydrological drivers of solute mobility and infer functional drivers in DOC and NO_3^- generation within and between catchments. In the Lake-influenced catchment, we found that daily flow-weighted DOC concentration was relatively stable across flow conditions, with no significant change in flow-weighted DOC concentration across 0–90th percentile flows. However, this stability was not conserved at monthly timescales. We found that median flow-weighted DOC concentration increased significantly across all months, driven using processes operating at low, dry, and mid-range flow conditions. It was only at these flow conditions that we observed statistically significant seasonal changes in DOC export.

Seasonal increases in flow-weighted DOC concentrations could be partially explained by seasonal thawing of active layer soils throughout the summer, which allows for deeper flowpaths to interact with subsurface sources of DOC (Lafrenière & Lamoureux, 2019). At baseflow and lower flow conditions, when discharge is generated from water stored in the catchment with longer residence time in tundra soils, it is possible that these conditions are accessing seasonally activated sources of terrestrial DOC (Fouché et al., 2017; Neff & Hooper, 2002; Zhang et al., 2017). However, there is much debate surrounding the influence of active layer thaw on DOC availability, as deep subsurface flow paths through newly thawed mineral soils may also facilitate greater adsorption or mineralization of dissolved organic matter and serve as a mechanism for DOC removal in these systems (Harms & Jones, 2012; Maclean et al., 1999; McClelland et al., 2007; Petrone et al., 2006). In-network lakes dispersed throughout the headwaters of the Lake-influenced catchment may also exert significant seasonal controls on DOC and nutrient export. While less affected by hydrologic transport than stream DOC concentrations, lakes can attenuate dissolved DOC and nutrient loads from the landscape while generating autochthonous DOC due to in-lake productivity (Arp et al., 2006; Kalinin et al., 2016). In snowmelt-influenced alpine and subalpine river networks, lake outlet DOC concentrations have been shown to increase throughout the flow season and serve as a DOC source for the downstream network during summer baseflow conditions (Goodman et al., 2011; Kalinin et al., 2016). Further, a study by Goodman et al. (2011) in a Lake-influenced alpine river network found that DOC exports in lake outflows were nearly two times greater than their inflows during baseflow conditions. Although we were unable to identify specific catchment DOC sources in this study, seasonal increases in Lake-influenced catchment DOC exports at dry and low flow conditions may represent an integrated network-scale response to both flow change and season, subsidized by lake and terrestrial DOC exports. Since DOC composition is strongly related to its source and biogeochemical journey from source to stream, further research exploring coupled variability in DOC concentration and composition at lake inlets and outlets is necessary to constrain the effects of lakes on networks with prevalent stream-lake interactions.

In contrast, we did not observe significant seasonal changes in flow-weighted DOC concentrations across months or flow conditions in the River-dominated catchment, suggesting that hydrological rather than temporal controls dominate DOC exports during the June–August portion of the flow season. Furthermore, differences in export behavior may also be influenced by lower soil carbon and nitrogen stocks in the Lake-influenced catchment, which could contribute to differences in source availability between catchments. However, it is important to note that this study does not capture “shoulder season” export behaviors, which can comprise a substantial proportion of annual solute export during the Arctic flow season caused by early season snowmelt (Townsend-Small et al., 2011) or late-season leaching of DOC and nutrients after plant senescence (Shogren et al., 2020).

The Lake-influenced catchment exhibited consistently lower flow-weighted NO_3^- concentrations than the River-dominated catchment across flow conditions. Inorganic nitrogen is scarce in tundra soils and surface waters; therefore, acute NO_3^- limitation in the Lake-influenced catchment is likely exacerbated by a combination of factors operating in the landscape (e.g., denitrification in water-logged tundra soils) and oligotrophic in-network lakes (e.g., biotic assimilation) (Harms et al., 2016; Kling et al., 2000; Shaver & Chapin, 1980). While overall NO_3^- yields increased from low to high flow conditions in both catchments, we found that this trend reversed when controlling for water yield, such that the highest flow conditions generated the lowest flow-weighted NO_3^- concentrations while low flow conditions generated the highest flow-weighted NO_3^- concentrations. In other words, limited NO_3^- source pools and generation processes in the landscape cannot maintain commensurate increases in NO_3^- export with water exports. This pattern is consistent with the diluting patterns of NO_3^- we observed during storm events (−FI) and uniquely reflects both the strength of terrestrial N-limitation as well as the strength of near-stream and in-stream NO_3^- production. For example, these Arctic river corridors can act as powerful reactors, particularly when drier conditions promote nitrification in near-stream oxygenated soils (Kling, 1995; McNamara et al., 2008). Also, when lower flows lead to longer residence times of water in the stream channel, there can be enhanced hyporheic exchange and regeneration of inorganic nutrients (Greenwald et al., 2008; Zarnetske et al., 2007, 2008). These sources of NO_3^- are overwhelmed at higher flows or during storm-events when NO_3^- sources are rapidly depleted. However, our data suggests that the lower flow conditions together (i.e., mid-range, dry, and low flow conditions) comprise over 50% of the average annual exports of NO_3^- in both catchments, suggesting that these catchment conditions are favorable to nitrate production and export.

As Arctic hydrological regimes intensify and storm incidence increases, flow-mediated changes in in-stream nutrient availability and residence time may also alter river ecosystem function (Kendrick et al., 2019; Myrstener, Gómez-Gener, et al., 2021). For example, daily rates of gross primary production in N-limited tundra streams in Arctic Sweden were shown to be tightly constrained by nutrient availability, and exhibited a strong positive correlation with inorganic N concentration during the flow season (Myrstener, Thomas, et al., 2021). Changes in resource supply driven by intensifying hydrological regimes, permafrost degradation, and changing terrestrial nutrient pools may therefore have far-reaching consequences that can alter the net-energy balance of Arctic surface water ecosystems, although these coupled changes remain largely unresolved.

5. Conclusion

This study highlights the critical role of catchment-specific characteristics and hydrological dynamics in shaping coupled exports of water, DOC, and NO_3^- in two Arctic headwater catchments. Our findings revealed that export patterns are strongly modulated by differences in hydrological connectivity, landscape structure, and water storage components, supporting our hypothesis that catchment characteristics drive distinct *C-Q* behaviors. In particular, the River-dominated catchment exhibited more synchronized and predictable *C-Q* behaviors during storm events, with consistent DOC enrichment and NO_3^- dilution reflecting a direct hydrological linkage to abundant DOC and limited NO_3^- sources. Conversely, the Lake-influenced catchment displayed more variable and often decoupled *C-Q* responses, likely driven by internal network mixing and buffering due to lake-induced attenuation and asynchronous source activation. While infrequent, high flows comprised a significant proportion of annual thaw-season solute export budgets in both catchments. Under future Arctic climate change scenarios, our findings suggest that an increase in precipitation, storm incidence, or intensity will likely result in dramatic increases in the lateral transport of carbon and nutrients from the landscape to surface waters, which has far-reaching consequences for downstream ecosystems to the Arctic Ocean (McClelland et al., 2007). Long-term permafrost degradation may further alter the seasonal dynamics we document here in ways that our 6-year record cannot resolve. The upper Kuparuk River has shown increasing discharge-corrected NO_3^- concentrations and declining DOC concentrations across decadal timescales, which have been attributed to deepening groundwater flow paths and increased mineral soil sorption of dissolved organic matter as permafrost thaws (Kendrick et al., 2018). These trajectories suggest that the seasonal active layer dynamics and terrestrial source pools that regulate solute export in our study catchments are likely shifting over longer timescales, and that continued high-frequency monitoring at these sites will be essential to detect these changes.

Our findings also highlight the limitations of relying solely on storm-event metrics to characterize catchment source dynamics or low frequency (e.g., monthly) monitoring efforts to capture solute exports. While storm events contributed disproportionately to annual thaw-season solute fluxes in both catchments, high daily DOC yields and shifting flow-weighted concentrations at longer timescales revealed emergent source dynamics that

were not detectable during individual storms. Notably, the Lake-influenced catchment exhibited signs of a seasonal transition in DOC source and lake-subsidized baseflow contributions, while the River-dominated catchment maintained a more hydrologically controlled pattern of progressive DOC source activation. Similarly, while NO_3^- exhibited consistent dilution patterns during high flows, flow-weighted concentrations at low to moderate flows reveal the strength of in-stream or near-stream nitrification—insights that would be overlooked without examining daily and monthly patterns.

Together, these findings emphasize that the solute export regime is not a fixed attribute of a catchment, but a dynamic property shaped by both flow condition and temporal resolution. Accounting for variability in solute availability, hydrological connectivity, and landscape buffering across timescales is essential to accurately quantify and interpret riverine carbon and nutrient fluxes in Arctic catchments.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

Daily estimated solute yields, flow-weighted concentrations, and water yields are freely available through the Arctic Data Center (ADC) (Rec et al., 2026a), along with storm-event solute yield data and storm characteristics (Rec et al., 2026b), and high-frequency solute data from 2017 to 2019 and 2021–2023 used in our analyses (Rec et al., 2026c). Discharge data associated with this manuscript were collected by the Arctic LTER program and are published separately by the Arctic LTER on the Environmental Data Initiative (EDI) data portal. The ADC and EDI are permanent data repositories that follow CARE data management principles (Collective Benefit, Authority to Control, Responsibility, and Ethics), which complement the FAIR principles (Findable, Accessible, Interoperable, and Reproducible) promoted by AGU's open data policies.

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