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Running Title:

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Seasonal dynamics and exports of elements from a first-order stream to a large inland lake in Michigan

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Abstract

Headwater streams are critical components of drainage systems, directly connecting terrestrial and downstream aquatic ecosystems. The amount of water in a stream can alter hydrologic connectivity between the stream and surrounding landscape, and is ultimately an important driver of what constituents headwater streams transport. There is a shortage of studies that explore concentration-discharge (*C*-*Q*) relationships in headwater systems, especially forested watersheds, where the hydrological and ecological processes that control the processing and export of solutes can be directly investigated. We sought to identify the temporal dynamics and spatial patterns of stream chemistry at three points along a forested headwater stream in northern Michigan and utilize concentration-discharge (*C*-*Q*) relationships to explore transport dynamics and potential sources of solutes in the stream. Along the stream, surface flow was seasonal in the main stem and perennial flow was spatially discontinuous for all but the lowest reaches. Spring snowmelt was the dominant hydrological event in the year with peak flows an order of magnitude larger at the mouth and upper reaches than annual mean discharge. All three *C*-*Q* shapes (positive, negative, flat) were observed at all locations along the stream, with a higher proportion of the analytes showing significant relationships at the mouth than at the mid or upper flumes. At the mouth, positive (flushing) *C*-*Q* shapes were observed for dissolved organic

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carbon and total suspended solids, while negative (dilution) *C-Q* shapes were observed for most cations (Na^+, Mg^{2+}, Ca^{2+}) and biologically cycled anions (NO_3^-, PO_4^{3-}, SO_4^{2-}). Most analytes displayed significant *C-Q* relationships at the mouth, indicating that discharge is a significant driving factor controlling stream chemistry. However, the importance of discharge appeared to decrease moving upstream to the headwaters where more localized or temporally-dynamic factors may become more important controls on stream solute patterns.

1 Introduction

Headwater streams are important conduits linking terrestrial and aquatic ecosystems, moving water, nutrients, and energy to downstream surface waters (Carpenter et al., 2005; Freeman, Pringle, & Jackson, 2007; Gomi, Sidle, & Richardson, 2002). Stream discharge is an important driver of the composition of dissolved and particulate matter in the stream and exported from a watershed. Changes in discharge can alter the hydrologic connectivity between streams and the surrounding landscape, as well as connections between ephemeral and perennially flowing stream reaches (Freeman et al., 2007; Pringle, 2003; Tetzlaff et al., 2007; Tockner, Penntzdorfer, Reiner, Schiemer, & Ward, 1999). Inputs from headwater streams can significantly influence the nutrient concentrations in higher order streams (Alexander, Boyer, Smith, Schwarz, & Moore, 2007; Gomi et al., 2002; MacDonald & Coe, 2007). In headwater systems, transport of material from terrestrial to aquatic zones is primarily influenced by runoff and shallow groundwater flow and biogeochemical cycling and transformations occurring in

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these systems can influence the larger drainage network (Brinson, 1993; Harvey & Gooseff, 2015; McClain et al., 2003; Raymond, Saiers, & Sobczak, 2016). While headwater streams may be small in size, they account for at least 70% of the total stream length in typical river networks and are by far the largest proportion (>96%) of streams and rivers in the world (Downing et al., 2012; Leopold, Wolman, & Miller, 1964; Marx et al., 2017). The Great Lakes contains 21% of the fresh surface water in the world and are primarily fed by small tributaries, which can significantly influence whole-lake budgets of dissolved and particulate nutrients (Marcarelli et al., 2018; Sterner et al., 2017). This influence of headwater streams can be substantial even across large catchments, such as the Great Lakes basin, and may become more consequential with changes in climate and weather patterns (Marcarelli et al., 2018). Given the significance of these streams to downstream rivers and lakes, we sought to investigate terrestrial-aquatic linkages within headwater watersheds by determining the temporal dynamics and spatial patterns of dissolved matter, especially carbon (C).

The relationship between solute concentration and stream discharge has long been used to investigate the transport of river materials and how changing hydrologic conditions impact water quality and nutrient exports (*e.g.*, Edwards, 1973; Foster & Walling, 1978; Walling & Webb, 1983; Williams, 1989). Concentration-discharge (*C*-*Q*) relationships have been used to identify positive (flushing), negative (dilution), and flat (often called chemostatic) solute trends (Godsey, Kirchner, & Clow, 2009; Moatar, Abbott, Minaudo, Curie, & Pinay, 2017). Solutes with positive *C*-*Q* relationships are often thought of as being transport-limited, solutes with negative

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C-Q relationships are source-limited, and for those with flat *C-Q* shapes neither process dominates (Basu et al., 2010; Salmon, Walter, Hedin, & Brown, 2001; Thomas, Abbott, Troccaz, Baudry, & Pinay, 2016). *C-Q* relationships are thought to be a reflection of solute distribution and availability throughout the watershed, the hydrologic connectivity between solute stores and the stream channel, and in-stream processing or reactivity (Moatar et al., 2017; Musolff, Schmidt, Selle, & Fleckenstein., 2015). Often, flat *C-Q* shapes are observed for solutes that have effectively unlimited stores homogenously distributed throughout the watershed, or where external inputs are high and consistent, such as nutrients in agricultural or urban watersheds (Duncan, Band, & Groffman, 2017; Herndon et al., 2015; Musolff et al., 2015; Thompson, Basu, Lascurain, Aubeneau, & Rao, 2011). Some studies consider all solutes with flat slopes to be chemostatic (*e.g.*, Godsey et al., 2009; Basu et al., 2010), while others distinguish between chemostatic solutes with high vs. low variability in concentration as a function of discharge (Thompson et al., 2011; Musolff et al., 2015).

In *C-Q* analyses, dissolved C, suspended sediment, and major cations (*e.g.*, Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (*e.g.*, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-) are often measured. The majority of these analytes are not conservative elements, *i.e.*, they can be bound in soil, biologically cycled, or transformed in the stream or surrounding soil. Because these differences in analyte sources and biogeochemical processing can influence their behavior, understanding their elemental properties can influence how we interpret their *C-Q* shapes. Dissolved organic carbon (DOC) is one of the most commonly measured solutes due to its importance in aquatic ecosystems and the C cycle

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(Elder, Rybicki, Carter, & Weintraub, 2000; Lambert et al., 2014; Lottig, Buffam, & Stanley, 2013; Marx et al., 2017). Much of the DOC measured in streams comes from terrestrial sources, such as organic-rich soil horizons in riparian zones or wetlands (Elder et al., 2000; Inamdar, Christopher, & Mitchell, 2004). Carbon can be stored in streams (*e.g.*, sedimentation) and transformed between organic and inorganic forms through microbial or photochemical oxidation or photosynthesis (Jonsson et al., 2007; Lottig et al., 2013; Schiff et al., 1997). Biologically cycled anions include NO_3^-, PO_4^{3-}, and SO_4^{2-}. In temperate forests, NO_3^- is a highly mobile form of a growth-limiting nutrient that is typically present in low concentrations, except where anthropogenic inputs or impacts are high; therefore, NO_3^- in streams is likely produced in riparian zones through nitrification (Bernhardt et al., 2005; Dittman, Driscoll, Groffman, & Fahey, 2007; Galloway & Cowling, 2002; Sebestyen et al., 2008). The primary source of PO_4^{3-} to streams comes from organic matter mineralization or PO_4^{3-} bound to suspended sediments, although it is ultimately derived from mineral weathering (Achat et al., 2010; Adams, Attiwill, & Polglase, 1989). Geologic weathering and organic matter mineralization are sources of SO_4^{2-}, although SO_4^{2-} from atmospheric deposition may constitute a large portion of the S capital in forested watersheds, especially those with a history of long-term elevated atmospheric deposition (Johnson, 1984; Mayer, Shanley, Bailey, & Mitchell, 2010). Major base cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) are derived both from parent material weathering and mineralization of organic matter. These biologically cycled cations can also be adsorbed onto the cation exchange complex in soil and taken up by vegetation (Likens, Bormann, Johnson, & Pierce, 1967; Likens et al., 1994;

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Likens et al., 1998; Williams, Szramek, Jin, Ku, & Walter, 2007). Geologic parent material weathering can also be a source of highly soluble anions, such as Cl^- and F^-, but typically concentrations are very low unless dominated by an anthropogenic source (*e.g.*, Cl^- due to additions of road salt) or maritime-related atmospheric deposition (Farrell, 1995; Jones & Sroka, 1997; Luczaj & Masarik, 2015; Williams et al., 2007).

Recently, *C-Q* relationships have been analyzed across a wide range of watersheds with differing catchment areas, climate conditions, lithologies, land covers, and land management methods (*e.g.*, Basu et al., 2010; Burns, Boyer, Elliott, & Kendall, 2009; Dupas et al. 2017; Godsey et al., 2009; Moatar et al., 2017; Musolff et al., 2015; Thomas et al., 2016). The *C-Q* relationships for many solutes varied across these studies, with Godsey et al. (2009), Basu et al. (2010), and Thomas et al. (2016) concluding that chemostatic patterns dominated parent material weathering elements such as Si, Na^+, Mg^{2+}, and Ca^{2+} (Godsey et al., 2009), and vegetation-limiting nutrients, such as NO_3^- and PO_4^{3-}, in agricultural watersheds (Basu et al., 2010; Thomas et al., 2016). DOC has been widely seen to have a positive, flushing *C-Q* relationship, particularly at high flows (Inamdar et al., 2004; Lambert et al., 2014; Moatar et al., 2017), but seen as chemostatic in some studies (Creed et al., 2015). Even Moatar et al. (2017), who observed significant *C-Q* relationships for elements seen as chemostatic in other studies, observed flat *C-Q* shapes for many solutes at low flows. Across all of these studies, solute concentrations varied less than discharge, suggesting that hydrological controls dominate stream chemistry even across catchments with varying sizes and physical characteristics. In contrast to

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the studies of larger watersheds where chemostatic *C*-*Q* trends dominated for many analytes, studies that focused on smaller headwater catchments (80-162 ha) observed significant positive or negative *C*-*Q* relationships for most analytes measured. Herndon et al. (2015), Hoagland et al. (2017), and Hunsaker & Johnson (2017) did not necessarily observe the same *C*-*Q* shape for all analytes, but they did observe significant *C*-*Q* relationships for Mn, Ca^{2+}, K^{+}, Cl^{-}, Fe, Al, DOC, and NO_3^{-}. Na^{+}, Mg^{2+}, SO_4^{2-}, and Si relationships that varied depending on study location.

Importantly, the number of studies that explore the *C*-*Q* relationships of a wide range of analytes in temperate watersheds is limited, especially in small forested watersheds where the hydrological and ecological processes that control the processing and export of solutes can be directly investigated. The literature bias towards larger watersheds means that these processes are often likely obscured by multiple land covers, anthropogenic activities, and altered (or even counteracting) natural hydrologic and biogeochemical processes (Burns et al., 2009; Duncan et al., 2017).

The importance of headwater streams to downstream water quantity and quality, especially in the Great Lakes basin, coupled with their under-representation in the literature, argues for more assessment of the temporal dynamics and spatial patterns of stream chemistry in such watersheds. Our forested 120 ha watershed in northern Michigan, USA, provides the opportunity to explore how *C*-*Q* relationships vary along a stream that is experiencing the same climatic conditions throughout the watershed, isolating the influence of hydrologic connectivity, and identifying the potential influence of heterogeneously distributed vegetation types and soil

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properties. In this analysis we are addressing three research questions: 1) what are the temporal and spatial patterns of discharge, suspended solids, dissolved C, cations, and anions along a first-order stream, 2) what *C-Q* relationships are observed at discrete sampling locations along the stream, and 3) what do these patterns indicate about connections between the stream and surrounding soils and landscape?

2 Methods

2.1 Study Area

We measured stream discharge and chemistry along Honeysuckle Creek, a headwater stream discharging into Michigan's 4th largest inland lake, Burt Lake (6,900 ha), which ultimately connects to Lake Huron. The 120 ha Honeysuckle Creek watershed is located within the University of Michigan Biological Station (UMBS) land holdings in northern Lower Michigan, USA (45.56°, -84.72°) (Figure 1). The climate of the region is continental with a mean annual temperature of 5.5°C and mean annual precipitation of 817 mm, including 294 cm of snow (Nave et al., 2017b). Mixed deciduous and conifer species dominate the forests of this landscape and the broader region, including *Populus* spp., *Acer* spp., *Pinus* spp., and *Quercus rubra*, with *Thuja occidentalis*, *Abies balsamea*, and *Tsuga canadensis* in the low-lying wetland areas (Nave et al., 2017a). The Honeysuckle Creek watershed and surrounding landscape is characterized by glacial and postglacial landforms that were formed in drift deposited at the end of the Laurentian glaciation (14,000-10,000 years before present) and modified by large,

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postglacial lakes (Lake Algonquin, Lake Nippissing; Spurr & Zumberge, 1956; Blewett & Winters, 1995; Lapin & Barnes, 1995). The limestone and shale bedrock is overlain by 100-200 m of glacial drift, with wasting ice depositing glacial till as moraines that were later capped by meters of outwash during the final stages of glacial retreat. The Honeysuckle Creek watershed begins at the top of an interlobate moraine (276 m above sea level, asl), has outwash, till, and lacustrine (dunes, beach ridges) landforms in the middle elevations (255 m to 190 m), and includes an outwash-lake plain wetland (190-181 m) along the shore of Burt Lake. Soils of the upper elevations of the watershed (*i.e.*, the uppermost ~1 km of the watershed) were formed in deep, coarse-textured outwash (Entic and Lamellic Haplorthods) with little water-holding capacity. In the middle (about 1 km) of the watershed, soils are finer-textured with restrictive glacial till close to the surface (Alfic Haplorthods, Alfic Epiaqods, Mollic Endoaquents) promoting episaturation and surface water in stream channels. Below 190 m elevation, the outwash-lake plain wetland soils are Terric Haplosaprists with consistent groundwater levels within 10 cm of the surface and perennial surface water in the stream (Nave et al., 2017a). Several seasonal sand tracks run through the watershed and a paved road runs between the mid and mouth flumes roughly parallel to the 190 m contour line.

2.2 Field Measurements

We installed modified Parshall flumes at three locations along Honeysuckle Creek (Figure 1) and measured stream stage and calculated stream discharge based on USGS methods (Kilpatrick & Schneider, 1983). We measured stream stage approximately weekly at all three

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flumes (mouth, mid, upper) from October 2015–September 2016 to capture stream dynamics over the course of an entire hydrologic year. In addition to stream discharge, we measured stream temperature at the mouth of the stream from October 2015–February 2016 (with Onset HOBO Pendant Temperature Data Loggers, Onset Computer Corporation, Bourne, MA) and May 2016–October 2016 (Solinst Levelogger, Solinst Inc., Georgetown, ON, CA). Meteorological (air temperature, precipitation, snow depth) measurements were taken at daily UMBS laboratory facilities approximately 3 km away from the watershed. Weekly chemical composition of precipitation at the UMBS facility (site MI09) was reported as part of the National Atmospheric Deposition Program (NRSP-3, 2018). Stream samples were taken at the same time as stream stage measurements from October 2015–August 2016. We collected water samples at each flume in HDPE bottles, which were transferred to a refrigerator (4°C) within 8 hours of sample collection. Soils were sampled at locations throughout the wetland (n=27) and upland (n=23) areas of the watershed for separate projects (2014–2017) and are being used in this analysis to provide context for the DOC $\delta^{13}C$ measured in the stream water. Wetland soil sampling methods are described in Nave et al. (2017a). Upland soils were collected as genetic horizons via pit-face or AMS slide-hammer coring.

2.3 Laboratory Analysis

In the UMBS Analytical Chemistry Laboratory, water samples were filtered through pre-ashed 0.7 µm glass-fiber filters within 24 hours of collection. Samples for cation analysis were acidified to 0.4% with trace metal grade HCl, and all samples were refrigerated at 4°C until

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analysis. The filters were then dried at 60°C for 12 hours and pre- and post-filter weights were used to determine total suspended solids (TSS) for each sample. Filtered water samples were analyzed for anions (Cl^-, F^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) with an ion chromatograph (Thermo Scientific Dionex Integrion HPIC system, Thermo Fisher Scientific, Inc., Miami, FL). DOC concentration and C stable isotope ratios were measured with a total organic carbon analyzer (Aurora 1030W TOC Analyzer, OI Analytical, Xylem Inc., College Station, TX) coupled to an isotope ratio mass spectrometer (Thermo Scientific Delta V Advantage IRMS, Thermo Fisher Scientific, Inc., Miami, FL). For water samples where anion, cation, or C concentrations were below analytical detection limits (Table S1), a value of zero was used in the following analysis. Organic soil samples taken in the wetland were processed according to Nave et al. (2017a). Upland soil samples were air-dried, weighed, and sieved (2 mm). All soil samples were ball milled and run for C concentration and $\delta^{13}C$ on a CHN analyzer (Costech Analytical Technologies, Inc., Valencia, CA) coupled to an isotope ratio mass spectrometer (Finnigan Delta Plus XL IRMS, Thermo Fisher Scientific Inc., Miami, FL). To infer the relative age of the soil C pools contributing to stream water DOC, a subset of soil samples were analyzed for radiocarbon (^{14}C) content. Wetland organic soil horizons (8 total from three representative profiles) were prepared for ^{14}C analysis by graphitization (Vogel, Southon, J.R., & Nelson., 1987), followed by measurement by accelerator mass spectrometry at Lawrence Livermore National Laboratory (Davis et al., 1990). We also present ^{14}C data for upland horizons (6 total from two representative profiles in the watershed) that were density

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separated (Heckman et al., 2014) and reported in Nave et al., (2019a). The density fractions of each upland soil horizon were graphitized and analyzed for ^{14}C content by the same methods used for wetland organic soil horizons. To express radiocarbon values for these upland soil horizons, we computed the ^{14}C value of the bulk material in each horizon as the weighted average ^{14}C value and mass proportion of each density fraction (free light, <1.85 g cm^{-3}; occluded light, <1.85 g cm^{-3} and liberated from within aggregates by sonication; heavy >1.85 g cm^{-3}). Radiocarbon abundances were normalized by the international radiocarbon standard, Oxalic Acid 1, and corrected for mass-dependent fractionation according to Stuiver & Polach (1977). In this manuscript we report ^{14}C values according to $\Delta^{14}C$ notation, as that is the most direct metric of ^{14}C abundance, carries fewer assumptions, and has a lower risk of mis-interpretation compared to other notations.

2.4 Data Analysis

We used non-parametric Kruskal Wallis One-Way ANOVA on Ranks with Dunn's Method of Comparisons tests to compare daily precipitation amounts to assess potential seasonal differences in precipitation patterns. Because we used two different temperature loggers to measure stream temperature at the stream mouth, there was a gap in data collection from February 11, 2016–May 4, 2016. During this period, we used an exponential regression to estimate mean daily stream temperature from 3-day mean air temperature. This relationship between air and stream temperature was strong based on coefficient of determination (r^2=0.838) and Nash Sutcliffe Efficiency (NSE=0.811) metrics (data not shown). We used Two-Way

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ANOVAs to assess temporal and spatial differences in stream chemical concentrations across the watershed. We used season (spring, summer, autumn, winter) and location (the three flumes) as the temporal and spatial factors, respectively. We utilized meteorological seasonal divisions [Spring (MAM), Summer (JJA), Autumn (SON), Winter (DJF)]. We set sample concentrations below analytical detection limit equal to zero and transformed non-normal data using squared and log transformations. We accepted results as statistically significant when $p<0.05$. Due to the very low number of samples where Br^- concentrations were above analytical detection limit, we have excluded Br^- from this analysis.

To assess the influence of stream discharge on chemical concentration, we examined the relationship between concentration (*C*) and discharge (*Q*) at each flume for each analyte. We used the power function that has been used by others (*e.g.*, Basu et al., 2010; Moatar et al., 2017; Musolff et al., 2015) to relate log-transformed *C* and *Q*. We used log(x+1) transformations of both *C* and *Q* for all analytes, except DOC $\delta^{13}C$ where we used log(x+30) transformations due to negative values, to include below detection limit (*i.e.*, zero) values in this analysis. This relationship takes the form:

$$C = aQ^b \tag{1}$$

where *C* is concentration, *Q* is discharge, *a* is a coefficient with units of concentration, and *b* is a unit-less exponent representing the slope of the log(x+1)-transformed *C*-*Q* relationship. The slope (*b*) of the *C*-*Q* relationship provides insights into the availability, transport capacity, and sources of elements across the watershed. *C*-*Q* relationships can be divided into positive ($b \geq 0$),

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negative ($b \leq 0$), or flat ($b=0$) shapes based on the p-value ($p<0.05$) (Godsey et al., 2009; Moatar et al., 2017; Musolff et al., 2015). Strength of the relationship was assessed based on the coefficient of determination (r^2). Positive slopes have been interpreted as enhanced, flushing, or transport-limited elements, while negative slopes have been interpreted as dilution or source-limited materials. Other researchers have observed that many elements exhibit flat *C-Q* shapes ($b=0$ or close to 0) and have described these elements as having no change in concentration with discharge (*e.g.*, Basu et al., 2010; Godsey et al., 2009). Following Thompson et al. (2011) and Musolff et al. (2015), we have used the ratio of coefficients of variation of analyte concentration and discharge (CV_C/CV_Q) to divide analytes with flat *C-Q* shapes into chemostatic ($CV_C/CV_Q \leq 0.5$), chemodynamic ($CV_C/CV_Q \geq 1.0$), or no distinct trend ($0.5 \leq CV_C/CV_Q \leq 0.1$) groups. While other researchers have explored *C-Q* relationships after segmenting their datasets into different flow regimes (*e.g.*, low, high flow; Herndon et al., 2015; Moatar et al., 2017), we grouped samples from all seasons together to strengthen statistical power for this analysis given the frequency of our sampling approach. We have used point color and shape in *C-Q* relationship figures to group points by season, which for the most part corresponds to different flow regimes. We used linear regressions to explore mineral and wetland soil $\Delta^{14}C$ and $\delta^{13}C$ distribution with depth in the soil profiles. We have included these data to provide context for the DOC quality (as interpreted from $\delta^{13}C$) in the stream. We used R (Version 3.4.3; R Core Team, 2017) and SigmaPlot (SYSTAT Software, San Jose, CA) to perform statistical analyses.

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3 Results

3.1 Stream Discharge and Precipitation Patterns

Throughout the year of study (October 2015–September 2016) Honeysuckle Creek flow was ephemeral and seasonal, with perennial flow only below 185 m elevation. During the spring snowmelt period (March–April), Honeysuckle Creek flowed continuously for 1.7 km from its headwaters at 236 m elevation to the mouth at 181 m. Stream flow was ephemeral at the upper flume (227 m) and for much of the stream reach above 206 m elevation, with surface water beginning to dry up in July and intermittent flow during late summer and autumn after large storm events. At the mid flume (195 m), surface water persisted even in the driest season, although during this time surface water downstream of the flume became disconnected from the perennially flowing stream below 185 m elevation. In the driest season, Honeysuckle Creek surface flow was continuous for an approximately 360 m long reach through the wetland to the confluence with Burt Lake. Stream discharge was highest at the mouth (1,126±809 L min^{-1}; mean ± SD), then the middle flume (186±285 L min^{-1}), and lowest at the upper flume (47±63 L min^{-1}). Across all flumes, discharge was the highest during the spring snowmelt period, ranging from 123 L min^{-1} at the upper flume to 2,627 L min^{-1} at the mouth, and lowest during August when there was no surface water at the upper flume and stream flow was 22-466 L min^{-1} at the other flumes (Figure 2). At the mouth, only spring and summer stream flows differed significantly, while at the mid flume, spring discharge was significantly larger than discharge at all other seasons. At the upper flume, stream flow during spring and winter was higher than

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summer and autumn flows, but not significantly different from each other. Stream temperatures at the mouth were warmest in the summer (13.6±1.6° C) and coldest in the winter (3.6±1.3° C), closely tracking air temperatures. Stream flow during the 2015-2016 period discussed here is within the range of base and peak flow conditions observed in subsequent years of measurements at this study site while still capturing similar seasonal patterns (Figure S1).

Precipitation during the 2015-2016 hydrologic year totaled 1,090 mm making it a wetter than average year when mean precipitation equals 817 mm. Precipitation during the winter and early spring period typically fell as snow and remained in the watershed until melt began in early March (Figure 2). Median daily precipitation amounts were similar in most seasons and only differed between winter and summer months ($p<0.05$) with less precipitation falling in summer. Inputs of cations and Cl^- due to precipitation were likely negligible, as seasonal precipitation concentrations of these analytes were two (Na^+, K^+, Cl^-) to three (Mg^{2+}, Ca^{2+}) orders of magnitude smaller than seasonal stream concentrations (Table 1). Concentrations of SO_4^{2-} in precipitation were only one order of magnitude smaller than concentrations in stream water, while seasonal NO_3^--N concentrations in precipitation (0.11-0.30 mg L^{-1}) were only slightly smaller than stream concentrations (0.43-0.48 mg L^{-1}).

3.2 Temporal Dynamics and Spatial Patterns of Stream Chemistry

Stream chemistry varied longitudinally along the stream, with the highest concentrations of all analytes generally measured at the mouth. The order of analytes with the highest to lowest concentrations varied slightly across flumes, but overall trends were similar. At all flumes, Ca^{2+}

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(30.6-40.8 mg L^{-1}), Mg^{2+} (10.6-13.6 mg L^{-1}), TSS (8.5-13.4 mg L^{-1}), DOC (3.5-4.5 mg L^{-1}), and SO_4^{2-} (3.0-4.3 mg L^{-1}) concentrations were the highest, while many anion concentrations were low [PO_4^{3-}-P (0.0035-0.0096 mg L^{-1}); F^- (0.036-0.048 mg L^{-1}); NO_3^--N (0.40-0.49 mg L^{-1}); Table 2].

To investigate temporal dynamics and spatial patterns along the stream, we compared analyte concentrations by season and location (flume; Table 3). Concentrations of major elements varied between locations along the stream and between seasons. Overall, concentrations of all analytes except TSS, DOC, and K^+ differed between flumes, and all analyte concentrations except Ca^{2+} and PO_4^{3-} had significant seasonal dynamics. Statistically significant season by location interactions were apparent for TSS, SO_4^{2-}, PO_4^{3-}, and K^+ (Table 3). Differences in analyte concentrations between flumes depended on the type of analyte (Table 2). Biologically cycled analytes (NO_3^-, PO_4^{3-}, SO_4^{2-}) were in higher concentrations at the mouth than the other flumes, along with Na^+ and Cl^-. The NO_3^-, SO_4^{2-}, and Cl^- concentrations also differed between the mid and upper flumes, with higher NO_3^- and SO_4^{2-} and lower Cl^- concentrations at the upper flume. The concentrations of some cations derived through parent material weathering and organic matter mineralization (Ca^{2+}, Mg^{2+}, and K^+ in summer) were not different at the mouth or upper flume and were lower at the mid flume (Table 2). Seasonal differences in analyte concentrations were not consistent for analytes within the same 'biogeochemical groups.' Specifically, concentrations of some analytes (*e.g.*, DOC, K^+, F^-) varied much more by season than by location, based on their Two-Way ANOVA F statistics (Table 3). In contrast, spatial

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differences in Na^+, Cl^-, and PO_4^{3-} concentration were much larger than seasonal differences.

3.3 Concentration-Discharge Relationships

Because observed seasonal differences in analyte concentrations might be due to seasonal differences in stream flow, we utilized *C-Q* relationships to better quantify the influence of discharge on chemical concentration in the stream at all three flumes. All three *C-Q* shapes (positive, negative, flat) were observed at all locations along the stream. Moving downstream, a larger proportion of the analytes displayed either a significant positive or negative shape as the contributing area increased from the upper, to the mid, and ultimately to the mouth flume. At the mouth, all analytes displayed either a positive or negative *C-Q* relationship except K^+ and F^-. Positive (flushing) *C-Q* relationships were observed for DOC and TSS at the mouth and mid flumes, and the DOC *C-Q* relationship showed a positive tendency (p=0.063) at the upper flume (Figure 3). A negative (dilution) *C-Q* relationship was observed for most cations (Na^+, Mg^{2+}, Ca^{2+}) and biologically cycled anions (NO_3^-, PO_4^{3-}, SO_4^{2-}), as well as Cl^- (Figure 4, 5). These relationships were most pronounced at the mouth, although dilution shapes were also observed for NO_3^-, Na^+, and Mg^{2+} at the mid flume and for Mg^{2+} at the upper flume.

At the mouth, K^+ and F^- displayed flat slopes with a smaller range of concentrations measured than variation in discharge. Moving upstream to the mid flume, more analytes displayed flat *C-Q* shapes (PO_4^{3-}, SO_4^{2-}, K^+, Ca^{2+}, Cl^-, F^-) and at the upper flume most analytes had flat slopes (NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Cl^-, F^-). For the analytes displaying flat *C-Q* shapes, we used CV_C/CV_Q to identify strongly chemostatic and strongly chemodynamic elements

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(Table 4). While most of these analytes could be grouped as chemostatic, PO_4^{3-} was chemodynamic at the mid flume and showed no strong trend at the upper flume, along with Ca^{2+} and F^-. The chemostatic analytes included SO_4^{2-}, NO_3^-, K^+, Ca^{2+}, Na^+, Cl^-, and F^-. Some of these analytes had chemostatic characteristics at one flume but had no distinct trend at other flumes, such as K^+, Ca^{2+}, and F^-, which were static at the mid flume, but showed no trend at the upper flume (Ca^{2+}, F^-) or mouth (K^+, F^-).

3.4 Carbon Isotopes in the Stream and Soil

At each flume, DOC $\delta^{13}C$ became more depleted as discharge (Figure 6) and DOC concentration increased (Figure 7). Seasonally, DOC $\delta^{13}C$ was most depleted in the spring, followed by winter, and most enriched in summer (Figure 6), and over the range of DOC concentrations (Figure 7), the upper (-26.57±0.27‰) and mid flumes (-26.67±0.43‰) had significantly more depleted DOC $\delta^{13}C$ than the mouth flume (-25.91±0.46‰). At the upper and mid flumes, DOC $\delta^{13}C$ and concentration were linearly related across the range of DOC concentrations, while the mouth flume showed asymptotic behavior. Soil $\delta^{13}C$ values were most depleted at the surface and became enriched with depth (Figure 8), and the most depleted DOC $\delta^{13}C$ values at the upper and mid flumes (*i.e.*, below *ca.* -27.0‰) were similar to horizons in the uppermost 5-15 cm of wetland and upland soil profiles. The generally more enriched DOC $\delta^{13}C$ of the mouth flume was, at its most enriched (*i.e.*, above *ca.* -25.5‰), similar to horizons below 50 cm, particularly in the deeper mineral soils of the uplands. In contrast with soil $\delta^{13}C$, soil $\Delta^{14}C$ showed the opposite pattern with depth, becoming increasingly depleted in the deeper

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horizons across upland and wetland profiles (Figure 8).

4 Discussion

While other researchers have found that many of the analytes they measured displayed chemostatic behavior and had flat *C-Q* shapes with slopes below $|b|<0.2$ (Basu et al., 2010; Godsey et al., 2009; Hunsaker & Johnson, 2017; Kim, Dietrich, Thurnhoffer, Bishop, & Fung, 2017; Thompson et al., 2011), we found that all positive and negative Honeysuckle Creek *C-Q* relationships, with the exception of Mg^{2+} at the upper flume, were strongly significant with slopes greater than $|b|>0.2$. Our results did generally agree with the findings of these researchers that solute concentrations vary less than discharge. Most of the analytes we measured displayed both temporal dynamics and spatial patterns, with differences in concentration at flumes and across seasons. Many of the differences we observed may be due to differences in seasonal stream flow, so *C-Q* relationships provided a direct analysis of the influence of discharge on stream chemistry on seasonal time scales. We observed positive *C-Q* shapes for DOC and TSS, and negative *C-Q* shapes for NO_3^-, PO_4^{3-}, SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+}, and Cl^-, with less significant relationships at the mid and upper flumes.

In Honeysuckle Creek, the divergent *C-Q* relationships for DOC (positive) vs. DOC $\delta^{13}C$ (negative), contextualized by differences between the three flumes, suggest that hydrologic connectivity, heterogeneous soils, and in-stream processing are key controls on the amount and source of DOC moving through the watershed. Regarding hydrologic connectivity, concurrency

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of higher discharge with higher DOC concentrations and more depleted $\delta^{13}C$ are congruent with the vertical distribution of C concentrations and ^{13}C signatures in soils, essentially suggesting that DOC concentration and DOC $\delta^{13}C$ are an integrative proxy for the portion of the soil profile with which water is interacting at any given flow stage. However, the increasing enrichment of DOC $\delta^{13}C$ along the stream reach (*i.e.*, from upper to mouth flumes) may reflect that in-stream DOC is being processed (*e.g.*, mineralized by heterotrophs) during transport down the stream (Herndon et al., 2017; Moatar et al., 2017). This potential is further intimated by DOC $\delta^{13}C$ values at the mouth that are more enriched than can be explained by even deep wetland soils that are present in this area. These most enriched DOC $\delta^{13}C$ values (which occur at the lowest flows) suggest a possibility of greater in-stream processing during these low, slow-flow conditions, or perhaps a hydrologic connection to deeper upland soils where enriched $\delta^{13}C$ values occur.

While the specific explanations for DOC/$\delta^{13}C$ patterns with discharge are not mutually exclusive, our ^{14}C results demonstrate a consequence of these *C-Q* patterns that is perhaps more important than the specific mechanism(s) responsible for them. Namely, at the higher flows during which Honeysuckle Creek interacts with more surficial soil horizons, it is transporting greater quantities of, and also more modern soil C, and therefore potentially favoring export of terrestrial C to aquatic ecosystems rather than *in situ* accumulation of SOC. The consequences of this flux to the watershed-level C balance or lake trophic dynamics are as yet unknown, but potentially significant. Other researchers have also observed transport-driven pulses of more depleted $\delta^{13}C$, modern (based on $\Delta^{14}C$) DOC from surficial soil horizons d $\delta^{13}C$ during snowmelt

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or after large rainfall events (Lambert, Pierson-Wickmann, Gruau, Thibault, & Jaffrezic, 2011; Sanderman, Lohse, Baldock, & Amundson, 2009; Schiff et al., 1997; Sebestyen et al., 2008).

Regardless of its age or degree of decomposition, the increase in DOC with discharge suggests it is a transport-limited solute, *i.e.*, that hydrologic connectivity is the ultimate driver of its concentration in the stream. This inference is congruent with the saturated variable source area (VSA) model (Andrews, Lin, Zhu, Jin, & Brantley, 2011; Boyer, Hornberger, Bencala, & McKnight, 1997; Inamdar et al., 2004; Lambert et al., 2014). The VSA model holds that rising water tables and more extensive soil saturation allow for flushing of soil C to the stream from distal wetland areas that are disconnected from the stream at lower flows (Diamond & Cohen, 2018; Gannon et al., 2015; Grabs, Bishop, Laudon, Lyon, & Seibert, 2012; Hornberger, Bencala, & McKnight, 1994; Brown, McDonnell, Burns, & Kendall, 1999; Inamdar et al., 2004; Lottig et al., 2013). Importantly, because TSS also showed a positive (flushing) *C*-*Q* relationship, it is likely that suspended solids account for an additional flux of C during high flows and peak events when saturated areas are most extensive and high-energy stream flows can transport particulate organic matter down-watershed.

In contrast to DOC and TSS, expanded connectivity between the stream and shallow soil horizons in riparian areas during high flows did not result in increased concentration of biologically cycled analytes. Specifically, negative *C*-*Q* relationships for NO_3^-, PO_4^{3-}, and SO_4^{2-} at the mouth and for NO_3^- at the mid flume suggests that the availability of these analytes for in-stream transport is limited by biological activity, with large inputs of snowmelt or precipitation

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diluting the concentrations. For example, NO_3^- is likely produced primarily in the stream or in very near-stream riparian areas during summer and autumn when low flow conditions favor net NO_3^- production due to increased nitrification and decreased denitrification as the extent of saturated soils shrinks (Burns et al., 2009; Duncan et al., 2017). NO_3^- availability in upland soils is very low, with practically no net nitrification in the top 30 cm of soil and very low concentrations in freely flowing soil water (<100 µg L^{-1} 10 cm below the surface; <50 µg L^{-1} at 60 cm) (Nave, Vogel, Gough, & Curtis, 2009; Nave et al., 2011, 2014). With soil water NO_3^- concentrations an order of magnitude less than stream NO_3^-, it is likely that in-stream or riparian zone biogeochemical processes and possibly precipitation are the primary sources of NO_3^- to the stream. In a forested watershed Duncan et al. (2017) observed a dilution pattern for NO_3^- when sampling at a weekly time step, however, high frequency sampling during storm events has revealed flushing of NO_3^- with concentrations increasing on the rising limb of storm hydrographs (Inamdar et al., 2004; Duncan et al., 2017; Hunsaker & Johnson, 2017). It is possible that similar phenomena could be occurring in our watershed as near-stream NO_3^- sources are flushed out during storm events and due to the slow production of NO_3^- in those riparian areas, concentrations remain low and are diluted even further, especially during snow melt. A low CV_C for NO_3^- (10-13%) and SO_4^{2-} (15-35%), and the chemostatic CV_C/CV_Q ratio for SO_4^{2-} at the mid and upper flumes and NO_3^- at the upper flume, suggests that the availability of these mobile elements is relatively consistent (Moatar et al., 2017). In contrast, PO_4^{3-} variability was high (CV_C 50-213%) and the CV_C/CV_Q ratio was chemodynamic at the mid flume and did not show a

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chemostatic trend at the upper flume. Higher variability in phosphorus (TP, PO_4^{3-}) has also been observed by Thompson et al. (2011), Musolff et al. (2015), Dupas et al. (2017), and Moatar et al. (2017) and this variability could be due to threshold driven variability of sediment-bound P, biological mediation, or to high rates of reactivity in streams being stronger controlling factors on concentration than discharge.

Negative *C*-*Q* relationships were also observed for several base cations (Na^+, Mg^{2+}, Ca^{2+}) at the mouth, mid (Na^+, Mg^{2+}), and even upper (Mg^{2+}) flumes. The *C*-*Q* plots for Ca^{2+} at the mid and upper and Na^+ at the upper flumes show a slight, though non-significant dilution tendency. Overall, the abundance of strong dilution patterns ($|b|>0.2$, except for Mg^{2+} at upper flume where $|b|=0.1$) at our site, contrast with findings by Godsey et al. (2009), Hunsaker & Johnson (2017), and Kim et al. (2017), who broadly observed base cations to have chemostatic or negative *C*-*Q* relationships with slopes close to 0 ($|b|<0.1$). In the Honeysuckle Creek watershed and across the local landscape, these major cations are present in the glacial parent materials and in soil exchangeable pools (Adams & Boyle, 1979, 1982; Jin, Williams, Szramek, Walter, & Hamilton, 2008; Nave et al., 2019b; Williams et al., 2007). While weathering at the deep soil-parent material interface may provide a small and stable baseline supply of these solutes to the stream, they are present at their highest soluble concentrations in the surface soils, where multiple factors control their availability. These include biotic factors such as rates of organic matter mineralization and vegetation uptake, and physical factors such as the soil pH and availability of cation exchange surfaces (Bigelow & Canham, 2015; Herndon et al., 2015; Hoagland et al.,

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2017). Thus, snowmelt or precipitation events that leach significant quantities of these cations from their available pools in surface horizons may interact with strong biotic limitations to their availability, leading to an apparent dilution effect if the mineral weathering baseline is a relatively small contribution to the quantities observed in streamflow. In contrast to the dilution patterns observed for the other major cations, K^+ displays a flat *C-Q* shape and chemostatic to neutral CV_C/CV_Q ratio. While parent material weathering is likely a primary source of K^+ (Adams & Boyle, 1982), biological processes unique to K^+ are likely controlling the availability and distribution of this cation (Likens et al., 1994; Salmon et al., 2001; Tripler, Kaushal, Likens, & Walter, 2006). In contrast to the major cations, excluding K^+, other parent material weathering byproducts, including the anions Cl^- and F^-, show no dilution trends. These anions are not bound up in any sink and are easily mobilized in soil and stream water. While neither Cl^- nor F^- had significant *C-Q* relationships, excepting the negative *C-Q* relationship for Cl^- at the mouth that is likely due to road salt applications to the paved road between the mid and the mouth flumes (Figure 1), they did differ somewhat in their levels of variability. Cl^- had lower CV_C (20-30%) and chemostatic CV_C/CV_Q ratios at the mid and upper flumes compared to F^-, which was more variable (CV_C=56-71%; no trend to slightly chemostatic CV_C/CV_Q ratio) but also measured at much lower concentrations. Musolff et al. (2015), Hunsaker & Johnson (2017), and Moatar et al. (2017) also observed low variability chemostatic trends for Cl^-.

At our study site, we observed that from the headwaters to the mouth of the stream, water fluxes and increasing discharge become a more dominant control on stream chemistry as the

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catchment area increased from 8.5 to 120 ha. Differences in the proportion of analytes with significant *C-Q* relationships (positive, negative) at each location suggest that, as the contributing area increases, stream waters are recording landscape variation in source areas, hydrologic connectivity, residence time, or in-stream biogeochemistry (Moatar et al., 2017; Singh, Inamdar, & Mitchell, 2015). The degree to which these discrete factors/processes (*e.g.*, connectivity, biogeochemistry) affect *C-Q* relationships is not clear, but may reflect differences in parent material distribution, groundwater inputs, or amount of wetland area in each subwatershed. At the upper flume, the lack of significant *C-Q* relationships for most analytes, suggests that the volume of water (*i.e.*, discharge) is likely not the primary factor controlling analyte concentrations in the stream at seasonal time scales, although the limited temporal resolution of our sampling design precludes detection of potentially rapid shifts in discharge and solute concentrations during storm events. As this flume is so near the headwater groundwater source, the amount and chemical characteristics of groundwater sources, as they interact with the soils formed in heterogenous glacial till are likely significant factors influencing stream chemistry. Moving down Honeysuckle Creek, the influence of discharge appears to increase, as more analytes display significant *C-Q* relationships.

Export of C, nutrients, and major ions from the Honeysuckle Creek watershed to Burt Lake is largest during the spring, with pulses during large summer storms. Spring snowmelt is the dominant hydrological event in the year; peak flows at the mouth and upper flumes are an order of magnitude larger than at other times of the year, and more than twice as large at the mid

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flume than annual mean discharge. During the hydrologic year, mean DOC loading from the mouth of the stream was 3,392 kg year^{-1}, with the largest loads in the spring (20 kg day^{-1}). Based on our isotopic data, spring DOC inputs to the lake consist of less decomposed, more surficial organic matter than at other times of the year and are likely to be dominated by wetland C with some upland sources mixed in (Elder et al., 2000; Lottig et al., 2013; Lambert et al., 2014; Marx et al., 2017). In the large northern basin of Burt Lake, which is fed only by first- and second-order streams similar to Honeysuckle Creek, DOC inputs from these small streams likely play a key subsidizing role in the C cycle of this aquatic ecosystem, just as small streams play important an important role in nutrient cycling of the Great Lakes especially in spring (Biddanda & Cotner, 2002; Marcarelli et al., 2018). Dissolved and particulate C are essential for maintaining heterotrophic processes within the lake, particularly during the spring when macroinvertebrate populations are booming, and fish are spawning (Carpenter et al., 2005; Frost, Kinsman, Johnston, & Larson, 2009; Lottig et al., 2013; McLaughlin & Kaplan, 2013; Tanentzap et al., 2017).

5 Conclusions

Stream discharge and chemistry along Honeysuckle Creek varied widely during the 2015-2016 hydrologic year. Stream discharge increased by an order of magnitude from the headwaters to the mouth, with the largest flows occurring in spring during the snowmelt period and during some large summer storms. Stream chemistry also varied longitudinally along the

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stream and all analytes were generally in the highest concentrations at the mouth. Many analytes displayed seasonal differences in concentration, likely due to changes in discharge, hydrologic connectivity, biological inputs, or microbial activity. Overall, the concentrations of all analytes measured displayed much less variation than the measured variation with discharge. However, all three *C-Q* shapes (positive, negative, flat) were observed at all locations along the stream. At the mouth, most analytes displayed significant positive or negative *C-Q* relationships, indicating that discharge is a significant driving factor controlling stream chemistry. The importance of discharge appeared to decrease moving upstream to the headwaters, suggesting that more localized (*e.g.*, heterogenous soils) or temporally dynamic (*e.g.*, event-based flow increases or decreases) factors may become more dominant controls on stream solute patterns. Small streams such as Honeysuckle Creek are an important conduit for energy, nutrients, and ions moving from the upland landscape to inland lakes.

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Tables

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Table 1: Weekly mean precipitation chemistry by season from October 2015–September 2016 (mean ± SD).

Analyte (mg L^{-1})	Autumn	Winter	Spring	Summer
NO_3^--N	0.11 ± 0.04	0.29 ± 0.18	0.17 ± 0.10	0.28 ± 0.21
SO_4^{2-}	0.40 ± 0.19	0.57 ± 0.38	0.56 ± 0.17	0.56 ± 0.34
Na^+	0.03 ± 0.02	0.06 ± 0.09	0.04 ± 0.03	0.03 ± 0.04
K^+	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02
Mg^{2+}	0.02 ± 0.01	0.02 ± 0.02	0.03 ± 0.02	0.05 ± 0.02
Ca^{2+}	0.09 ± 0.05	0.20 ± 0.30	0.22 ± 0.13	0.28 ± 0.23
Cl^-	0.04 ± 0.04	0.10 ± 0.14	0.05 ± 0.40	0.07 ± 0.07

Table 2: Mean stream water analyte concentration ± SD during October 2015–August 2016 sample period. Superscript letters denote significant differences in concentration by location; see Table 3 for location, season, and interaction p-values. Asterisks beneath table indicate significant location by season interactions.

Analyte (mg L^{-1})	Mouth	Mid	Upper
TSS †	13.05 ± 12.69*a*	13.44 ± 13.94*a*	8.45 ± 8.41*b*
DOC	4.5 ± 3.1*a*	4.3 ± 1.9*a*	3.5 ± 1.23*a*
NO_3^--N	0.493 ± 0.048*a*	0.400 ± 0.053*b*	0.451 ± 0.045*c*
PO_4^{3-}-P ‡	0.01 ± 0.005*a*	0.004 ± 0.01*b*	0.003 ± 0.002*b*
SO_4^2 §	4.31 ± 0.66*a*	2.98 ± 1.04*b*	3.28 ± 1.16*c*
Na^+	5.59 ± 1.14*a*	1.46 ± 0.53*b*	1.16 ± 0.24*b*
K^+ ¶	1.08 ± 0.48*a*	1.18 ± 0.41*a*	1.03 ± 0.37*a*
Mg^{2+}	13.51 ± 2.15*a*	10.59 ± 2.53*b*	13.61 ± 4.62*a*
Ca^{2+}	34.85 ± 5.41*a*	30.58 ± 18.48*b*	40.79 ± 33.04*a*
Cl^-	6.35 ± 1.29*a*	0.51 ± 0.15*b*	0.45 ± 0.13*c*
F^-	0.048 ± 0.027*a*	0.046 ± 0.027*a*	0.036 ± 0.026*b*
DOC $\delta^{13}C$ ‰	-25.91 ± 0.46*a*	-26.67 ± 0.43*b*	-26.57 ± 0.27*b*

† Interaction: Mouth, Mid greater than Upper in spring; no difference between locations in other seasons

‡ Interaction: Mouth greater than Mid, Upper in autumn, winter; Mouth greater than Mid in spring, summer

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§ Interaction: All locations different in spring, summer; no difference between locations in autumn

¶ Interaction: Mid lower than Mouth and Upper in summer; no difference between locations in other seasons

Table 3: Two-Way ANOVA results for the comparison of stream analyte concentration by location (flume) and season. F statistic and p-values are given for the location, season, and interaction effects for each analyte.

Analyte	Location		Season		Interaction	
	F	p-value	F	p-value	F	p-value
TSS	0.414	0.662	4.389	0.007	2.711	0.019
DOC	0.906	0.408	18.779	<0.001	0.901	0.498
DOC $\delta^{13}C$	37.266	<0.001	9.252	<0.001	0.416	0.416
NO_3^--N	21.933	<0.001	4.435	0.016	0.964	0.435
PO_4^{3-}-P	31.004	<0.001	8.786	0.092	2.298	0.044
SO_4^{2-}	43.741	<0.001	49.106	<0.001	7.838	<0.001
Na^+	216.963	<0.001	6.981	<0.001	1.188	0.323
K^+	1.555	0.218	13.348	<0.001	2.485	0.031
Mg^{2+}	15.728	<0.001	16.533	<0.001	1.249	0.292
Ca^{2+}	5.191	0.008	2.085	0.11	0.837	0.546
Cl^-	910.496	<0.001	3.217	0.028	1.669	0.141
F^-	4.632	0.013	28.120	<0.001	0.752	0.610

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Table 4: For analytes with no significant *C-Q* slope (flat shape), solute coefficient of variation CV_C and the CV_C/CV_Q ratio are presented here to indicate analytes trending towards chemostatic ($CV_C/CV_Q \leq 0.5$) and chemodynamic ($CV_C/CV_Q \geq 1.0$) behavior based on variability. Analytes are organized by location (flume) and CV_C/CV_Q ratio, beginning with the most variable chemodynamic analytes (noted with a D), followed by analytes with no distinct trend (noted with N), and ending with low-variability chemostatic analytes (noted with S).

Location	Analyte	CV_C (%)	CV_C/CV_Q	Trend
Mouth	F^-	56	0.83	N
	K^+	43	0.61	N
Mid	PO_4^{3-}-P	213	1.5	D
	Ca^{2+}	60	0.42	S
	F^-	60	0.41	S
	K^+	35	0.24	S
	SO_4^{2-}	35	0.24	S
	Cl^-	30	0.21	S
Upper	Ca^{2+}	81	0.82	N
	F^-	71	0.72	N
	PO_4^{3-}-P	65	0.66	N
	K^+	40	0.40	S
	SO_4^{2-}	35	0.36	S
	Cl^-	30	0.30	S
	Na^+	21	0.21	S
	NO_3^--N	10	0.12	S

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Figure Legends

Figure 1: Honeysuckle Creek watershed (black outline) and subwatersheds (mid flume is gray, upper flume is white) in northern Lower Michigan (see inset). Three flumes were located along Honeysuckle Creek (mouth at 181 m elevation, mid around 200 m, upper around 230 m; triangles). A paved road (dashed line) runs roughly parallel to the 190 m and 200 m elevation contour lines.

Figure 2: Honeysuckle Creek discharge at all three flumes (mouth, mid, upper) and stream temperature at the mouth shown in the top panel (A) during the 2015-2016 hydrologic year. Note: stream temperature during Feb 12-May 4, 2016 was estimated from air temperature as described in the Methods. Precipitation and snow depth are shown in the bottom panel (B). Over this time period, discharge was highest at the mouth (1,126±809 L min^{-1}; mean ± SD), then the middle flume (186±285 L min^{-1}), and lowest at the upper flume (47±63 L min^{-1}).

Figure 3: *C-Q* relationships for TSS, C, and biologically cycled anions (NO_3^-, PO_4^{3-}, SO_4^{2-}) at all three flumes (mouth, mid, upper), with season indicated by point shape and color. Power relationship significance and strength assessed by p-values and r^2 values; slope (*b*) of the relationship is also given. Statistically significant regressions are indicated by solid ($p<0.05$) and dashed ($0.05<p<0.1$) lines.

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Figure 4: *C-Q* relationships for cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) at all three flumes (mouth, mid, upper), with season indicated by point shape and color. Power relationship significance and strength assessed by p-values and r^2 values; slope (*b*) of the relationship is also given.

Figure 5: *C-Q* relationships for anions (Cl^-, F^-) at all three flumes (mouth, mid, upper), with season indicated by point shape and color. Power relationship significance and strength assessed by p-values and r^2 values; slope (*b*) of the relationship is also given.

Figure 6: *C-Q* relationships for DOC $\delta^{13}C$ at all three flumes (mouth, mid, upper), with season indicated by point shape and color. Power relationship significance and strength assessed by p-values and r^2 values; slope (*b*) of the relationship is also given.

Figure 7: Stream DOC and DOC $\delta^{13}C$ at the mouth (triangle), mid (square), and upper (circle) flumes. The upper (-26.57±0.27‰) and mid (-26.67±0.43‰) flumes had significantly more depleted DOC $\delta^{13}C$ than the mouth (-25.91±0.46‰). DOC was most depleted in the spring, followed by winter, and most enriched in summer. There are no DOC $\delta^{13}C$ samples from the autumn season.

Figure 8: Soil $\delta^{13}C$ (panel A) and $\Delta^{14}C$ (panel B) from wetland and upland soil samples by horizon depth. Linear regressions are shown with significance and strength assessed by p-values

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and r^2 values.

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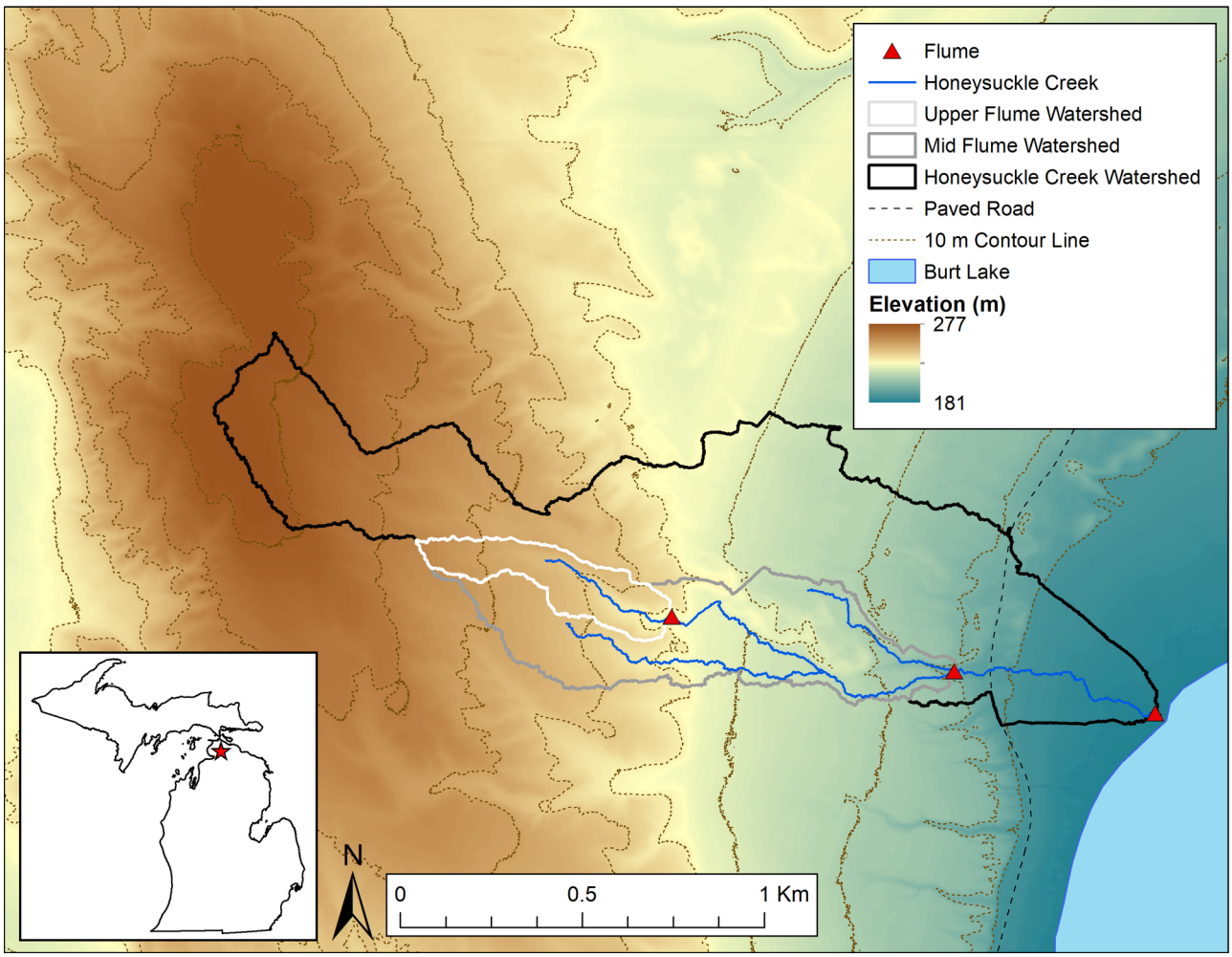

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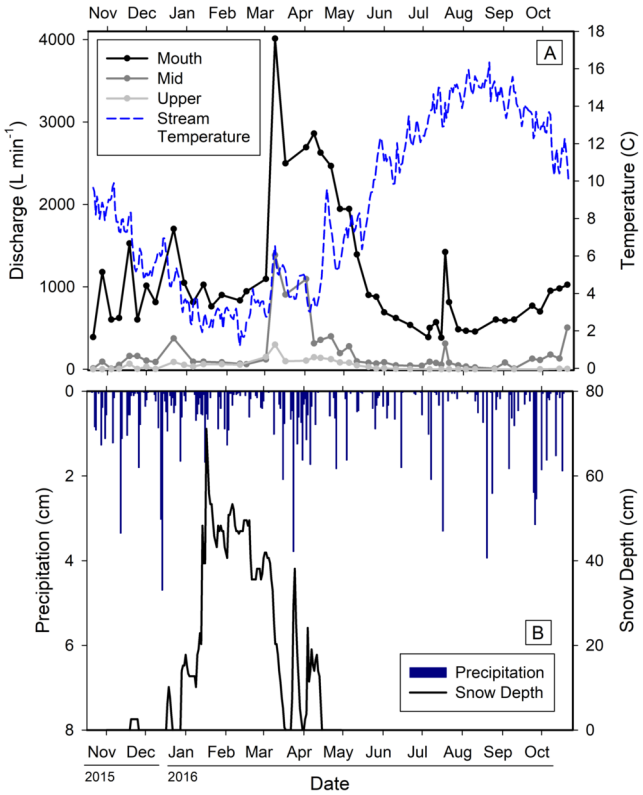

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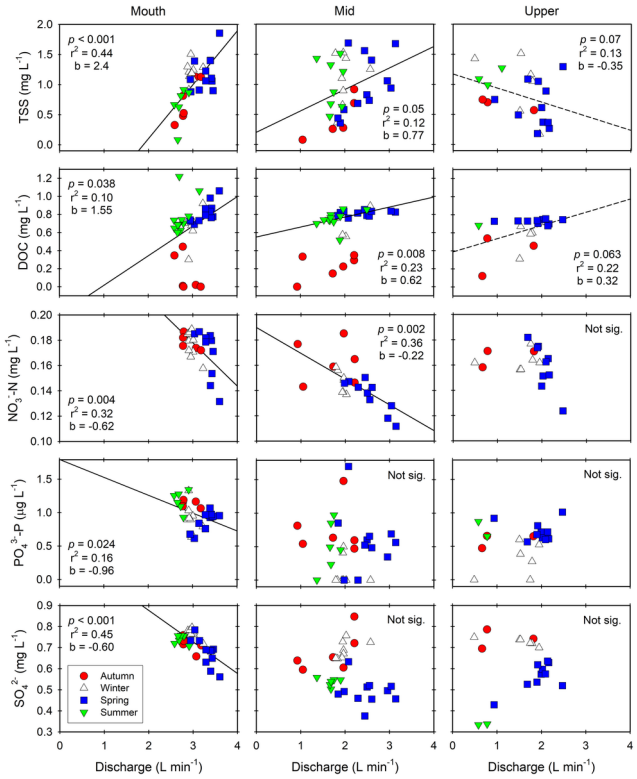

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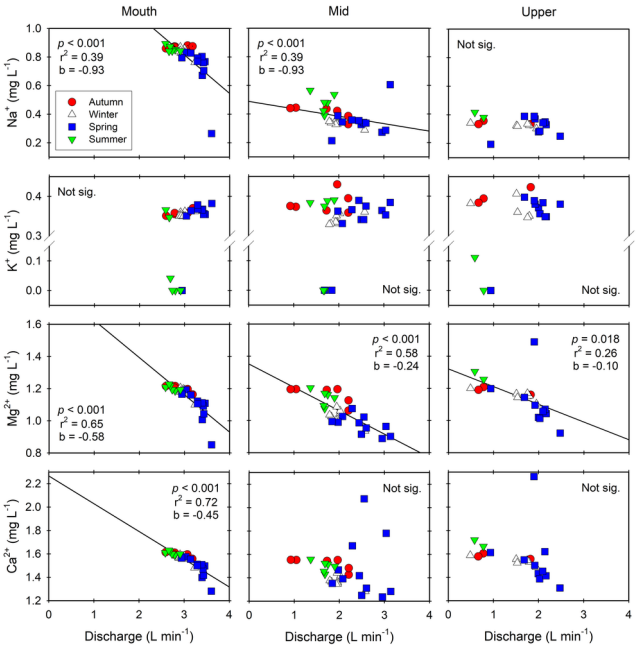

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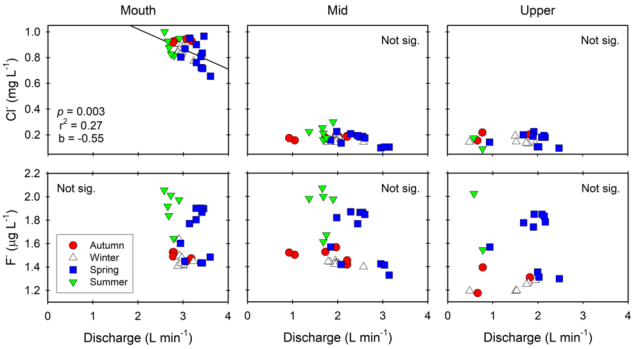

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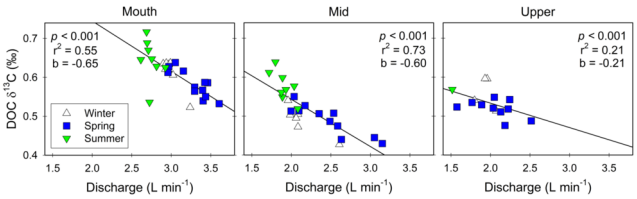

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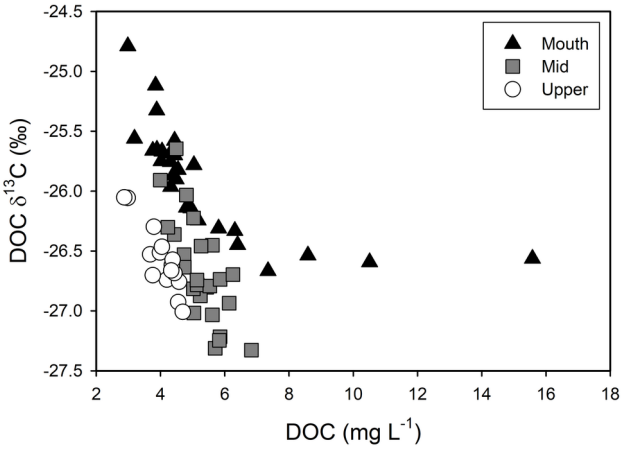

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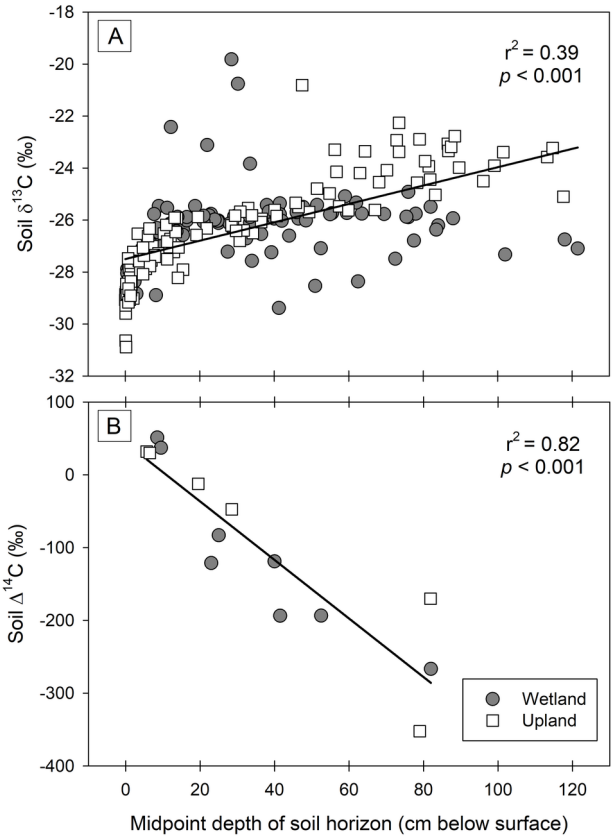

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