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# Hydrological and catchment controls on event-scale dissolved organic carbon dynamics in boreal headwater streams

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Running Title: Controls on stream DOC in boreal forests

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/hyp.14279

## ABSTRACT

Hydrological events transport large proportions of annual or seasonal dissolved organic carbon (DOC) loads from catchments to streams. The timing, magnitude and intensity of these events are very sensitive to changes in temperature and precipitation patterns, particularly across the boreal region where snowpacks are declining and summer droughts are increasing. It is important to understand how landscape characteristics modulate event-scale DOC dynamics in order to scale up predictions from sites across regions, and to understand how climatic changes will influence DOC dynamics across the boreal forest. The goal of this study was to assess variability in DOC concentrations in boreal headwater streams across catchments with varying physiographic characteristics (e.g. size, proportion of wetland) during a range of hydrological events (e.g. spring snowmelt, summer/fall storm events). From 2016 to 2017, continuous discharge and sub-daily chemistry grab samples were collected from three adjacent study catchments located at the International Institute for Sustainable Development – Experimental Lakes Area in northwestern Ontario, Canada. Catchment differences were more apparent in summer and fall events and less apparent during early spring melt events. Hysteresis analysis suggested that DOC sources were proximal to the stream for all events at a catchment dominated by a large wetland near the outlet, but distal from the stream at the catchments that lacked significant wetland coverage during the summer and fall. Wetland coverage also influenced responses of DOC export to antecedent moisture; at the wetland-dominated catchment, there were consistent negative relationships between DOC concentrations and antecedent moisture, while at the catchments without large wetlands, the relationships were positive or not significant. These results emphasize the utility of sub-daily sampling for inferring catchment DOC transport processes, and the importance of considering catchment-specific factors when predicting event-scale DOC behaviour.

## KEY WORDS

Dissolved organic carbon; hysteresis; storm event; snowmelt; solute export; climate change; boreal forest; antecedent moisture

## INTRODUCTION

The boreal ecozone is a complex mosaic of lakes, streams, wetlands and forests that contain vast stores of carbon (Kurz et al., 2013). Understanding how watersheds and aquatic ecosystems process carbon is important for protecting water quality and for understanding the global carbon balance (Cole et al., 2007; Tranvik et al., 2009). Dissolved organic carbon (DOC) also plays an integral role in the biogeochemistry and ecology of surface waters in forested watersheds (Schiff, Aravena, Trumbore, & Dillon, 1990; Dillon & Molot, 1997; Laudon et al., 2012). It has strong effects on physical properties such as light attenuation (and subsequently the depths of both the thermocline and photic zone), lake heat budgets, and autotrophic productivity that sustains aquatic food webs (Ask et al., 2009; Seekell, Lapierre, & Karlsson, 2015). Dissolved organic carbon provides an important energy and nutrient source for primary productivity (Dillon & Molot, 1997; Creed, Beall, Clair, Dillon, & Hesslein, 2008; Eimers, Buttle, & Watmough, 2008), is important in the mobility, persistence and toxicity of metals (complexation), and affects the acid-base chemistry of surface waters (Schiff et al., 1990; Dillon & Molot, 1997; Gergel, Turner, & Kratz, 1999; Eimers, Watmough, Buttle, & Dillon, 2008). Given the importance of DOC to freshwater systems, there has been substantial research attention given to its fate under a changing climate.

There is substantial evidence that transport of DOC to lakes and streams across the Northern Hemisphere is changing in response to declines in sulphate deposition (i.e. recovery from acid rain) and changing precipitation patterns associated with climate change (Monteith et al., 2007, Imtiazy et al. 2020). Increased temperatures and intensifying hydrological regimes are fundamentally altering catchment hydrology and carbon (C) cycling (Campbell, Driscoll, Pourmokhtarian, & Hayhoe, 2009), which ultimately impacts DOC export to streams and lakes and aquatic ecosystem functions (Solomon et al., 2015). Observational studies have demonstrated that these changes are not uniform across the landscape; for instance, adjacent streams can have opposite trajectories of changes in DOC loading, particularly when they differ in terms of the location and organization of wetlands within the catchments (Schiff et al., 1998).

Dissolved organic carbon export to streams and lakes depends on the magnitude and connectivity of sources of DOC within catchments as well as hydrological dynamics (Hinton, Schiff, & English, 1997; Richardson, 2012; Lambert et al., 2013; McGlynn & McDonnell, 2003b). Hydrological connectivity between DOC sources and the surface waters draining the catchment varies through time as flowpaths are activated during runoff events; these events are key in deciphering patterns and dynamics of DOC across the landscape (Ågren et al., 2008; James & Roulet, 2009; Laudon et al., 2011).

Forested wetlands are hot spots of C accumulation due to saturated conditions and low rates of decomposition (Moore, Roulet, & Waddington, 1998; Creed et al., 2008). The proportion of wetlands within catchments is perhaps the single most important determinant of the magnitude of DOC export at local to regional scales (Eckhardt & Moore, 1990; Creed et al., 2008; Laudon et al., 2011). Patterns of DOC export also depend on the presence and spatial arrangement of wetlands. Streams draining wetland-dominated catchments maintain high concentrations of DOC under baseflow conditions, but concentrations may decrease during spring runoff due to dilution (Ågren et al., 2008; Eimers, Buttle, & Watmough, 2008; Laudon et al., 2011). Conversely, DOC concentrations from catchments with little or no wetland coverage peak before discharge during snowmelt and then decline rapidly as rising water tables flush out DOC-rich soil water (Hornberger, Bencala, & McKnight, 1994; Boyer, Hornberger, Bencala, & McKnight,1997; McGlynn & McDonnell, 2003b; van Verseveld, McDonnell, & Lajtha, 2008). This same pattern has been observed during summer storms in catchments dominated by mineral soils (Inamdar & Mitchell, 2006). Furthermore, wetland hydrology and C cycling are very sensitive to climate change, particularly hydrological intensification (Creed, Hwang, Lutz, & Way, 2015).

At northern latitudes, increasing temperatures and increasing variability in precipitation patterns are projected over the next few decades (Collins et al., 2013). Shifts in the seasonal distribution of precipitation and more frequent and intense events could impact DOC cycling. For example, events that result in preferential subsurface or saturated overland flow through the upper soil horizons from intense summer or fall rain events could result in larger pulses of DOC concentration in streams (Hornberger et al., 1994; McGlynn & McDonnell, 2003b); these pulses may have important biological implications by influencing stream water acidity, metal mobility, and speciation (Eimers, Watmough, Buttle, & Dillon, 2008). The magnitude of DOC response to high flow events depends on the season, catchment antecedent moisture conditions and the duration and extent of the storm (McClain et al., 2003; Inamdar, O'Leary, Mitchell, & Riley, 2006). In wetland-dominated catchments, high DOC concentration pore waters from wetlands can mix with more dilute, new event water, resulting in lower DOC concentrations at the peak of storms (Laudon, Sjöblom, Buffam, Seibert, & Mörth, 2007; Vidon et al., 2010; Tiwari, Sponseller, & Laudon 2019). The predicted changes in intensity and frequency of storms due to climate change will have important implications for the export of DOC from catchments, although the direction and magnitude of the response may vary across the landscape (Inamdar et al., 2006).

Given the importance of storm events to DOC dynamics and their sensitivity to climate change, there is a pressing need to understand within-storm DOC dynamics. A widely-used approach is to examine concentration-discharge (c-Q) relationships to investigate how solute (in this case, DOC) sources and transport vary by hydrological condition and watershed characteristics (Basu et al., 2010). Examining the hysteretic behavior of DOC during storm events can also yield valuable insights into source and transport dynamics (Vaughan et al., 2017; Werner et al., 2019). The direction of change in DOC concentration relative to discharge over the course of the event can infer whether DOC sources are near to and/or spatially connected to the stream or far from and/or spatially disconnected from the stream (McGlynn & McDonnell 2003a). Patterns of hysteresis can vary seasonally; during dry summers and early fall months, increased DOC concentrations in wetland pore water can arise as a result of low flushing and high decomposition rates under lower water tables and warmer conditions (Moore, Matos, and Roulet, 2003; Schiff et al., 1998). However, work from other sites has found that season matters less than antecedent conditions in predicting hysteretic behavior (Vaughan et al. 2017; Vaughan, Bowden, Shanley, Vermilyea, & Schroth, 2019).

The goal of this study was to assess variability in DOC concentrations in boreal headwater streams across catchments with varying physiographic characteristics (e.g. size, proportion of wetland) during a range of hydrological events (e.g. spring snowmelt, summer/fall storm events). To address this goal, we addressed two specific research objectives across three forested catchments of varying size and wetland proportions:

1. Compare DOC transport dynamics among high flow events (i.e., spring snowmelt, summer/fall storms) to evaluate how sources and flowpaths of DOC vary among events and catchments; and,
2. Investigate variability in the relationship between DOC concentration and a) discharge (Q) and b) antecedent moisture condition (AMC) among seasons and catchments.

## METHODS

### *Study Site*

The International Institute for Sustainable Development - Experimental Lakes Area research station (IISD-ELA) is located approximately 55 km east southeast of Kenora, Ontario, Canada (49°40’N and 93°44’W, at 360-380 metres above mean sea level) (Brunskill & Schindler, 1971; Schindler et al., 1996). Several dozen lakes were set aside for whole ecosystem studies as well as several long-term reference lakes to monitor changes to meteorology, hydrology and the physical, chemical and biological properties of lakes and their respective watersheds (Parker, Schindler, Beaty, Stainton, & Kasian, 2009). The reference lake with the longest record (1969-present) and most thoroughly studied catchment and lake system at IISD-ELA is Lake 239 (L239; Figure 1). Lake 239 drains three small catchments (see below for details) via first-order streams as well as a larger, ungauged area (Schindler et al., 1996). Soils in these three catchments are thin orthic brunisols, generally <1m in depth covering pink Precambrian granodiorite (Brunskill & Schindler 1971; Parker et al., 2009). Forests consist of old-growth *Pinus banksiana*, *Picea glauca*, and *Picea mariana* with smaller quantities of *Populus* *tremuloides, Betula papyrifera,* and *P. resinosa* with a well-developed understory of mosses and smaller vascular plants (Brunskill & Schindler, 1971; Parker et al., 2009). These catchments do not have any logging or management history; however, a major windstorm and two fires swept parts of the L239 catchment during the 1970s and 1980s, although the effects of this fire on streamflow and chemistry are hard to disentangle from concurrent changes in climate (Emmerton et al., 2018).

The largest catchment (1.7 km$^2$) of L239 is at the eastern side of the lake (herein referred to as the 'upland-large') and is well defined by a bedrock ridge with a maximum elevation of 67 m above lake level. About 80% of this catchment is forested upland, 10% rock outcrop, 6% valley bottom, and 4% wetland (Schindler et al., 1996). A small wetland is in the upper portion of the catchment with the lower part dominated by deep glacial overburden with quaternary deposits of sand and till (Schindler et al., 1996). A narrow (0.4 – 1.0 m) stream channel runs a length of approximately 1.4 km with a small delta at the stream mouth as it enters L239 (Parker et al., 2009). Vegetation and soils within this upland-large catchment were heavily damaged by a large windstorm (1973) and subsequent (1974, 1980) forest fires that took years to decades to recover from (Schindler et al., 1996; Parker et al., 2009). The northwest catchment (herein referred to as the 'upland-small') is the second largest (0.56 km$^2$) and is largely upland with forest cover similar to the upland-large catchment. It was slightly damaged in the 1973 windstorm and extensively burned during the 1980 fire. This catchment consists of a small (<0.02 km$^2$) wetland near the bottom of the catchment, which represents ~3.5 % of the catchment area, before a short stream segment (~100 m) enters L239 (Schindler et al., 1996; Parker et al., 2009). The northeast catchment (herein referred to as 'wetland-dominated') is the smallest of the three catchments (0.12 km$^2$) and contains a wooded *Sphagnum* bog (0.04 km$^2$) near the lower end that comprises ~ 30% of the catchment area. The upland part of the wetland-dominated catchment was damaged in the 1973 windstorm and most, including half of the wetland, was burned in the 1974 fire and again in the 1980 fire (Brunskill & Schindler, 1971; Schindler et al., 1996; Parker et al., 2009).

### ***Sample Collection***

Stage levels at each of the three catchment weirs were recorded using either an OTT Thalimedes or Sutron Stage Discharge Recorder at 10-minute intervals, downloaded weekly, and then converted to discharge volumes (m$^3$ s$^{-1}$) using rating curves for each of the three respective catchments. Discharge data were summed to hourly and daily time steps.

Samples for water chemistry were typically collected weekly (occasionally bi-weekly or longer during 'no flow' periods) during the ice-free season at each of the weirs of the three monitored catchments. Grab samples were collected twice daily during the beginning of the snowmelt period (24 February 2017 – 19 April 2017). We also collected higher frequency water samples during storm events in the summer and fall of 2016 (1 August 2016 – 31 October 2016) and from 2 May 2017 until 23 September 2017 (herein referred to as the "field season") using automated Teledyne ISCO 6712 full-size portable water samplers (referred to as 'ISCOs'). The ISCOs at each of the three study sites were equipped with a Teledyne ISCO 1650 liquid level actuator conductivity probe that was triggered by an increase in stream stage level during storm events. Samples were then collected at a frequency of 1– 12 hours for the duration of the storm, with the frequency varying among events. There were two major gaps in sampling during 2017: from 11

August and 15 September, 2017 because all three streams ceased flowing due to dry conditions; additionally, samples were also not available for the upland-large catchment between 14 July and 15 September due to rodent damage to the actuator cables. Routine samples, spring grab samples and ISCO storm samples were combined to make the complete field season dataset. We immediately filtered all samples through a pre-ignited (at 550°C for 16 hours) Whatman 42.5 mm glass fiber filters (GF/F) and stored at 4°C for further analysis. We performed DOC analysis with the Shimadzu TOC VCPH + TNM-1 Total Organic Carbon and Total Nitrogen Analyzer with Gas Purification Kit. The data that support the findings of this study are openly available through the Lake Winnipeg DataStream (IISD-Experimental Lakes Area, 2019).

### *Data analysis*

To investigate DOC transport dynamics in each catchment, we performed three different analyses on the high flow events. First, we used qualitative hysteresis loops and quantitative hysteresis and flushing indices to investigate the DOC response in streams to high flow events across the three catchments. This approach assesses whether DOC transport within the catchments was transport-limited or source-limited, increased or decreased on the rising limb of the snowmelt or storm hydrographs and whether these responses varied by hydrological condition. Second, we evaluated c-Q relationships from the entire field season dataset to assess how patterns and controls on DOC dynamics vary among catchments and seasons. Finally, we evaluated the correlations between antecedent moisture conditions (AMC) and stream DOC concentrations at the three catchments.

We manually delineated high flow events using the discharge volumes, rainfall records and the dates and times at which the ISCO automatic water samplers were initiated. Events were retained for analysis if there were at least two DOC samples collected on the rising limb and two collected on the falling limb. High flow events were categorized as: 1) Early Snowmelt (first peak of snowmelt), 2) Late Snowmelt (second peak of snowmelt), 3) Summer (June, July, August), or 4) Fall (September, October, November).

We calculated a quantitative hysteresis index (HI) and a flushing index (FI) for each storm. The hysteresis index is based on normalized discharge and storm DOC concentrations (Lloyd, Freer, Johnes, & Collins, 2016b; Vaughan et al., 2017), as follows:

$$Q_{i,norm} = \frac{Q_i - Q_{min}}{Q_{max} - Q_{min}} , \qquad \text{(Equation 1)}$$

$$C_{i,norm} = \frac{C_i - C_{min}}{C_{max} - C_{min}} , \qquad \text{(Equation 2)}$$

where $Q_i$ and $C_i$ are the normalized (range = 0 to 1) and unitless discharge and solute concentration values at time $i$, $Q_{max}$ and $Q_{min}$ are the maximum and minimum discharge values in the storm, and $C_{max}$ and $C_{min}$are the maximum and minimum DOC concentrations of the storm (Vaughan et al., 2017). We interpolated the DOC concentration by linear regression at 10% intervals of the normalized discharge on both the rising and falling limbs using two adjacent measurements (Vaughan et al., 2017). We determined the hysteresis index at each discharge interval ($HI_j$) by subtracting the normalized falling limb concentrations ($C_{j,falling}$) from the rising limb concentrations ($C_{j,rising}$):

$$HI_j = C_{j,rising} - C_{j,falling.} \qquad \text{(Equation 3)}$$

We only calculated the HI for intervals where data existed for both the rising and falling limbs because not all high flow events returned to their initial discharge condition (Lloyd et al., 2016b; Vaughan et al., 2017). We chose a 10% discharge interval because there were enough samples on both limbs to accommodate a simple linear regression interpolation of concentration measurements. A positive HI indicates that DOC sources are close to the stream, while a negative HI indicates that DOC sources are located distal to the stream (Lloyd et al., 2016b; Vaughan et al., 2017). This proximity can either be spatial or temporal, with deeper flowpaths taking a longer time to reach the stream outlet (Evans and Davies, 1998).

We characterized high flow events using a FI which was calculated by subtracting the normalized DOC concentration (Equation 2) at the beginning of the high flow event ($C_{initial,norm}$) from the normalized DOC concentration at the peak of the high flow event ($C_{Qpeak,norm}$) using Equation 4 (FI; Vaughan et al., 2017):

$$FI = C_{Qpeak,norm} - C_{initial,norm\,.} \qquad \text{(Equation 4)}$$

Positive FI values indicate increased DOC concentration or "flushing" on the rising limb of a snowmelt or storm hydrograph; negative FI values indicate a diluting effect with declining DOC values on the rising limb of the hydrograph.

We evaluated relationships between DOC concentration and discharge (c-Q) on a seasonal basis by calculating the slope (β) of the c-Q relationships and the ratio of the coefficients of variation between concentration and discharge ($CV_c/CV_q$). The combination of these two metrics helped categorize weak c-Q relationships (Musolff, Schmidt, Selle, & Fleckenstein, 2015). If β is ~0, and $CV_c/CV_q$ is low, this may indicate chemostasis. If β is ~0, and $CV_c/CV_q$ is high, this may indicate that concentration varied significantly, but independently of discharge. Generally, four possible relationships exist: 1) chemodynamic "up" (when β is positive) which is described as transport-limited since delivery to the stream is dependent on the capacity of the catchment to move the DOC and not by DOC availability or production; 2) chemodynamic "down" behavior (when β is negative) is attributed to dilution during high flows and are described as source-limited since delivery to the stream is determined by DOC abundance rather than the ability of the catchment to transport them to the stream (Moatar, Abbott, Minaudo, Curie, & Pinay, 2017); 3) chemostatic or flat behavior (when β is approximately 0 and $CV_c/CV_q$ is low) which is attributed to homogenous and uniform distribution of elements in the catchment indicating that changes in hydrological connectivity and flowpath do not affect DOC concentration (Moatar et al., 2017); and 4) where DOC concentration varied independently of discharge (i.e. when β is approximately 0 and $CV_c/CV_q$ is high). The β parameter was considered to be approximately 0 when the slope of the c-Q line was not significant (Moatar et al., 2017).

Finally, we correlated DOC concentrations with measures of antecedent moisture during the summer and fall. We were unable to assess antecedent moisture during the spring, as very few discharge measurements were taken prior to the onset of snowmelt. We estimated the antecedent moisture conditions (AMC) by summing the discharge measurements for different time periods: 2 days prior to the date of measurement, 7 days prior and 14 days prior. We used these measurements of the AMC as a proxy for catchment saturation conditions (Ali & Roy, 2010). We tested relationships between discharge and each of the AMC (2, 7 and 14 days) and DOC concentrations on the date in question using Pearson's correlation coefficients. We also assessed the correlations between discharge and each of the AMC using Pearson's correlation coefficients. All correlations were performed at a significance level of $\alpha = 0.05$.

## RESULTS

### ***Field Data Summary***

During the study period, total discharge from these catchments ranged from 302 mm to 385 mm with the highest water yield occurring in the wetland-dominated catchment. Spring and Fall periods had very similar levels of discharge in all catchments, ranging from 101 mm season$^{-1}$ to 144 mm season$^{-1}$. The Summer period had the lowest total discharge ranging from 49 mm season$^{-1}$ to 90 mm season$^{-1}$, which was ~40-60% lower than during the Spring or Fall periods (Figure S1). Measurable snowmelt began on March 26, 2017 and continued for 24 days until April 19, 2017. During the summer, there was a period of negligible precipitation, which caused all three streams to cease flowing from August 11 until September 15, 2017, when a storm event with more than 40 mm of precipitation fell in one 24-hour period and resulted in streamflow within all three catchments (Figure S1). Dissolved organic carbon concentrations were consistently highest at the wetland-dominated catchment (ranging from 12.6 – 78.7 mg L$^{-}$1) compared with the upland-large catchment (ranging from 11.3 – 30.2 mg L$^{-}$1) and the upland-small catchment (ranging from 11.0 – 41.4 mg L$^{-}$1) (Figure S2).

### *Hysteresis Analysis*

The HI was negative for all high flow events within the two upland dominated catchments (median for the upland-large = -0.386; median for the upland-small = -0.213), except during early snowmelt (upland-large HI = 0.183; upland-small HI = 0.398) (Figure 2). The FI was generally positive across all seasons for streams within the upland dominated catchments, with a single exception during early snowmelt in the upland-small catchment, where FI values were negative. While there were distinct patterns associated with the early snowmelt event, the late snowmelt, fall and summer events were not substantially different in terms of the FI and HI values at these upland-dominated catchments. In contrast to the upland dominated catchments, the HI index was positive for all events in the wetland-dominated catchment (median = 0.304) and the FI values spanned a range from -0.672 to +1.000 (Figure 2).

### *Concentration-discharge relationships*

Relationships between DOC and discharge were significant and moderately negative for both the wetland (p = <0.0001, $r^2$ = 0.427, β = -0.159) and upland-small (p = <0.0001, $r^2$ = 0.544, β = -0.118) catchment in the spring. The remaining relationships were chemostatic, which was indicated by low $r^2$ values, high p values, β values close to 0 and low $CV_c/CV_q$ values suggesting that DOC concentrations were independent of discharge (Figure 3).

### *Antecedent Moisture Conditions*

There were significant correlations between discharge and AMC, with the strength of the correlation declining as the length of the AMC increased (Table S1). In all but one case, the correlation between discharge and DOC concentration was not as strong as the relationship between discharge and each AMC. The upland-large catchment exhibited positive relationships with DOC for each AMC during both the summer and the fall (correlation coefficients ranging from 0.323 to 0.677; $p<0.001$); there was no significant relationship between DOC and discharge during the summer ($p>0.05$), and only a weak relationship during the fall ($r = 0.292$; $p = 0.04$; Table 1). The pattern was opposite in the wetland-dominated catchment in the summer, where correlations between DOC concentrations were negative for each AMC in the summer (correlation coefficients ranging from -0.460 to -0.721; $p<0.001$), while in the fall there was only one significant positive relationship with the 2-day AMC ($r = 0.372$; $p = 0.02$). There was a weak negative correlation with discharge in the summer ($r = -0.290$; $p = 0.02$) and no significant correlation with discharge in the fall (Table 1).. The upland-small catchment exhibited generally poor relationships between AMC and DOC concentration except for two relationships in the fall for the 7-day ($r = -0.378$, $p = 0.01$) and 14-day AMCs ($r = -0.533$, $p <0.001$); Table 1) The summertime at the upland-small catchment was the one exception where the correlation was stronger with discharge ($r = 0.248$; $p = 0.04$), while there were no significant relationships with any AMC.

## DISCUSSION

Storm and snowmelt events play an important role in the transport of DOC from catchments to streams (Raymond & Saiers, 2010; Casson et al., 2014), and the timing and magnitude of DOC export is highly dependent on event characteristics (Inamdar et al., 2006). Given the projected changes in the timing and magnitude of snowmelt and the frequency and intensity of precipitation associated with climate change, understanding event-scale dynamics is critical for projecting C losses from catchment soils and wetlands to receiving waters, effects on a wide range of limnological processes and the subsequent degradation of DOC and enhanced losses of $CO_2$ to the atmosphere (e.g. Hall et al. 2018). This study examined how catchment characteristics (e.g.. size and proportion of wetland) affected DOC transport dynamics during high flow events and the relationship between AMC and DOC concentrations. At the wetland-dominated catchment, DOC sources were proximal to the stream for all events. Conversely, hysteresis analysis at the upland-dominated catchments suggested that DOC sources were located distal to the stream, except during the early snowmelt period. These upland-dominated catchments exhibited transport-limited dynamics; delivery of DOC to the stream was dependent on the capacity of the catchment to move the solute and not by the DOC availability or production capacity of the catchment (Moatar et al., 2017). Catchment features also influenced responses of DOC export to AMC. At the wetland-dominated catchment, DOC tended to decrease as AMC increased throughout the summer. The upland-large catchment responded in the opposite way; DOC concentrations increased with increased moisture within the catchment, while the upland-small catchment had few significant relationships between DOC and AMC. These results also emphasize the importance of considering catchment-specific factors when predicting event-scale DOC behaviour.

### ***Dissolved organic carbon transport dynamics during high flow events***

The three catchments at IISD-ELA displayed different seasonal hysteretic DOC transport dynamics. The early snowmelt phase was distinct from other events, in that the hysteresis dynamics were consistent across catchments. Positive HI values during this phase suggest a dominance of DOC sources located close to the stream. These dynamics are perhaps an indication of shallow, subsurface flowpaths or high concentrations of DOC at the snowpack-soil interface (Sebestyen et al., 2008; Ågren et al., 2010; Casson et al., 2014) that are rapidly mobilized to the stream. Infiltration into frozen soils typically increases as snowmelt progresses (Costa et al., 2017), and therefore differences in catchment topography and flowpaths can become more pronounced as soils thaw and deeper flowpaths are activated. This mechanism is less important in catchments with riparian wetlands, which typically maintain their connection to the stream throughout the winter (Casson, Eimers, Watmough, & Richardson, 2019) and which have larger pools of DOC which can dominate stream DOC export even during snowmelt (Eimers, Buttle, & Watmough, 2008). The magnitude of DOC export during snowmelt and its sensitivity to climate change highlight the importance of understanding catchment-scale controls on transport mechanisms (Ågren et al 2010, Laudon et al 2011).

During late snowmelt, summer and fall events, there were distinct differences in DOC behavior among catchments. At the two upland-dominated catchments, the negative HI and positive FI values are characteristic of an early flush of materials from proximal sources resulting in higher concentrations on the rising limb, followed by enrichment from distal sources later in the event (Creed et al., 1996; McGlynn & McDonnell, 2003b; Hood, Gooseff, & Johnson, 2006; Vaughan et al., 2017). This pattern may arise from change in hydrological connectivity as the storm progressed. High DOC in the wetland or proximal, shallow soil pore water may be flushed in the early part of the event. As the catchment becomes saturated, the upland portion of the catchment becomes hydrologically connected to the stream thereby increasing the contribution of DOC-rich water from uplands during the latter part of high flow events (McGlynn & McDonnell, 2003b). Catchments with a greater proportion of upland or mineral soils typically have a larger proportion of DOC that is adsorbed onto the mineral soils (Qualls & Haines, 1991; Creed, Webster, Braun, Bourbonnière, & Beall, 2013). This adsorption may create a time-lagged transport of DOC to the stream during high flow events (Hagedorn, Scleppi, Waldner, & Flühler, 2000; Inamdar & Mitchell, 2006). The wetland-dominated catchment had positive HI values during all storm events, indicating a dominance of DOC sources proximal to the stream. This catchment has a large wetland located close to the stream outlet which likely sustains high stream DOC concentrations across all event types.

The transport of DOC in forested catchments is sensitive to precipitation events and numerous studies have documented both the importance of storms for DOC export to surface waters (Hinton et al., 1997; Bernal, Butturini, & Sabater, 2002; Wilson, Saiers, Raymond, & Sobczak, 2013) and the role of AMC in regulating DOC concentrations (Biron et al., 1999; Raymond & Saiers., 2010). Storms following drier conditions can result in higher DOC concentrations due to greater accumulation of flushable organic carbon between events and changes in hydrological flowpaths as different areas of a catchment become connected during storm events (Raymond & Saiers, 2010). We found little seasonal difference in the catchment hysteretic behavior between the summer storms following relatively wet conditions and the fall storms which followed a long period of hydrological disconnection. This is in contrast to previous work at a nearby catchment which suggested that wetter AMC may result in enhanced flow through shallow organic soils, and therefore flushing of DOC from these layers (Oswald & Branfireun, 2014). We found more pronounced hysteretic behavior during a late fall event compared with a May event when the ground was still saturated from snowmelt when looking at small sub-catchment units. The HI was negative at the two upland dominated catchments in all cases except for the early snowmelt. This suggests distal sources of DOC during the event, resulting in the peak in concentrations before the peak in discharge. These sources of DOC did not depend on AMC, as the hysteretic behavior was similar during summer and fall.

### ***Relationships with discharge and antecedent moisture***

Classifying relationships between DOC concentration and discharge at seasonal or annual scales can give a great deal of information about catchment behavior and the relative influence of DOC sources vs. hydrological transport in controlling DOC stream concentrations (Creed, McKnight, et al., 2015; Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011). At the IISD-ELA study catchments, seasonal c-Q relationships were generally flat, with the exception of the spring in the wetland and upland-small catchments, when the relationships were moderately negative. While meta-analyses across diverse catchment and land-use types have shown some consistency in predicting DOC from discharge (Zarnetske et al., 2018), work from other small boreal catchments has also suggested that weak c-Q relationships are common, and additional analyses such as including AMC or examining event-scale patterns are needed to understand hydrological controls on DOC concentrations in streams (Oswald & Branfireun, 2014; Ali et al., 2017). The increasing availability of high frequency sondes to measure parameters such as chromophoric dissolved organic matter fluorescence will help elucidate these fine-scale dynamics (Pellerin et al. 2012; Carstea et al. 2020)

The relationships between DOC and AMC help to provide more insight into mechanisms underlying the differences in DOC dynamics among seasons and catchments. While there were correlations between discharge and AMC, in all but one case AMC was a better predictor of DOC compared with discharge, suggesting that antecedent moisture plays an important role in controlling DOC export to streams. At the wetland-dominated catchment, there were inverse relationships between DOC concentration and AMC throughout the summer. This result suggests that the wetland near the outlet was a consistently high supply of DOC to the stream via preferential flowpaths on top of and through the wetland even during dry conditions. As the catchment wets up, this DOC-rich water is diluted by lower concentrations from upland portions of the catchment. Extended droughts, such as the one observed between the summer and the fall period can lead to water table drawdown and increased carbon mineralization in forested wetlands (Creed, Hwang, et al., 2015; Senar, Webster, & Creed, 2018), which can result a flush of high DOC concentrations when the shallow subsurface layers of the wetland reconnect to the stream (Ledesma et al. 2015). Given the projections for increased drought intensity and frequency in this region (Collins et al., 2013), understanding these mechanisms is critical.

Patterns of DOC in the upland-large catchment were opposite from those observed in the wetland-dominated catchment. While the overall concentrations were lower at this catchment compared with the wetland-dominated catchment, DOC concentrations were higher during high flow, likely due to accumulated DOC in the upland portions of the catchment being flushed from the shallow sub-surfaces (Eimers, Buttle, & Watmough, 2008). DOC concentrations peaked after the peak in discharge. In contrast, the upland-small catchment, which had similar hysteretic behavior to the upland-large catchment, did not exhibit any significant relationships between AMC and DOC concentration during the summer and fall seasons. The result at the upland-large catchment follows similar results from other studies that have documented large increases in upland stream DOC concentrations during periods of high flow and were attributed to flushing of DOC sources in the catchment (Boyer et al., 1997; McGlynn & McDonnell, 2003b). Drier conditions in upland-dominated catchments can create disconnected flowpaths which limit the ability of DOC to reach the stream whereas wet conditions promote connectivity. Therefore, as flow increases, DOC is more readily available to be transported to the stream (Boyer et al., 1997; Stieglitz et al., 2003). This positive DOC–AMC relationship in the upland-large catchment may be explained by increased connectivity between saturated areas and a larger proportion of the catchment contributing to runoff as flow increases, even if the total magnitude of the DOC pool is smaller than the pool available to be transported from the wetland. However, the lack of strong results at the upland-small catchment warrants further investigation into how size or arrangement of catchment features might mediate this mechanism.

## CONCLUSIONS

Given the large stores of C in catchments and inland waters across the boreal zone, understanding the responses of streams to more intense and frequent summer storms will be critical for predicting future trajectories of C fluxes from watersheds to receiving waters. DOC dynamics during high flow events depend both on catchment characteristics and time-variant hydrological dynamics such as antecedent moisture. Examining catchment-specific responses help explain divergent trends in stream DOC concentrations, even from proximal systems (Eimers, Watmough, & Buttle, 2008), which is critical for resolving debates in the literature around drivers of regional changes to DOC concentrations and loads (Imtiazy et al., 2020; Houle et al., 2020). Understanding how landscape and climate factors interact to drive DOC loads to lakes is critical for calibrating models of organic C cycling in lakes (McCullough et al., 2018) as well as terrestrial C balance models (Bona et al., 2020). Given the projections for increased frequency and intensity of both storms and droughts, process-based studies such as this one are particularly valuable when considering how stream DOC dynamics respond to changing climatic drivers.

## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

## ACKNOWLEDGMENTS

This work would not have been possible without the hard work and dedication of IISD-ELA staff and students, both past and present. In particular, we thank Ken Sandilands, Paul Fafard, Justin Hubbard and Sonya Havens. This work was funded by an NSERC Discovery Grant to NJC.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available through the Lake Winnipeg DataStream at http://doi.org/10.25976/r3kp-7m22.

## LIST OF FIGURE & TABLE CAPTIONS

Figure 1: Location of the NE (wetland-dominated), NW (upland-small) and E (upland-large) catchments for the Lake 239 watershed and the gauged weir locations for each catchment.

Figure 2: Hysteresis and flushing indices for each high flow event captured at three study catchments between 2016 and 2017.

Figure 3: Slope of the linear ln(concentration)-ln(discharge) relationships (beta) vs. the coefficient of variation of concentration divided by the coefficient of variation of discharge for each study catchment and each season. The diagonal lines represent the theoretical bounds on these data (Musolff et al. 2015).

Table 1: Pearson correlation statistics for relationships between discharge and DOC concentration and antecedent moisture and DOC concentration for three study catchments during summer and fall. Antecedent moisture condition was calculated by summing the discharge measurements for different time periods: 2 days prior to the date of measurement, 7 days prior and 14 days prior.

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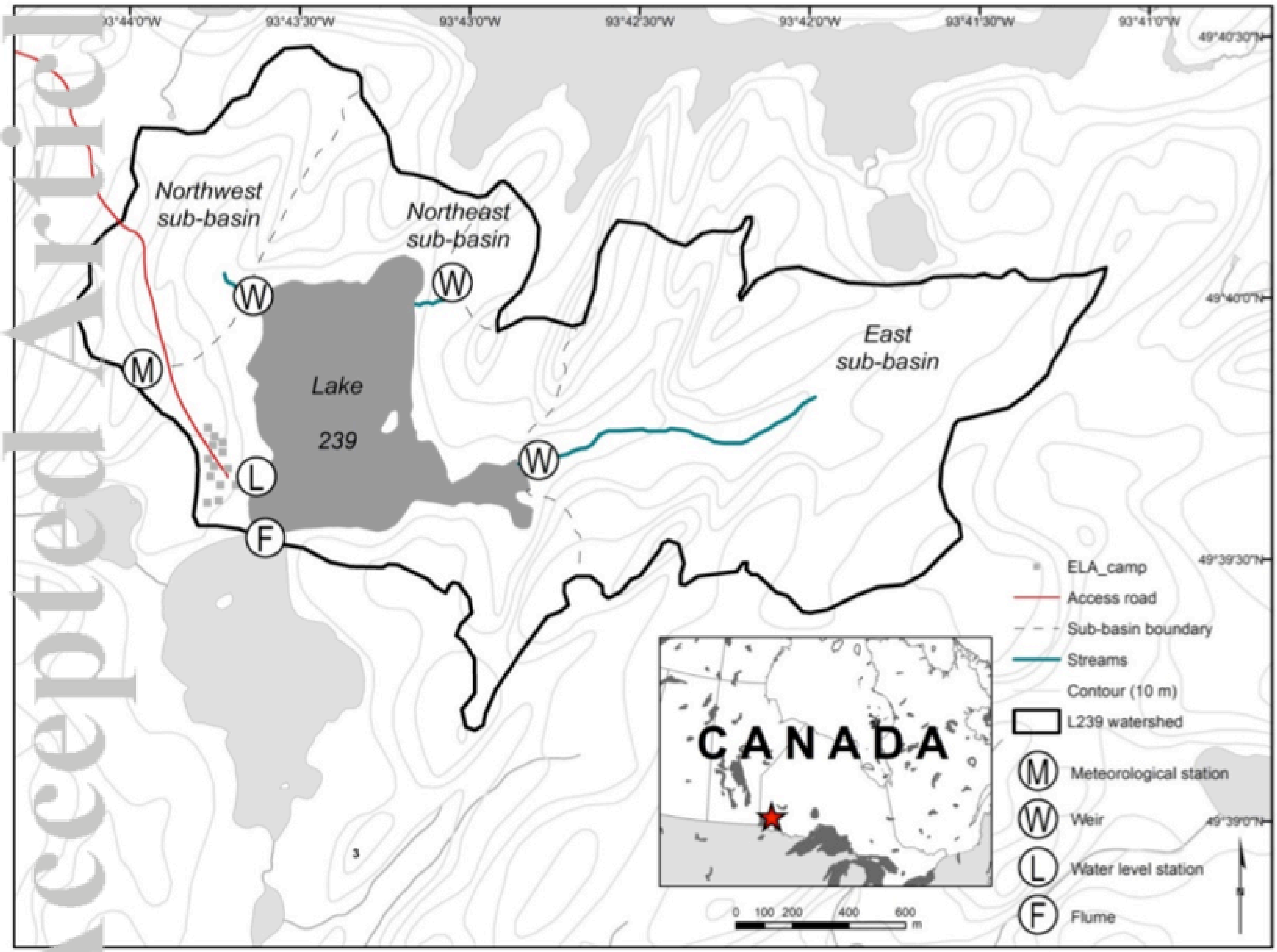

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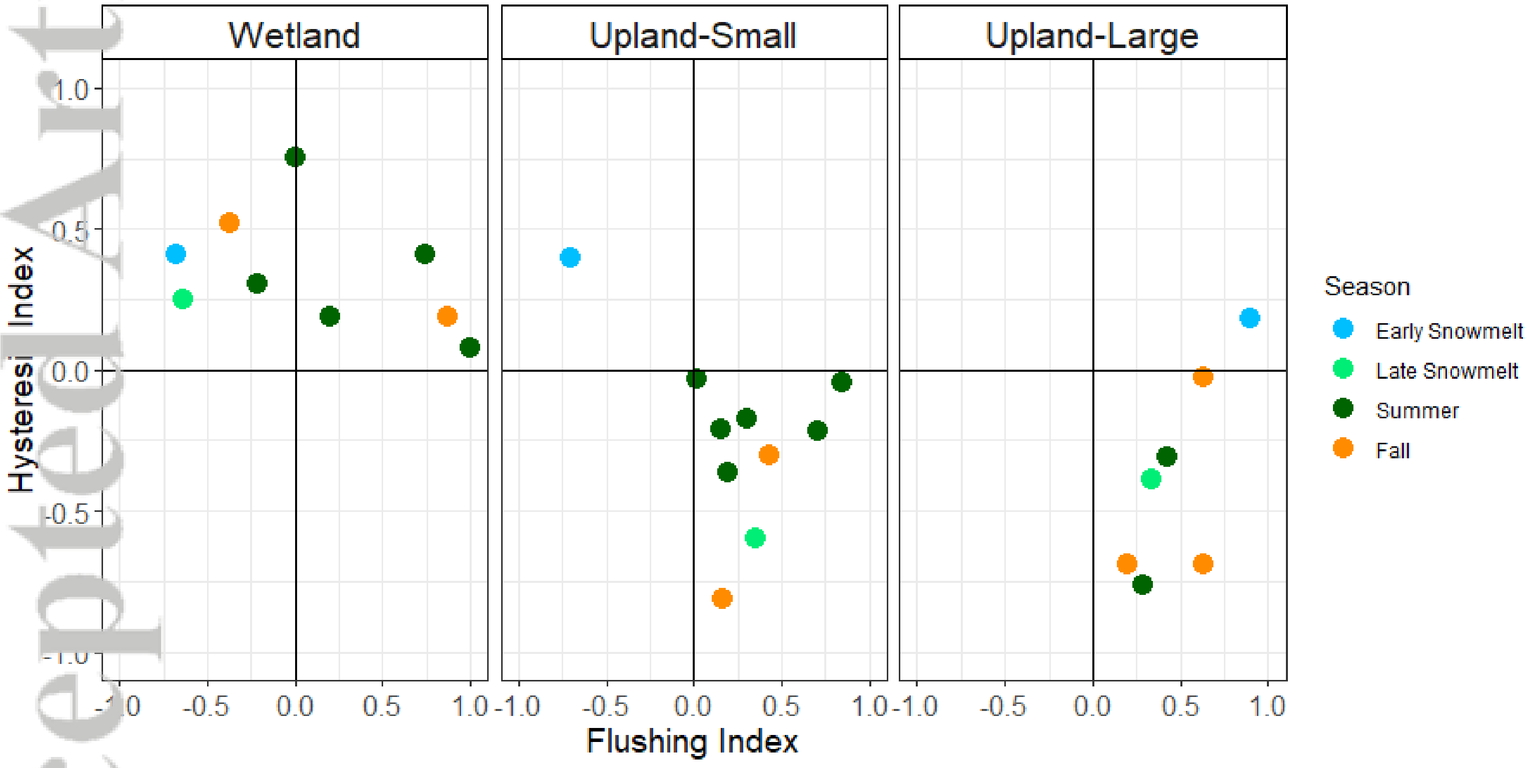

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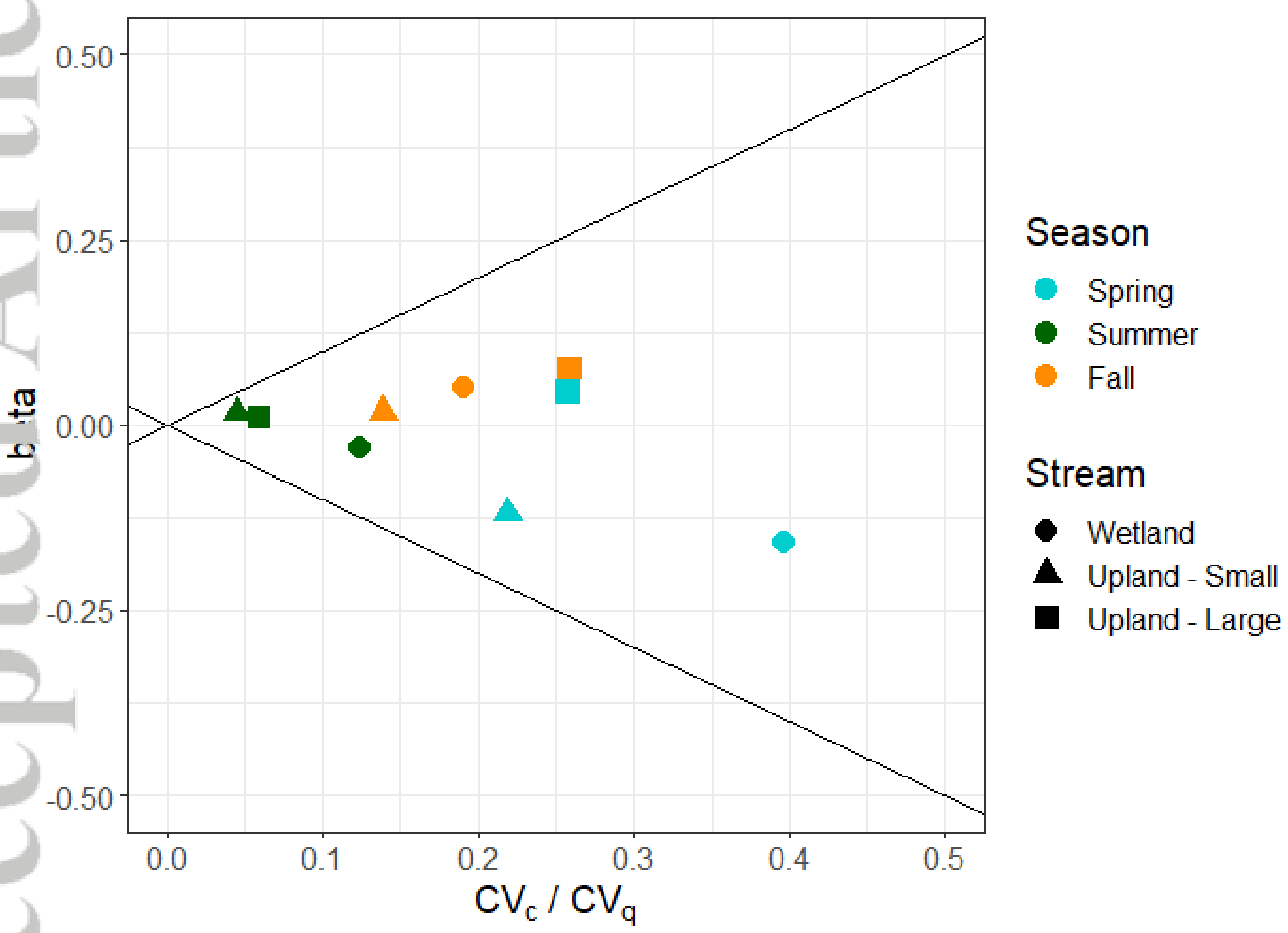

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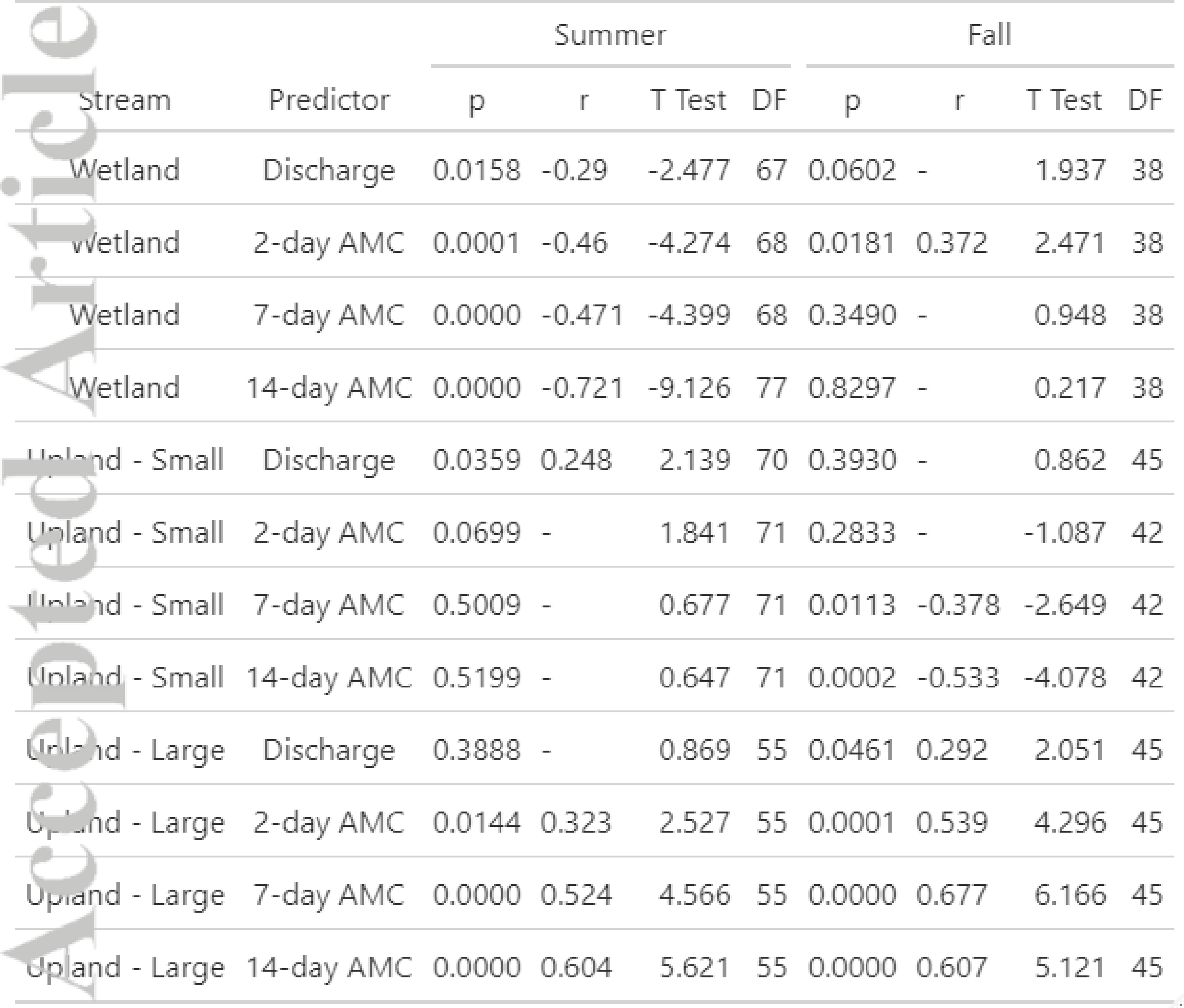

| | | Summer | | | | Fall | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stream | Predictor | p | r | T Test | DF | p | r | T Test | DF |
| Wetland | Discharge | 0.0158 | -0.29 | -2.477 | 67 | 0.0602 | - | 1.937 | 38 |
| Wetland | 2-day AMC | 0.0001 | -0.46 | -4.274 | 68 | 0.0181 | 0.372 | 2.471 | 38 |
| Wetland | 7-day AMC | 0.0000 | -0.471 | -4.399 | 68 | 0.3490 | - | 0.948 | 38 |
| Wetland | 14-day AMC | 0.0000 | -0.721 | -9.126 | 77 | 0.8297 | - | 0.217 | 38 |
| Upland - Small | Discharge | 0.0359 | 0.248 | 2.139 | 70 | 0.3930 | - | 0.862 | 45 |
| Upland - Small | 2-day AMC | 0.0699 | - | 1.841 | 71 | 0.2833 | - | -1.087 | 42 |
| Upland - Small | 7-day AMC | 0.5009 | - | 0.677 | 71 | 0.0113 | -0.378 | -2.649 | 42 |
| Upland - Small | 14-day AMC | 0.5199 | - | 0.647 | 71 | 0.0002 | -0.533 | -4.078 | 42 |
| Upland - Large | Discharge | 0.3888 | - | 0.869 | 55 | 0.0461 | 0.292 | 2.051 | 45 |
| Upland - Large | 2-day AMC | 0.0144 | 0.323 | 2.527 | 55 | 0.0001 | 0.539 | 4.296 | 45 |
| Upland - Large | 7-day AMC | 0.0000 | 0.524 | 4.566 | 55 | 0.0000 | 0.677 | 6.166 | 45 |
| Upland - Large | 14-day AMC | 0.0000 | 0.604 | 5.621 | 55 | 0.0000 | 0.607 | 5.121 | 45 |

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