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UNDERSTANDING THE MECHANISMS CONTROLLING THE
CONCENTRATION-DISCHARGE RELATIONSHIPS OF STREAMS IN
NORTHEASTERN AND NORTH MIDWESTERN UNITED STATES

By

Veronica Porter

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Forest Ecology and Management

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2020

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
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College of Forest Resources and Environmental Science

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Table of Contents

Preface	vi
Acknowledgements.....	vii
Abstract.....	viii
1 Chapter 1: Concentration-Discharge Relationships.....	1
1.1 INTRODUCTION.....	1
1.2 REFERENCES.....	3
2 Chapter 2: Controls on Long-Term, Annual, and Seasonal Solute Export Patterns in a Forested Headwater Watershed in Northeastern U.S.	6
2.1 Abstract	6
2.2 INTRODUCTION.....	7
2.3 SITE DESCRIPTION.....	10
2.4 METHODOLOGY	11
2.4.1 Sample Collection.....	11
2.4.2 Data Preparation.....	12
2.4.3 Concentration-Discharge Analysis	13
2.4.4 Diagnostic Tools of Mixing Models and End-Member Mixing Analysis	14
2.5 RESULTS.....	15
2.5.1 Hydrologic and Hydrochemical Characteristics	15
2.5.1.1 Annual Precipitation and Chemistry	15
2.5.1.2 Streamflow and Stream Water Chemistry	15
2.5.1.3 Spatiotemporal and Vertical Variation of Solute Concentrations in the Soil Water and Groundwater	16
2.5.2 C-Q Relationships in Streamflow	17
2.5.2.1 Multi-Annual C-Q Relationships.....	17
2.5.2.2 Yearly C-Q Relationships	17
2.5.2.3 Seasonal C-Q Relationships.....	18
2.5.3 End-Member Mixing Analysis	19
2.5.3.1 Conservative Solutes and the Number of End-Members	19
2.5.3.2 Determination of End-Members	19
2.5.3.3 End-Member Contributions	21
2.6 DISCUSSION	22
2.6.1 Multi-Annual Pattern	22
2.6.2 Yearly Pattern	24

2.6.3	Seasonal Pattern	26
2.7	CONCLUSION	27
2.8	REFERENCES	28
2.9	TABLES AND FIGURES.....	34
2.9.1	Tables.....	34
2.9.2	Figures.....	37
	38	
2.10	APPENDIX 2.A SUPPLEMENTAL TABLES	47
2.11	APPENDIX 2.B SUPPLEMENTAL FIGURES	62
3	Chapter 3: Synoptic Diagnosis of Catchment Hydrologic and Biogeochemical Processes and Climate and Land Use Change Effects in the Great Lakes Basin.....	64
3.1	Abstract	64
3.2	INTRODUCTION.....	65
3.3	SITE DESCRIPTION.....	68
3.4	METHODOLOGY	69
3.4.1	Data Sources and Preparation	69
3.4.2	Concentration-Discharge Analysis	71
3.4.3	Correlation Between C-Q Coefficients and Catchment Characteristics	72
3.5	RESULTS.....	73
3.5.1	Solute Concentration-Discharge Patterns	73
3.5.2	Catchment Characteristics and Concentration-Discharge Patterns...74	
3.5.2.1	R ² and Catchment Characteristics	74
3.5.2.2	Correlation Between b-Coefficients from all Sites and Catchment Characteristics	74
3.6	DISCUSSION	75
3.6.1	Insight into Contrasting Solute Distributions	76
3.6.2	Importance of Snow Abundance on Hydrologic Processes	77
3.6.3	Land-Use Impacts on Solute Transport and Hydrologic Flowpaths.79	
3.6.3.1	Prevalent Transport Dynamics in Forested Catchments.79	
3.6.3.2	Prevalent Transport Dynamics in Urbanized Catchments 80	
3.6.3.3	Prevalent Transport Dynamics in Areas with Agriculture 80	
3.6.3.4	Nutrient Export and Water Quality Concerns.....	82
3.7	CONCLUSION	83
3.8	REFERENCES	84

3.9	TABLES AND FIGURES.....	90
3.9.1	Tables.....	90
3.9.2	Figures.....	91
3.10	APPENDIX 3.A: SUPPLEMENTAL TABLES	101
4	Conclusion	105
4.1	REFERENCES.....	107

Preface

The chapters of this thesis are composed of two multi-author, journal articles that are in preparation to be submitted for publication in the scientific journals: *Hydrological Processes* (Chapter 2) and *Journal of Great Lakes Research* (Chapter 3). For these articles, I primarily led the research (study design, data analysis, and interpretation) and wrote the manuscripts. The data used for Chapter 2 was collected by numerous researchers and technicians at Sleepers River Research Watershed and the data in Chapter 3 was collected by USGS as part of their water watch program in addition to multiple public datasets. Both articles were written in collaboration with Fengjing Liu who also acquired the funding, guided the studies, assisted with the end-member mixing analysis, and edited the manuscripts. Stephen Sebestyen and Jamie Shanley aided in data analysis questions and draft revisions of Chapter 2.

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Abstract

Concentration-discharge (C - Q) relationships, concentration expressed as a power-law function of stream discharge ($C = aQ^b$), are an easy and efficient way to gain insight into solute export processes within a catchment. Despite decades of research, we have limited understanding of the controls on C - Q relationships, consequently making it difficult to confidently apply findings to unstudied catchments. Additionally, there is limited knowledge on how changes in climate and land uses may affect solute export by modifying solute availability and stream water chemistry at catchment scales.

The goal in Chapter 2 was to close some of those knowledge gaps by understanding factors controlling variation in stream water chemistry between timescales through end-member mixing analysis and concentration-discharge analysis. Over a decadal timescale, major nutrients and some trace elements exhibited a positive relationship with discharge (positive b for flushing), while major ions, particularly geogenic ions, displayed a contrasting pattern of dilution (negative b). I found a key factor controlling export, represented by the slope of the C - Q power-law relation, is the vertical distribution of solutes between shallow to deeper flowpaths. A negative b -coefficient corresponds to an increase in solute concentrations with depth, while a positive b is caused by a decrease. When solute concentrations varied greatly between deep and shallow flowpaths, the magnitude of the b -coefficient was higher than when there was little variation in concentrations. Interannual variability was much lower for conservative solutes (resulting from mixing rather than chemical equilibrium over a short time period, e.g., days) than for non-conservative solutes, making the export pattern of conservative solutes, mostly geogenic ones, more predictable and useful in forensic hydrology. During snowmelt, the magnitudes of b -coefficients of most solutes were higher on the falling than rising limbs due to greater contributions of saturation overland flow. These findings indicate that seasonal stream chemistry will likely shift under new climate conditions as precipitation patterns change with a decrease in snow abundance and earlier snowmelt.

The objective in Chapter 3 was to examine patterns in C - Q relationships throughout 138 catchments within the Great Lakes Basin (GLB) and the catchment physical and environmental factors (e.g., land-use and precipitation pattern) controlling the C - Q behaviors. Major geogenic ions were consistently diluted throughout the GLB during periods of high flow, while major nutrients and trace elements were enriched. Snow abundance and land-use were frequently correlated to the R^2 values of C - Q relationships and the pattern and intensity of changes in solute concentrations. In more forested areas, the strength of C - Q relations (R^2) for specific conductance (SC) increased, while that of sulfate and ammonium decreased. There was also increased dilution of SC, calcium, and magnesium and increased enrichment of phosphorus in catchments with more forested area. The results indicate that under future conditions of increasing urban areas and decreasing snow abundance, the C - Q power-law relationships may become weakened for major geogenic solutes, suggesting that solute export for multiple solutes will become more chemostatic and the buffering capacity for nutrients such as NO_3^- and contaminants will be reduced.

1 Chapter 1: Concentration-Discharge Relationships

1.1 INTRODUCTION

Analyzing the relationship between solute concentrations and changes in stream discharge is a valuable analytical method used to study hydrological processes and solute export processes at a catchment scale. Many studies have shown that concentration-discharge (C - Q) analysis is a useful tool in understanding the internal processes controlling streamflow generation, solute distribution and availability, export flowpaths, and timing of export (Duncan, Welty, Kemper, Groffman, & Band 2017; Hofmeister et al., 2019). Shifts in C - Q relations across spatial-temporal scales and varying landscapes reflect dominant flowpaths and solute availability controlling stream water chemistry creating an effective way to understand integrated biological and hydrological processes within catchments (Hofmeister et al., 2019; Zimmer, Pellerin, Burns, & Petrochenkov 2019). Concentration-discharge relationships can be one tool to improve the understanding of hydrologic mechanisms and predict potential impacts of climate change on the quality and quantity of future water resources. (Hunsaker & Johnson, 2017; Litt, Gardner, Ogden, & Lyons 2015)

One benefit of the C - Q analytical method is that it does not require high-frequency sampling or data collection from multiple water sources, making it a relatively inexpensive but effective method to gain an understanding of hydrological and biogeochemical processes occurring within a catchment. To calculate C - Q relationships, data collection involves simultaneously measuring stream discharge and the concentration of a solute either by in situ measurements or grab samples typically at the outlet of the catchment. The concentration-discharge relationship is represented by a power-law function such that:

$$C = aQ^b \quad (1)$$

Where C represents concentration of a solute, Q stream discharge, and a and b are constants. This relationship can also be examined in the logarithmic space with b representing the slope of the line:

$$\log(C) = \log(a) + b \cdot \log(Q) + \epsilon \quad (2)$$

where ε is the error (Hofmeister et al., 2019; Zimmer et al., 2019). The strength of the C - Q relation is measured by the coefficient of determination (R^2) which indicates how much of variation in solute concentration is explained by variation in stream discharge. The significance of the relationship is measured by the p -value of the regression with a value of less than 0.05, 0.01 or 0.001.

When using the logarithmic scale, the slope (b) indicates the trend of solute concentration with flat slopes ($-0.1 < b \leq 0.1$) indicating chemostatic behavior, positive slopes ($b > 0$) indicating a flushing response, and negative slopes ($-0.1 \geq b$) occurring with dilution (Evans & Davies, 1998; Herndon, Dere, Sullivan, Norris, Reynolds, & Brantley 2015; Hofmeister et al., 2019; Zimmer et al., 2019). Solutes with positive slopes are theorized as transport-limited, those with negative slopes are source limited, and those with no slope are dominated by neither process (Hofmeister et al. 2019, Godsey et al. 2009, Zimmer et al. 2019).

The slope may also change between the rising and falling limbs of snowmelt or event hydrographs, creating a hysteresis pattern. Clockwise hysteresis occurs when the rising limb has higher solute concentrations than the falling during the same values of stream discharge, often related to mineral weathering in the vadose or saturated zone (Evans & Davies, 1998). An anti-clockwise hysteresis is the reverse where the rising limb has lower solute concentrations than the falling (Evans & Davies, 1998). Evans & Davies (1998) argued that one can infer dominant mixing components from the direction and shape of the hysteresis. This should be done cautiously since changes in stream chemistry does not always reflect the timing of inflows (Chanet & Hornberger, 2003). Hysteretic flushing patterns are often associated with transient (short-term) water sources and flowpaths that intersect surface soils with higher organic carbon content and higher hydraulic conductivity than deeper soils (Bishop, Seibert, Nyberg, & Rodhe, 2011; Duncan et al., 2017; Kendall, Shanley, & McDonald, 1999; McIntosh et al., 2017). Additionally, hysteretic patterns can reveal information on the moisture content of soils since well-drained soils are less likely to exhibit a dilution effect compared to less well-drained soils (McIntosh et al., 2017)

Thus, *C-Q* analysis provides a diagnostic tool to quickly and efficiently assess water quality changes in response to stream flow changes by reflecting the internal catchment structures (e.g., hydrologic pathways) influencing hydrological, biogeochemical, and ecological functions (Liu, Conklin, & Shaw, 2017). However, research investigating *C-Q* relationships is still young. The general patterns of *C-Q* relationships are readily observed, yet, the underlying causes of variability over timescales and drivers (e.g., water and energy inputs) are still debated (Chanet, Rice, & Hornberger, 2002; McIntosh et al., 2017). This knowledge gap makes extrapolating findings from *C-Q* analysis to unstudied catchments difficult. Teasing out the factors contributing to this unknown variability is made more difficult with climate change and changes in land use, which can exacerbate the natural complexity of these systems. However, understanding these interactions between natural processes and human activities is necessary in balancing environmental conservation and human development (Hunsaker & Johnson, 2017). Thus, the goal of this thesis is to bridge this knowledge gap by furthering our understanding of factors controlling *C-Q* relationships by focusing on the influences of climate, the critical zone, and land-use with the aim to increase the applicability and interpretation of *C-Q* relationships as a tool to solve water management issues.

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2 Chapter 2: Controls on Long-Term, Annual, and Seasonal Solute Export Patterns in a Forested Headwater Watershed in Northeastern U.S.

2.1 Abstract

The objective of this study was to compare responses in stream water chemistry to changes in discharge over decadal, annual, and seasonal timescales to better understand solute export patterns using concentration-discharge (C - Q) relationships and end-member-mixing analysis (EMMA). C - Q power-law relationships ($C=aQ^b$) were assessed using 15 solutes for water years 1992-2015 at W-9 of Sleepers River Research Watershed (0.405 km²), Vermont. Over a decadal timescale, NO₃⁻, DOC, and Fe exhibited a positive relationship with discharge (flushing), while SC, Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Si, Sr, Ba, and Mn displayed a negative relationship (dilution). Cl⁻ and Al were chemostatic. The power-law relationship is primarily controlled by vertical distribution of solutes from shallow to deeper flowpaths. A negative b -coefficient corresponds to an increase with depth while a positive b -coefficient corresponds to a decrease. The b -coefficient decreased significantly ($p < 0.05$) with an increase in concentration ratio between deeper and shallow end-members for geogenic solutes. Geogenic solutes that are conservative, distinct, and temporally relatively constant in the three end-members identified by EMMA, showed consistent annual C - Q patterns. However, C - Q patterns for the remaining solutes did change between years, more frequently switching from chemodynamic to chemostatic behavior than remaining chemodynamic and switching the b -coefficient sign. During snowmelt with greater contributions of saturation overland flow, the power-law relations became stronger and the b -coefficients of geogenic solutes were frequently more negative on the falling than rising limbs. As snowmelt timing and precipitation intensities are likely to change in the future, concentration-discharge relationships in streamflow could change, particularly at the seasonal scale.

2.2 INTRODUCTION

For decades, hydrologists have studied processes governing solute export through concentration-discharge ($C-Q$) analysis to better understand export behavior in relation to catchment characteristics, precipitation patterns, biotic, and abiotic processes (Bieroza, Heathwaite, Bechmann, Kyllmar, & Jordan, 2018; Evans & Davies, 1998; Godsey et al., 2009; Hall 1970; Hall 1971; Johnson, Likens, Bormann, Fisher, & Pierce, 1969; Moater, Abbott, Minaudo, Curie, & Pinay, 2017; Pinder & Jones, 1969). Limited by chemical data, few studies have focused on the long-term patterns of $C-Q$ relationships. Thus, we have minimal understanding of how the $C-Q$ relationship changes in response changes in precipitation, namely increases in rainfall intensity and declining snow abundance. Understanding export process dynamics is particularly important since these processes will likely change under predicted climate conditions. These climatic changes will modify many of the dominant factors controlling solute export such as snow cover extent, snowmelt timing, winter temperatures, duration of seasons, and stream discharge (Hidalgo et al., 2009; Derksen & Brown, 2012; Pierce & Cayan, 2013; Demaria, Roundy, Wi, & Palmer, 2016). These changes will continue to occur as concentrations of greenhouse gases rise and further modify water budget partitioning, solute export, and nutrient cycling processes, which will have important implications for water quality and watershed management (Markstrom & Hay, 2009; Maher, Shanley, Bailey, & Mitchell, 2010; Krause et al., 2017).

Shifts in climate patterns are particularly concerning for snow-dominated systems which are considered especially vulnerable to climate change (Field et al., 2014). In these ecosystems, winter precipitation and the snowmelt period heavily influence stream water chemistry by rapid elution and transport of contaminants from snowpack and surficial soils into nearby streams (Bishop, Grip, & O'Neill, 1990; Bishop, Grip, & Piggott, 1990; Bishop 1991; Boyer, Hornberger, Bencala, & McKnight, 2000; Carroll et al., 2018; Ericson, Holmen, & Latkovich, 1980). Additionally, precipitation patterns are expected to change to shorter and more intense events, thereby changing nutrient and sediment mobilization by modifying the sequence of activation and contribution of hydrological flowpaths (Field

et al., 2014; Winnick, Carroll, & Williams, 2017). By understanding current linkages between solute export, activation of hydrologic flowpaths, and end-member contributions, we can better identify the implications of these changes on stream water chemistry and better address future water quality vulnerabilities.

Long-term research sites provide a valuable opportunity to study such linkages by providing large, detailed datasets spanning numerous years, allowing researchers to determine underlying mechanisms across multiple timescales and factors influencing interannual variations. Sleepers River Research Watershed (SRRW), founded in 1957, is a long-term research site in Vermont, USA, where research has focused on hydrological processes, particularly streamflow generation, and biogeochemical processes (Shanley, Sebestyen, McDonnell, McGlynn, & Dunne, 2015). Saturation overland flow (SOF) was first identified at SRRW in the 1960's through highly permeable surficial soils over a variable source area (VSA) (Dunne & Black, 1970). These processes were determined influential in shaping stream water chemistry by channeling up to 40% of event water along preferential flowpaths (Kendall, Shanley, & McDonnell, 1999; Shanley, Kendall, Smith, Wolock, & McDonnell, 2002). Recent research from SRRW has found that SOF, coupled with existing biogeochemical processes, strongly shapes timing and yield of nutrient export during storm and melt events especially for nitrate (NO_3^-), sulfate (SO_4^{2-}), and dissolved organic carbon (DOC), which have highest concentrations in surface soils (Doctor et al., 2008; Ohte et al., 2004; Sebestyen et al., 2008; Sebestyen, Shanley, Boyer, Kendall, & Doctor, 2014; Sebestyen et al., 2019). Findings also revealed seasonal fluctuations in DOC and nitrogen concentrations during autumn due to leaf fall shifting microbial activity and seasonal hydrological changes (Sebestyen et al., 2014). These findings indicate solute export will change with changes in climate especially since storm intensities are predicted to rise, increasing the frequency and duration of SOF.

A useful tool in understanding solute export is end-member mixing analysis (EMMA), which reveals the source end-members and contributions responsible for stream chemistry. A few studies have used EMMA at SRRW to discover that either two or three end-members were necessary to recreate stream chemistry (Kendall, Shanley, &

McDonnell, 1999; Ohte et al. 2004; Sebestyen et al., 2008, Shanley et al., 2015; Smith 1997). Kendall et al. (1999) showed that 94% of the variance in stream chemistry could be explained by a two-component mixture of groundwater high in base cations and an O-horizon/overland flow water high in DOC. Smith (1997) also used EMMA to find three end-members, including precipitation (rain and meltwater), soil water, and groundwater. Both studies selected the chemical species as conservative tracers based on assumptions and their behavior in the catchment (Kendall et al, 1999; Smith 1997). Two of these studies occurred before diagnostic tools of mixing models (DTMM) were developed, which are tools to select conservative tracers and determine the number of end-members (Hooper, 2003). Sebestyen et al. (2008) used DTMM but performed EMMA only over the 2004 snowmelt period. A recent study has demonstrated that combining end-member mixing analysis and concentration-discharge relationships strongly enhances watershed hydrologic and biogeochemical studies and provides physically meaningful results of end-member mixing analysis (Liu, Conklin, & Shaw, 2017).

Previous studies at SRRW have significantly improved our understanding on the controls of solute export, especially of the importance of SOF during storm and snowmelt events and how export may respond to a changing climate. However, these studies focused on hydrologic and biogeochemical processes at seasonal scales within a limited time period and typically did not examine interannual variability and long-term trends. By combining DTMM and EMMA using hydrologic and hydrochemical data collected at SRRW from 1992 to 2015 water years, I examined concentration-discharge relationships at multiple temporal scales, varying from seasonal to annual to decadal. The overarching goal was to investigate the linkages between changes in stream chemistry and shifts in end-member contributions across ranging timescales to better predict how climate-induced hydrological patterns will influence solute export. Specifically, the objectives were to (1) examine solute export patterns and variability at varying temporal scales; and (2) determine the factors that control solute export processes and *C-Q* dynamics at varying timescales.

2.3 SITE DESCRIPTION

Sleepers River Research Watershed (44° 28'N, 72° 9'W), a long-term research watershed located in rural north-eastern Vermont, was established in 1957 by the Agricultural Research Service (ARS) of the United States Department of Agriculture (USDA). Watershed 9 (W-9) is a 0.405 km² forested sub-basin included in Sleepers River Research Watershed. Elevation ranges from 524 to 679 m and is dominated by south-facing slopes ranging from 0 to 90% with a mean of 13 (Shanley, Sundquist, & Kendall, 1995). Temperature ranges from an average of -10°C in winter to 12°C in summer with an annual mean of 4.6°C (Shanley, Kram, Hruska, & Bullen, 2004). The area is impacted by acid rain, but the high buffering capacity from carbonates in bedrock and till limits the negative impacts (Hornbeck, Bailey, Buso, & Shanley, 1997). There are also chronically high nitrogen inputs typical in northeastern United States with the average total N input from 1978 to 1998 of 13.2 kg ha⁻¹a⁻¹ (Campbell et al. 2004). Mean annual precipitation of 1100 mm falls evenly over seasons throughout the year with 25-35% of precipitation falling as snow, and snow typically accumulating from December until late March or April (Shanley et al., 2015; Armfield et al., 2019).

The catchment is on the Waits River formation, composed of a quartz-mica phyllite with beds of calcareous granulite, covered by 1-4.5 m of fine silty calcareous glacial till from the Wisconsin glaciation ~10,000 years B.P. (Shanley, Hjerdt, McDonnell, & Kendall, 2003; Shanley et al., 2015; Hall 1959). The catchment drains into Pope Brook which joins with Sleepers River and later becomes the Connecticut River (Shanley, Mayer, Mitchell, & Bailey, 2008; Mayer et al., 2010).

Soils belong to Spodosol, Inceptisol, and Histosol soil orders that range from 50 to 70 cm depth on top of up to three meters of dense till and silt (Shanley et al., 2008; Mayer et al., 2010). Soil hydraulic conductivities exponentially decrease with depth while water levels in upland areas vary over several meters depending on antecedent wetness conditions (Kendall et al., 1999; Shanley et al., 2003). The forest overstory at W-9 is dominated by sugar maple, yellow birch, and white ash with an understory of striped maple, sugar maple,

hobblebush, balsam fir, and red spruce (Sebestyen et al., 2008). The forest was last harvested in 1960 when there was a selective harvest, and the forest was partially logged in 1929 (Sebestyen et al., 2008).

2.4 METHODOLOGY

2.4.1 Sample Collection

Hydrologic and meteorological variables were measured for the water years 1992 to 2015 with each water year beginning October 1 and ending September 30. Stream stage was measured at a 120° V-notch weir and discharge was calculated using a stage-discharge relationship following standard stream gauging protocols (Rantz, 1982). Discharge was calculated every 5 minutes. The stream chemistry sampling frequency varied over the period, ranging from weekly to higher frequency event sampling triggered by changes in stream discharge that varied from minutes to hours or days based on variations in stream discharge.

Soil water and groundwater samples were collected from numerous zero-tension lysimeters, piezometers, and wells throughout the catchment. The soil water was collected from three sets of 2-3 nested shallow soil zero-tension lysimeters (names starting with LYS in Table 2.A.1) along a hillslope transect (Figure 2.1). The shallowest lysimeters (SH) are just under the O-horizon (0.05-0.1 m), the middle depth (MID) is at the top of the B-horizon (~0.3 m), and the deepest (DP) is at the bottom of the B-horizon (0.7-1 m). Samples from the lysimeters were collected after a rainfall or melt event. The inlets of the lysimeters at the middle and deep depths were frequently under the top of the water table. Six piezometers (T1-T6) were deployed at two locations in the riparian zone along the stream. Groundwater samples were also collected from 36 groundwater wells (BW-##) at varying depths and sampling frequency at various landscape positions, including riparian zone, hillslope, hillslope bench, and hillslope hollow (Figure 2.1; Table 2.A.1). There were between 1 to 30 samples collected at 32 of the wells for each solute. There were only 4 wells where samples were collected more frequently with 30 to 166 samples collected for each solute (Table 2.A.1). Precipitation was measured using a weighing bucket gage at the

meteorological station (R29) in a clearing adjacent to the stream gauge. Precipitation chemistry samples were collected from a polyethylene bucket in a wet-only precipitation collector near the weighing bucket after each event or weekly.

2.4.2 Data Preparation

Specific conductance (SC) and the concentrations of 14 solutes were investigated in the study: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), dissolved organic carbon (DOC), silicon (Si), strontium (Sr), aluminum (Al), barium (Ba), iron (Fe), and manganese (Mn). Quality of ionic stream water concentrations was checked using charge balance whenever chemistry was complete for a sample. Charge balance was calculated as the percent of difference between the sum of cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and the sum of anions (Cl^- , NO_3^- , SO_4^{2-} , and HCO_3^-) to the total of both cations and anions, all expressed in $\mu\text{eq L}^{-1}$. Most of the samples with a charge balance greater than 5% resulted from missing values of bicarbonate (HCO_3^-). Around 80% of the stream water chemistry samples measured HCO_3^- . A few samples were identified as outliers and discarded because an obvious reason for charge imbalance was not identified.

To look at seasonal variability in solute export mechanisms, each water year was divided into four periods: the dormant season (Oct. 1 – beginning of snowmelt), the rising limb of snowmelt (the beginning of snowmelt to date of peak streamflow during snowmelt), the falling limb of snowmelt (peak snowmelt to the return to baseflow conditions), and the growing season (return to base flow to Sept. 30). For each water year, the snowmelt period was visually identified as the date ranges during the rising and falling limbs using stream discharge, precipitation, and temperature data. The rising limb of the snowmelt period started when there was a steady, persistent increase in stream discharge that was coupled with consecutive mean daily temperatures greater than 0°C . The falling limb began after peak streamflow and continued until streamflow returned to near baseflow conditions.

Years that had less than 20 data points were discarded for the annual C - Q analysis because there were too few samples, but these points were included in the multi-annual C - Q relationship analysis. Similarly, seasons were excluded in the seasonal C - Q analysis if they had less than 5 data points. The rising and falling limbs of snowmelt frequently had the fewest data points, ranging from 5 to 52 with a mean of 16 and a standard deviation of 13.

2.4.3 Concentration-Discharge Analysis

All C - Q analyses were calculated on $\log_{10}$ - $\log_{10}$ scales across seasonal, annual, and multi-annual timescales with the equation: $\log(C) = \log(a) + b \cdot \log(Q)$ (Hofmeister et al., 2019; Zimmer et al., 2019). Solute concentration is C , stream discharge is Q , and a and b are constants from the line of best fit. Export patterns were chemostatic if $-0.1 \leq b \leq 0.1$, meaning concentration varied little with changes in stream discharge. Patterns were chemodynamic if $|b| > 0.1$ (dilution: $b < -0.1$ or mobilization: $b > 0.1$), meaning concentration varied significantly with stream discharge (Herndon et al., 2015). The strength of the C - Q relation is measured by the coefficient of determination (R^2) which measures how much of variation in solute concentration is explained by variation in stream discharge. Student's t -test was used to determine whether the best-fit slope was significantly different from zero ($p < 0.05$). For each timescale, the CV_C/CV_Q was calculated by calculating the coefficient of variation (CV) of the solute concentrations and dividing by the coefficient of variation of stream discharge using the equation from Thompson, Basu, Lascrain, Aubeneau, & Rao (2011):

$$\frac{CV_C}{CV_Q} = \frac{\mu_Q \sigma_C}{\mu_C \sigma_Q}$$

CV_C/CV_Q measures the degree of chemostasis v. chemodynamics and can be used with the b -coefficient to provide a more robust assessment of what is occurring in the catchment. Chemostatic behavior is $CV_C/CV_Q < 1$ (Thompson et al., 2011). $CV_C/CV_Q \sim 1$ indicates chemodynamic behavior, but the sign of the b -coefficient must be considered to determine whether the chemodynamic pattern is flushing or dilution. $CV_C/CV_Q > 1$

indicates greater variability in the solute concentrations and that discharge is not the sole factor influencing concentrations.

2.4.4 Diagnostic Tools of Mixing Models and End-Member Mixing Analysis

Diagnostic tools of mixing models (Hooper, 2003) and end-member mixing analysis (Christophersen and Hooper, 1992) were combined to determine conservative tracers, the number of end-members, and the contribution of end-members to streamflow, as detailed in previous studies (Liu et al., 2008; Liu et al., 2017; Liu, Hunsaker, & Bales, 2013; Frisbee, Phillips, Campbell, Liu, & Sanchez, 2011). In contrast to previous applications, the number of end-members and conservative tracers were not evaluated by the R^2 and p values from the distribution of residuals between measured and projected streamflow chemistry using eigenvectors extracted from streamflow chemistry itself. Instead, they were examined by the cumulated, squared and then scaled eigenvectors by eigenvalues. This quantity, in correspondence to each solute, essentially represents the fraction of the total variance explained by cumulative principal components. Using this value is virtually the same as using R^2 and p values from the residual distribution, as this value is equal to 1 minus R^2 . The advantage of using squared and scaled eigenvectors is twofold: it is clearer how much variance is retained within the chosen mixing dimensions and it is easier to use from a computing/coding, operational perspective. With numerous samples, even a low R^2 may still be significant at $\alpha = 0.001$, as encountered in Liu, Lerch, Yang, and Peters (2020), and can make determining the number of end-members and conservative tracers difficult. In addition, simulated streamflow chemistry using EMMA results was validated using Nash-Sutcliffe Efficiency (NSE), instead of combining slope, R^2 and p value in observed-simulated scatterplots.

2.5 RESULTS

2.5.1 Hydrologic and Hydrochemical Characteristics

2.5.1.1 *Annual Precipitation and Chemistry*

Annual precipitation in the Sleepers River Watershed ranged from 1043 mm to 1685 mm from water years 1992 to 2015, with a mean of 1332 mm (Table 2.A.2). Water years 1995 and 2001 were the driest with annual precipitation of 1057 and 1043 mm, respectively. Overall, however, there were not extremely dry or wet years over the study period (Figure 2.B.1a). Median solute concentrations in precipitation were much lower than those in stream water for all solutes except NO_3^- (Table 2.A.1). The median pH in precipitation was 4.7. Solute concentrations and pH values varied dramatically through the study period (temporal variation not plotted but implicitly shown by the quartile range in Table 2.A.1). Like many areas on the eastern coast of the US, this watershed is impacted by acid rain caused by anthropogenic activities creating low pH (Campbell et al., 2004).

2.5.1.2 *Streamflow and Stream Water Chemistry*

Streamflow ranged from near zero to $1929.6 \text{ m}^3 \text{ h}^{-1}$ with a mean of $36.0 \text{ m}^3 \text{ h}^{-1}$. The 25%, 50%, and 75% quartiles were 10.8, 21.6, and $54.0 \text{ m}^3 \text{ h}^{-1}$. Snowmelt typically dominated the annual hydrograph but was not always the period of highest discharge, and streamflow was frequently lower and less variable during the growing season from mid to late summer when air temperatures and evapotranspiration were highest (Figure 2.B.1b). The 25%, 50%, and 75% quartiles of streamflow during sampling were 14.4, 39.6, and $111.6 \text{ m}^3 \text{ h}^{-1}$. Thus, the measured stream chemistry emphasizes stream chemistry during periods of higher flows due to the automated sampling regime that was triggered by increases in discharge. However, this is not problematic since this study focused on analyzing stream behavior during storm or snowmelt events and not on characterizing baseflow conditions.

Solute concentrations in stream water varied slightly over seasons and events, as demonstrated by Ca^{2+} , Cl^- , NO_3^- , and DOC in Figures 2.B.1c-1e. The SC and median

concentrations of all solutes except NO_3^- were highest during the growing and dormant period. Most solutes had lowest median concentrations during the snowmelt period, except DOC, which was lowest during the dormant period, and NO_3^- , which was lowest during the growing and dormant season (Table 2.A.3). Unlike other solutes, median DOC, NO_3^- , and Fe concentrations in stream water were higher during high flow conditions (e.g., $\text{NO}_3^- = 0.9 \text{ mg L}^{-1}$, $\text{DOC} = 3.6 \text{ mg L}^{-1}$, and $\text{Fe} = 17.1 \text{ } \mu\text{g L}^{-1}$ at the 95th flow percentile) compared to low flow conditions (e.g., $\text{NO}_3^- = 0.5 \text{ mg L}^{-1}$, $\text{DOC} = 1.3 \text{ mg L}^{-1}$, $\text{Fe} = 8.7 \text{ } \mu\text{g L}^{-1}$ at the 5th flow percentile) (Table 2.A.4).

2.5.1.3 Spatiotemporal and Vertical Variation of Solute Concentrations in the Soil Water and Groundwater

SC and most solutes (SC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , Si, and Sr) had higher median concentrations in ground water, while others (NO_3^- , DOC, Al, Ba, Fe, and Mn) had higher median concentrations in the soil water 0.1 to 0.4 meters deep (Figure 2.2; Table 2.A.1; Table 2.A.4). For example, median Ca^{2+} concentration from all years was 0.9, 27.6, and 28.4 mg L^{-1} at shallow upslope lysimeter UP SH (0.1 m deep), hillslope hollow well BW18 (1.0 m deep), and piezometer T1 (2.2 m deep), respectively, while median NO_3^- concentration was 1.0, 0.9, and 0.5 mg L^{-1} at the same sites. Although Cl^- had a slightly higher median (0.4) in the BW18 well samples than those at the lysimeter and piezometer, concentrations changed little with depth ($\text{sd} = 0.06 \text{ mg L}^{-1}$). Most solutes retained the same vertical distribution of concentrations throughout the soil profile across all seasons (Table 2.A.5). Cl^- changed between seasons with the highest median concentrations shifting to the mid-depth lysimeters (0.4 m) in the dormant period and deep lysimeters (1 m) during the rising limb of snowmelt. NO_3^- also changed by having high median concentrations in the mid-depth lysimeters during the dormant and rising limb and shifting to wells during the growing season (Figure 2.2c). Lastly, the highest median concentrations of Ba ($8.8 \text{ } \mu\text{g L}^{-1}$) shifted to the mid-depth lysimeters during the falling limb (Table 2.A.5).

The solute concentrations in groundwater often varied with the geographic location of the wells (Table 2.A.6). Riparian wells had the highest median concentrations of SC,

Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, Sr, and Ba, while the hillslope hollow wells had highest median concentrations of Cl⁻ and Al (Table 2.A.1). The hillslope wells had on average higher median concentrations of Na⁺ (1.1 mg L⁻¹) and Si (11.0 mg L⁻¹) while the hillslope bench wells had the highest median concentrations of NO₃⁻.

2.5.2 C-Q Relationships in Streamflow

2.5.2.1 Multi-Annual C-Q Relationships

Of the studied solutes all but Al had significant ($p < 0.05$) multi-annual C-Q relationships created using data from water years 1992 to 2015 (Figure 2.3). The R² values for the significant relationships ranged from 0.03 to 0.82 (Table 2.1). Most geogenic solutes (Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Sr) had C-Q relationships with higher R² values ($R^2 = 0.48 - 0.82$), while Cl⁻, NO₃⁻, DOC, Ba, Fe, Mn and Si had much lower R² values (0.03 - 0.38). SC, Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Mn, Sr, and Ba exhibited chemodynamic dilution patterns ($b < -0.1$), while NO₃⁻, DOC, and Fe exhibited a flushing response ($b > 0.1$). Cl⁻ and Si were the only two solutes showing chemostatic behaviors, as their b -coefficient < 0.1 and > -0.1 following Herndon et al. (2015). CV_C/CV_Q values for all solutes ranged from 0.13 to 1.75 with a mean of 0.42 and a standard deviation of 0.44 (Table 2.1). SC, Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, SO₄²⁻, Si, Sr, and Ba had lower CV_C/CV_Q values (0.13 – 0.21) than NO₃⁻ and DOC (0.41 - 0.54). Some of the trace elements (Al, Fe, and Mn) had the highest CV_C/CV_Q values ranging from 0.87 - 1.75.

2.5.2.2 Yearly C-Q Relationships

Seven solutes (SC, Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, and Sr) had significant C-Q relationships in all water years, in which data was available (Table 2.2; Figure 2.4). The remaining eight solutes had C-Q relationships that changed between years with some having 1 to 12 years with insignificant annual C-Q relationships. Major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺ and SO₄²⁻) had the most significant C-Q relationships while Cl⁻, nutrients (NO₃⁻ and DOC), trace elements (Al, Ba, Fe, and Mn) and Si had multiple years with insignificant annual C-Q relationships (Figure 2.4).

The annual C - Q relationships were consistent with the multi-annual ones for most solutes (Figures 2.3 and 2.5). However, SC, K^+ , Cl^- , NO_3^- , SO_4^{2-} , DOC, Si, Al had at least one year where the C - Q pattern changed. These eight solutes shifted between a chemodynamic behavior to a chemostatic behavior. Al was the only solute that had significant annual C - Q relationships for all three C - Q patterns. CV_C/CV_Q mean values for all the solutes ranged from 0.14 to 1.51 with standard deviations ranging from 0.02 to 0.55 (Table 2.2). Most CV_C/CV_Q values were less than 0.50, while DOC, Al, and Fe were between 0.50 and 1.0 (Table 2.2).

2.5.2.3 Seasonal C - Q Relationships

The seasonal C - Q relationships for the four periods (dormant, snowmelt rising, snowmelt falling, growing) created for each individual year showed that nearly all solutes had the highest $|b|$ during the falling limb of snowmelt (Figure 2.6). Only NO_3^- , DOC, and Al had the highest median $|b|$ -coefficients during the dormant period and Si had its highest $|b|$ -coefficient during the growing season. Most solutes had lower median $|b|$ -coefficients on the rising limb than the falling limb of snowmelt. Only Si and Al had a higher median $|b|$ -coefficient on the rising limb than the falling limb.

Some solutes had individual seasonal export patterns that differed from the multi-annual pattern. The median b -coefficient for Si remained chemostatic for all periods except the growing season where it was diluted. SC, K^+ , NO_3^- , Ba, and Mn also had periods during which the median b -coefficient showed evidence of chemostasis (Figure 2.6). Conversely, during the seasons where Al had significant C - Q relationships, the medians of all four periods showed evidence of flushing. Aside from those six solutes, all others had seasonal median b -coefficients consistent with their respective multi-annual C - Q relationship.

When concentration was plotted against discharge during the snowmelt period, few solutes showed consistent visible hysteresis patterns (Figure 2.B.2). NO_3^- and DOC were the only solutes that seemed to show weak hysteretic behavior with NO_3^- exhibiting a clockwise pattern and DOC exhibiting a much narrower and unclear clockwise pattern.

2.5.3 End-Member Mixing Analysis

2.5.3.1 Conservative Solutes and the Number of End-Members

Using the diagnostic tools of mixing models (DTMM), seven major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-}) were tested for conservative behavior and the number of end-members contributing to streamflow using samples collected from water years 1992 to 2015 ($n = 2420$). The first principal component (PC1) explained 54% of the total variance of seven ions, while the second (PC2) explained 16% (Table 2.3). By PC1, the variances of Ca^{2+} , Mg^{2+} , and Na^+ were explained by 85-90%, those of K^+ and SO_4^{2-} by 71% and 47%, respectively, and those of Cl^- and NO_3^- only by 8% and 18% (Table 2.3). Based on the high % of variance explained by the first principal component, Ca^{2+} , Mg^{2+} , and Na^+ could be considered to be conservative under 1-D (two end-members), which is consistent with Kendall et al. (1999). However, the increase in cumulative variance explained by 2-D was marginal for these ions (Table 2.3). Thus, 2-D (three end-members) was deemed to be more appropriate, similarly to Smith (1997). The RRMSE values were lower in 1-D and 2-D for Ca^{2+} , Mg^{2+} , and Na^+ than for other ions, but the values of K^+ , Cl^- , NO_3^- and SO_4^{2-} were not unusually high compared to other studies (e.g., Liu et al., 2020; Liu et al., 2013).

2.5.3.2 Determination of End-Members

A mixing diagram was developed using PC1 and PC2 extracted from Ca^{2+} , Mg^{2+} , and Na^+ concentrations in streamflow, along with projected principal components of soil water and groundwater using their median concentrations, to identify the three end-members that control streamflow (Figure 2.7). Geometrically, a triangle was sought to bound most stream samples. Many combinations of three potential end-members served as viable vertices. Potential end-members that plotted well within the stream sample cloud were rejected because they did not bound the stream samples, and they appeared to be a mixture of other end-members, similar to stream samples. Listed in Table 2.4 were examples of potential end-member combinations. From a geometrical perspective, UP SH, BW30A, and BW6 would be the best combination to bound most stream samples (M1 in

Table 2.4). Although only 6.1% of stream samples were outsiders, this model was rejected because NSE was so poor for Ca^{2+} (0.44) and Mg^{2+} (0.23). A triangle of UP SH, T2, and BW18 (M2), which tightly bound 87% of stream samples, significantly improved NSE values for Ca^{2+} , Mg^{2+} , and Na^+ (0.94-1.00) and marginally for SO_4^{2-} and Sr. The remaining trials, we supplemented either one or two of UP SH, T2, and BW18 end-members to identify the best combination. Substituting UP SH with precipitation changed the modeling results only slightly (e.g., M2 vs M9 and M7 vs M3). Any trials substituting BW18 with nearby neighbors worsened the modeling (e.g., M4, M6, M8, and M10), indicating that BW18 was necessary. Substituting T4 for either T1 or T2 produced poor NSE values for Ca^{2+} and Mg^{2+} even if both UP SH and BW18 were used (e.g., M5). In summary, four best, competing models were identified, which were composed of UP SH/precipitation, T1/T2, and BW18 (M2, M3, M7, and M9).

The end-members in these four competing models were further evaluated from a hydrologic perspective. UP SH, a soil lysimeter placed 10 cm below the soil surface in an upslope location, represented soil water that was derived from infiltration of snowmelt and rainfall (Kendall et al., 1999; Shanley et al., 2002). Both UP SH and precipitation worked well in EMMA because they had similar ionic concentrations, particularly of Ca^{2+} , Mg^{2+} , and Na^+ (Table S1), and plotted very closely to each other in the mixing diagram (Figure 2.7). With hindsight, the mean fractional contribution of corresponding end-members between alternative models had a difference $< 3\%$ with a R^2 of almost 1.0 when either UP SH or precipitation was used (M3 vs M7 and M2 vs M9).

T1 and T2 were co-located in a riparian zone and differed only in screened depth (T1's screen centered at 2.2 m while T2's at 1.5 m). Comparing the results of M2 and M3, NSE was almost identical for Ca^{2+} , Mg^{2+} , and Na^+ and slightly better for SC and Sr from M3 (Table 2.4). The total number of samples outside the triangle (therefore negative solutions for at least one end-member) was about the same, but the number of samples with a negative contribution of SOF from M3 was much higher than that from M2 (219 vs 147), while that number of hillslope hollow (characterized by BW18) was much lower from M3 than from M2 (40 vs 122). Examination of ionic concentrations in stream samples outside

the triangle of M3 revealed that samples below the UP SH-T1 side and above the UP SH-BW18 side had abnormally high or low concentrations for one or two tracers compared to samples collected within the day or a few days apart if there were no samples collected the same day. However, abnormal ionic concentrations were hardly identified for those unbounded on the T1-BW18 side. Interestingly, these unbounded points, with negative contributions of SOF, occurred during very low flows ($< 0.006 \text{ m}^3\text{s}^{-1}$), regardless of whether T1 or T2 was used. Having more samples with negative contributions of SOF (zero after corrected following Liu et al., 2004) during low flows was more plausible than having more samples with negative contributions of hillslope hollow groundwater (which turned out to dominate baseflow; see below). Therefore, M3 was superior to M2.

2.5.3.3 *End-Member Contributions*

The results of M3 indicated that streamflow was dominated by hillslope groundwater from hollows, with a mean of 0.44 and a standard deviation of 0.16 from water years 1992 to 2015. The contributions of riparian groundwater and SOF were comparable, with a mean of 0.27 and 0.29, respectively, and a standard deviation of 0.18 and 0.17. The contributions of the three end-members varied annually and seasonally and between the rising to falling limbs of snowmelt (Figure 2.8). SOF contributed least during the dormant period and growing season (median < 0.20) and dominated the snowmelt period, with higher contributions on the falling limb than the rising limb. Riparian groundwater has almost an opposite pattern compared to SOF, with lower contributions during the snowmelt period (median < 0.25), but the contribution was still slightly higher in the falling limb than the rising limb. The fractional contribution of hillslope groundwater from hollows was higher during the dormant and growing seasons than the snowmelt period and significantly higher than riparian flow during the same seasons. The fractional contribution of hillslope groundwater from hollows was higher on the rising limb than the falling limb contrary to both SOF and riparian groundwater.

2.6 DISCUSSION

By combining the results from EMMA and the C - Q analysis, this study determines the solute export patterns at multi-timescales and the key factors controlling annual or seasonal shifts in export at W-9. The multi-annual C - Q relationships provide the “big picture” of long-term solute concentration variation while the C - Q relationships at the annual and seasonal timescales reveal increasingly more specific patterns in stream water chemistry. In the multi-annual C - Q relationships, major geogenic ions and major nutrients have contrasting patterns (Figure 2.3). The concentrations of major ions become diluted during periods of high streamflow while the concentrations of major nutrients and some trace elements enrich with increasing streamflow. This contrast is caused by the distribution of solute concentrations throughout the soil profile (Table 2.A.1; Table 2.A.4; Figure 2.2) and, subsequently, the conservative behavior and contrasting solute concentrations in contributing end-members, consistent with Evans & Davies (1998).

2.6.1 Multi-Annual Pattern

The solute concentrations throughout the soil profile create unique concentrations in end-members. Geogenic solutes (Ca^{2+} , Mg^{2+} , Na^+ , and Sr) with strong C - Q relationships ($R^2 > 0.60$) had vertical heterogeneity throughout the soil profile with increasing concentrations at deeper depths, particularly for the end-members determined by EMMA (Figure 2.2; Table 2.A.1). DOC had one of the highest $|b|$ -coefficients and contrasting DOC concentrations in the surficial soils vs the deeper soils, with median concentrations an order of magnitude higher in surficial soils (Figure 2.2; Table 2.1; Table 2A.1). Conversely, Cl^- lacked vertical heterogeneity with only slight and inconsistent changes in solute concentrations throughout the soil profile, leading to an extremely low b -coefficient (0.04) although the Cl^- - Q relationship was significant (Figure 2.3). The b -coefficients of geogenic solutes (SC , Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , K^+ , SO_4^{2-} , Si , and Sr) were negatively correlated with the ratio between shallow and deep end-member median solute concentrations ($p < 0.05$) (Figure 2.9). These results indicate that vertical heterogeneity in solute concentrations is a key factor controlling the b -coefficient and the strength of the C - Q relationship. An

increase in solute concentrations with depth creates a negative b , while a decrease creates a positive b . This field observation-based finding agrees with a hypothetical numerical modeling result by Chen, Tague, Melack, & Keller (2020). However, if source pools are not large enough in volume, as suggested by Ackerer et al. (2020), the C - Q power-law may be very weak. Source limitation may explain why Ba and Mn do not exhibit flushing patterns despite having higher median concentrations in the shallow soils.

Contrasting C - Q patterns and solute vertical distribution throughout the soil profile revealed which major flowpaths became active during high flow events. The flushing patterns of NO_3^- and DOC and their high concentrations in surface soils indicate that a significant amount of water flowed through or over shallow soils during periods of high flow, as supported by EMMA. Several prior studies at SRRW indicated that SOF greatly shapes NO_3^- and DOC export (Dunne and Black, 1970; Kendall et al., 1999; Shanley et al., 2002; Sebestyen et al., 2008; Sebestyen et al., 2014; Sebestyen et al., 2019). SOF begins heavily contributing to streamflow during storm events once precipitation wets the nutrient-rich shallow soils (Dunne and Black, 1970; Kendall et al., 1999).

It is worth noting that though Si- Q had a significant power-law relation at multi-annual scale based on p value, its b was extremely low (-0.05) like that of Cl^- (Figure 2.4). Silica has a significant biogenic cycling component and the dissolution of opal phytoliths contained in leaf litter confound the shallow to deep concentration profile. When mixed, this shallow source counters dilution to make the b -coefficient less negative. Additionally, over the 24-year-long sampling period, SO_4^{2-} concentrations in streamflow were systematically lower after 2008 than before 2008 and were consistently under-estimated using the EMMA results before 2008 but over-estimated after 2008 (Figure 2.10). This decreasing trend is a result of the declining intensity of acid rain deposition in the northeastern United States and has been observed at Hubbard Brook Experimental Forest (Fuss, Driscoll, & Campbell, 2015). Using data from 2008 to 2015 in simulating stream chemistry by the EMMA results, NSE becomes 0.56 and 0.55 for SO_4^{2-} and Si, respectively, significantly higher than their values for the entire period (M3 results in Table 4). Si appears to have become at least quasi-conservative after 2008.

2.6.2 Yearly Pattern

The variation of C - Q power-law coefficients over years is stronger for some solutes than others (Figures 2.4 and 2.5). A key factor controlling this variability is whether the solute behaves conservatively and whether solute concentrations in end-members are relatively stable over time (Evans and Davis, 1998). The DTMM determined Ca^{2+} , Mg^{2+} , and Na^+ were conservative (Table 2.3). Using their median concentrations in EMMA, their concentrations in streamflow were very well simulated (e.g., Ca^{2+} in Figure 2.10), suggesting their concentrations in end-members were relatively constant over time.

Chloride and NO_3^- were among the solutes that were determined non-conservative and had they some of the most interannual variation, with multiple insignificant C - Q annual relationships. Both R^2 and $|b|$ values for Si became relatively high and stable after 2008, consistent with Si behaving quasi-conservatively after 2008. DOC was assumed conservative by Kendall et al. (1999), but this study's EMMA results significantly underestimated DOC concentrations (Figure 2.10), showing that DOC concentrations in our SOF end-member were too low and also varied dramatically over time. A doubling of DOC concentrations in SOF improved the mean values but not the overall temporal pattern. Trace elements (other than Sr) were deemed to be non-conservative because their concentrations in streamflow were not well simulated using the EMMA results (Table 2.4). Their annual C - Q relationships had greater variability as well (Figures 2.4 and 2.5). Since Al and Fe can be co-transported with DOC and colloidal materials, it is not surprising that all three solutes have high interannual variability since all are controlled by similar processes (Chorover, Derry, & McDowell, 2017). Non-conservative behavior degrades the C - Q relationship and creates more variable concentrations due to factors such as instream processes, biotic processes, plant uptake, anthropogenic additions, and colloid formation and transport. The latter process tends to mobilize nutrients and trace metals (Mulholland and Hill, 1997).

Furthermore, both NO_3^- and DOC concentrations are mainly delivered to the stream via shallow flowpaths, with the amount of seasonal quick flow as one of the main factors

explaining seasonal variation of stream NO_3^- loading and the single factor explaining DOC loading (Kendall et al., 1999; Shanley et al., 2002; Sebestyen et al., 2008, Sebestyen, Boyer, & Shanley, 2009). Hence, the C - Q relationships deteriorate from variability in production and uptake/degradation of NO_3^- and DOC due to weather and wetting/drying cycles.

Like many areas of the US, there is high nitrogen deposition in SRRW. Nitrate can be quickly transported to the stream during storms and snowmelt without being transformed or immobilized by biological uptake (Campbell et al., 2004; Sebestyen et al., 2008; Sebestyen et al., 2019). New N inputs may be highly variable and thus further weaken the C - Q relationship. Prior studies from SRRW show that NO_3^- is source limited, meaning that NO_3^- becomes progressively depleted over long events such as snowmelt (Sebestyen et al., 2008), further eroding the C - Q relation.

For those solutes with high interannual variation, b -coefficients more frequently switched from flushing or diluting to chemostatic behaviors than from flushing to diluting (or vice versa). Only Al had significant ($p < 0.05$) annual C - Q relationships where the b -coefficient was positive one year and negative in another. This result reveals that, for most solutes, flushing or diluting patterns are relatively stable, rarely switching between chemodynamic patterns.

It is important to note that neither the b -coefficient nor CV_C/CV_Q were necessarily good indicators of mixing and strength of the C - Q relationship, as is seen in the multi-annual and annual C - Q relationships. Results for Ca^{2+} , Mg^{2+} , and Na^+ showed that strong mixing does not require a b near -1 (Godsey, 2009). Here, these major ions had high R^2 values and small p values, but $|b|$ was only 0.11-0.15 (Tables 2.1 and 2.2), which would be considered chemostatic by the thresholds in Godsey et al. (2009). Meanwhile, CV_C/CV_Q is also low for these major ions and higher for NO_3^- and DOC (Tables 2.1 and 2.2). DOC has a b of 0.26 and CV_C/CV_Q of 0.54, but it cannot be predicted by conservative mixing and its annual C - Q varies significantly (Figure 2.5). The EMMA results showed that C - Q

relationships with low b -coefficients can still be strong when there is strong mixing among distinct end-members with unique concentrations.

2.6.3 Seasonal Pattern

The seasonal C - Q relationships indicated that there was intra-annual variation over seasons throughout the year. During the dormant and growing seasons, the C - Q patterns were frequently similar (Figure 2.6). EMMA fractional contributions indicate that the growing and dormant seasons have similar end-member contributions, with groundwater from hillslope hollows contributing the highest fraction followed by riparian groundwater and Surface Overland Flow (Figure 2.8). Surface Overland Flow and riparian groundwater contribute slightly more during the growing season possibly because of high intensity summer storms that enhance SOF.

During the snowmelt period, the C - Q relationships showed that the median intensity of solute export for most solutes changed between the rising and falling limb of snowmelt. Most solutes had smaller median $|b|$ coefficients on the rising limb than the falling limb of snowmelt (Figure 2.6). Only Si and Al had larger median $|b|$ coefficients on the rising limb compared to the falling limb. The EMMA results indicate that the proportional contributions of hillslope hollow groundwater decreased and that of SOF and riparian groundwater increased during the falling limb of snowmelt (Figure 2.8). The difference in solute concentrations of major ions (except NO_3^-) was significant between SOF (characterized by UP SH) and either riparian groundwater (T1) or hillslope hollow groundwater (BW18) (Figure 2.2). The increase in fractional contribution of SOF during the falling limb (Figure 2.8) increases the $|b|$ value for all solutes except Si and Al (Figure 2.6). Because solute concentrations in groundwater from riparian zone and hillslope hollow are very close (Figure 2.2), relative changes in fractional contributions between riparian and hillslope hollow groundwater do not change much stream chemistry. Thus, a hysteresis was not observed for most solutes. Similar to DOC, NO_3^- is an exception because its concentration was much higher in SOF based on the above discussion and also somewhat different between riparian groundwater and hillslope groundwater (Figure 2.2), resulting

in a subtle hysteresis (Figure 2.B.2). Certain studies have found hysteretic patterns in data from individual years (Kendall et al., 1999; Sebestyen et al., 2014). Since our study combined the data from all years to study snowmelt hysteresis, it is possible that the hysteresis seen within individual years becomes obscured when looking at all data due to interannual variation.

Changing C - Q patterns between seasons also means that timing of solute export and nutrient availability might shift in a future climate as snow melt occurs earlier, dormant season ends earlier, and the growing season becomes longer. Coupled with results from existing studies on precipitation patterns and influence of storm events on stream nutrient loadings, the observed seasonal patterns from my study of C - Q analysis and EMMA reinforce the theory that climate change effects on the frequency and magnitude of storm events will drive future patterns of stream nutrient loadings (Sebestyen et al., 2009). With a warmer climate, solute export during snowmelt will continue to occur earlier in the year. Additionally, during the growing season, there will be greater proportional contributions of SOF as more intense and precipitation events are projected in the future (Hayhoe et al. 2007), causing more water to flow through quick flowpaths. Increased storm intensity will also increase DOC export since DOC had a flushing pattern, consistent with Sebestyen et al. (2008).

The observed seasonal variation in C - Q relationships also has implications for sampling regime and data analysis. If sampling is not conducted representatively throughout the year, researchers can potentially draw inaccurate conclusions from the constructed relationships. This seasonal variation particularly poses a challenge for collecting representative NO_3^- and DOC samples from surficial soils.

2.7 CONCLUSION

The power-law relationship between concentration and discharge in streamflow is primarily controlled by vertical distribution of solutes in source waters, an increase with depth generating a negative b -coefficient (dilution) while a decrease with depth generating a positive b -coefficient (flushing). The strength (R^2) and direction (b -coefficient) of the

power-law depends on (1) conservative behavior of solutes, (2) distinctiveness of solute concentrations among source waters, (3) temporal variability of solute concentrations in source waters. Solutes that are conservative with distinct and relatively constant concentrations in source waters, show a strong and persistent power-law relation over variable timescales such as Ca^{2+} , Mg^{2+} , Na^+ , and Sr of this study. The strength of the power-law cannot be solely measured by the magnitude of b -coefficient and CV_Q/CV_C . A $|b|$ -coefficient as low as 0.15, like those of Ca^{2+} , Mg^{2+} , Na^+ , and Sr in this study, could still be considered a strong power-law relationship and interpreted primarily as a result of mixing. The power-law relationships of some solutes such as nutrients in this study could change over timescales due to non-conservative behavior, variable source stores, and/or intermittent flow pathways. With a change in snowmelt timing and precipitation intensities in the future, concentration-discharge relationship in streamflow could change, particularly at the seasonal scale.

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2.9 TABLES AND FIGURES

2.9.1 Tables

Table 2.1. Multi-annual C - Q coefficients, CV_c/CV_Q , and root mean squared error (RMSE) for the 15 solutes.

Species	# samples	R^2	p	a	b	RMSE	CV_c/CV_Q
SC (μ s)	693	0.54	< 0.001	1.73	-0.13	0.076	0.164
Ca ²⁺ (mg L ⁻¹)	2406	0.76	< 0.001	1.00	-0.16	0.056	0.155
Mg ²⁺ (mg L ⁻¹)	2406	0.82	< 0.001	-0.31	-0.15	0.043	0.145
Na ⁺ (mg L ⁻¹)	2406	0.70	< 0.001	-0.53	-0.16	0.065	0.163
K ⁺ (mg L ⁻¹)	2398	0.48	< 0.001	-0.19	-0.11	0.072	0.147
Cl ⁻ (mg L ⁻¹)	2406	0.03	< 0.001	-0.61	-0.04	0.141	0.211
NO ₃ ⁻ (mg L ⁻¹)	2406	0.07	< 0.001	0.09	0.13	0.293	0.412
SO ₄ ²⁻ (mg L ⁻¹)	2387	0.50	< 0.001	0.47	-0.16	0.097	0.182
DOC (mg L ⁻¹)	1890	0.30	< 0.001	0.80	0.26	0.244	0.541
Si (mg L ⁻¹)	2300	0.14	< 0.001	0.61	-0.05	0.082	0.125
Sr (μ g L ⁻¹)	1058	0.67	< 0.001	1.62	-0.17	0.070	0.175
Al (μ g L ⁻¹)	1501	0.00	0.59	1.24	0.01	0.512	0.977
Ba (μ g L ⁻¹)	1058	0.38	< 0.001	0.65	-0.14	0.104	0.212
Fe (μ g L ⁻¹)	1057	0.15	< 0.001	1.49	0.29	0.421	0.866
Mn (μ g L ⁻¹)	1056	0.04	< 0.001	-0.27	-0.21	0.608	1.752

Table 2.2. Summary statistics of annual C - Q relationships from years with significant relationships ($p < 0.05$).

Species	Sig/Total Years	Mean R^2 (sd)	Mean b (sd)	Mean CV_c/CV_Q (sd)
SC (μ s)	10/10	0.62 (0.21)	-0.13 (0.04)	0.16 (0.06)
Ca ²⁺ (mg L ⁻¹)	24/24	0.77 (0.09)	-0.15 (0.02)	0.16 (0.05)
Mg ²⁺ (mg L ⁻¹)	24/24	0.81 (0.07)	-0.15 (0.02)	0.16 (0.04)
Na ⁺ (mg L ⁻¹)	24/24	0.72 (0.11)	-0.15 (0.02)	0.17 (0.05)
K ⁺ (mg L ⁻¹)	24/24	0.48 (0.18)	-0.11 (0.03)	0.15 (0.04)
Cl ⁻ (mg L ⁻¹)	12/24	0.12 (0.09)	-0.05 (0.08)	0.22 (0.11)
NO ₃ ⁻ (mg L ⁻¹)	18/24	0.18 (0.14)	0.17 (0.09)	0.42 (0.13)
SO ₄ ²⁻ (mg L ⁻¹)	24/24	0.6 (0.19)	-0.12 (0.05)	0.14 (0.05)
DOC (mg L ⁻¹)	19/24	0.34 (0.19)	0.26 (0.11)	0.52 (0.2)
Si (mg L ⁻¹)	14/24	0.51 (0.25)	-0.08 (0.09)	0.15 (0.07)
Sr (μ g L ⁻¹)	8/8	0.74 (0.07)	-0.18 (0.01)	0.19 (0.02)
Al (μ g L ⁻¹)	11/17	0.26 (0.15)	0.26 (0.2)	0.62 (0.29)
Ba (μ g L ⁻¹)	7/8	0.53 (0.13)	-0.14 (0.02)	0.19 (0.02)
Fe (μ g L ⁻¹)	6/8	0.23 (0.17)	0.34 (0.17)	0.82 (0.34)
Mn (μ g L ⁻¹)	6/8	0.08 (0.04)	-0.3 (0.09)	1.51 (0.55)

Table 2.3. The results of diagnostic tools of mixing models using concentrations of major ions (n = 2420)

		Ca²⁺	Mg²⁺	Na⁺	K⁺	Cl⁻	NO₃⁻	SO₄²⁻
Accumulative	1-D	85	90	88	71	8	18	47
Variance	2-D	89	90	89	72	65	54	63
Explained (%)	3-D	91	92	91	77	97	89	74
RRMSE	1-D	0.2	0.15	0.19	0.27	0.66	1.21	0.48
(%)	2-D	0.17	0.15	0.18	0.27	0.4	0.91	0.41
	3-D	0.15	0.14	0.16	0.24	0.12	0.44	0.34

Table 2.4. Evaluation of alternative end-member mixing models using Nash-Sutcliffe Efficiency (NSE) and percent of samples outside the triangle.

Model Code	End-members	Out-siders (%)	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)
M1	UP SH; BW39A; BW6	6.1	0.64	0.44	0.23	0.98	0.01	-0.09	-55.9	-0.32	-1.11	-2.34	0.79	-10.66	-3.13
M2	UP SH; T2; BW18	13.1	0.26	0.96	0.94	1	0.06	-0.01	0.05	0.26	-0.11	-0.99	0.82	-4.57	-0.71
M3	UP SH; T1; BW18	12.7	0.44	0.95	0.93	1	-0.67	-0.03	0.07	0.27	-0.08	-0.3	0.86	-4.48	-0.7
M4	UP SH; T2; BW6	11.7	0.41	0.72	0.62	0.99	0	-0.05	-23.49	-0.12	-1.01	-1.51	0.73	-9.57	-2.59
M5	UP SH; T4; BW18	5.1	0.62	0.43	0.22	0.98	-1.56	-0.01	-69.48	0.01	-0.6	0.03	0.68	-7.17	-1.2
M6	UP SH; T1; BW26	9.2	0.52	0.41	0.19	0.98	-0.45	0	0.07	0.38	-0.19	-0.64	0.26	-5.57	-1.17
M7	PPT; T1; BW18	12.1	0.4	0.96	0.94	1	0.44	-0.06	0.03	0.27	-0.81	-0.7	0.85	-0.09	-0.16
M8	UP SH; T1; 8/9/2011 PPT; T2;	9.4		0.92	0.89	1	-0.3	-0.56	-0.09	-0.29	-3.54	-0.7	0.75	-6.15	-3.59
M9	BW18	12.2	0.18	0.96	0.94	1	0.39	-0.07	-0.01	0.26	-0.79	-0.9	0.83	-0.19	-0.22
M10	PPT; T2; BW17	10.9	-1.15	0.89	0.85	1	0	-0.12	-0.17	0.17	-0.66	-0.92		-0.65	

Note: the simulation cannot be done for Ba and Mn because their concentrations in hillslope (both bench and hollow) samples were not available.

2.9.2 Figures

Figure 2.1. Map of sampling locations including W-9 stream gauge, precipitation gauge (R29), soil lysimeters, piezometers (T-#), and groundwater wells (BW-##).

Figure 2.2. Depth profiles of Ca^{2+} , NO_3^- , and DOC concentrations in soil lysimeters, piezometers, and selected groundwater wells using all data collected during the 1992-2015 water years. Note that depth increases toward the right of the graphs and top of the page within each sample group. Solute concentrations in precipitation, high (5%) and low (95%) flows of all years are shown for comparison. Data for all groundwater wells are summarized in Table S1.

Figure 2.3. C - Q relationships at the multi-annual timescales for water years 1992-2015. All relationships were calculated on the log_{10} - log_{10} scale with red indicating insignificant C - Q relationships ($p < 0.05$).

Figure 2.4. Temporal variation of the R^2 values from the yearly C - Q relationships. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale with red indicating insignificant C - Q relationships ($p < 0.05$).

Figure 2.5. Temporal variation of the b -coefficients from the yearly C - Q relationships. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale. Red indicates an insignificant C - Q relationship ($p < 0.05$), and the light red shaded section indicates the range of b where the relationship is considered chemostatic.

Figure 2.6. Boxplots of the b -coefficients from the seasonal C - Q relationships during the four periods: dormant, rising limb of snowmelt, falling limb of snowmelt, and growing season. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale, and only those with significant relationships ($p < 0.05$) were included in the statistics. The red line indicates the b -coefficient from the multiannual C - Q relationships.

Figure 2.7. Mixing diagram using the first two principal components (PC1 and PC2) constructed from Ca^{2+} , Mg^{2+} , and Na^+ . Triangles show examples of alternative models with varying end-members. Sites with labels are discussed in the text. The final selected end-members were UP SH, T1, and BW18.

Figure 2.8. Boxplots of fractional contributions of saturation overland flow, riparian groundwater, and hillslope groundwater from hollows across the four seasons

Figure 2.9. Variation of b -coefficients with geogenic solute concentration (SC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , Si, and Sr) ratios between T1 and UP SH (a) and BW18 and UP SH (b).

Figure 2.10. Measured (blue) vs modelled (red) stream concentrations for Ca^{2+} , SO_4^{2-} , NO_3^- , and DOC using the EMMA results. Note that an additional curve (orange) was shown for modelled NO_3^- results with hypothetically increased concentrations in saturation overland flow (see text).

2.10 APPENDIX 2.A SUPPLEMENTAL TABLES

Supplemental Table 2.A.1: Summary of solute concentrations in all types of samples collected during water years 1992-2015, including 25%, 50%, 75% quartiles, the sample period, and the number of samples.

		SC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	DOC	Si	Sr	Al	Ba	Fe	Mn	
Station	pH	(μS cm ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	
W-9	Median	7.6	108	21.6	1	0.6	1.1	0.3	0.7	6.3	1.6	5.3	87.3	15.4	8.1	8.6	1.4
	25%	7.3	92.9	17.6	0.8	0.5	0.9	0.3	0.5	5.1	1.2	4.6	70.9	7.1	6.7	4.2	0.6
	75%	7.7	122.2	24.8	1.2	0.7	1.3	0.4	1.1	7.6	2.6	6	103.5	30	9.9	17	3.3
	Date	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	2008-	1993-	2008-	2008-	2008-
	Range	2015	2007	2015	2015	2015	2015	2015	2015	2015	2015	2015	2015	2015	2015	2015	2015
n	1760	693	2336	2336	2336	2336	2336	2336	2336	1837	2321	988	1431	988	987	986	
PPT	Median	4.7	12.6	0.1	0	0.1	0.1	0.1	0.9	0.8	0.8	0.1	0.7	6	0.7	5.1	2
	25%	4.4	6.9	0.1	0	0	0	0.1	0.5	0.4	0.5	0	0.4	2.7	0.4	2.6	1
	75%	5.2	20.4	0.2	0	0.1	0.1	0.2	1.6	1.6	1.4	0.2	1.3	10	2.4	11.2	3
	Date	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1991-	1999-	1991-	2007-	1991-	2007-
	Range	2020	2020	2020	2020	2020	2020	2020	2020	2020	2020	2020	2018	2020	2017	2020	2020
n	1090	967	1795	1777	1736	1730	1722	1756	1794	1428	1400	378	1286	265	1511	518	
LYS LO SH	Median	6.9	45	6.8	0.5	0.7	0.2	0.3	0.2	3.9	1.3	7	35.1	31.6	2.7	14.7	0.2
	25%	6.5	32	4.6	0.4	0.5	0.1	0.2	0.1	3	0.7	6.3	26.4	7.1	2.3	1.8	0.1
	75%	7.2	57.8	7.3	0.6	0.8	0.3	0.4	2.3	4.8	3.5	7.7	41.5	81.9	5	38.5	0.5
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range	2013	2002	2013	2013	2013	2013	2013	2013	2013	2013	2013	2013	2013	2013	2013	2013
n	71	62	95	104	104	94	111	90	111	103	103	74	67	47	60	46	
LYS LO DP	Median	6.9	52.4	6.4	0.5	0.8	0.2	0.3	0.1	4.1	0.7	7.1	37	6.3	2.5	1.6	0.2
	25%	6.6	43.3	5.8	0.5	0.7	0.1	0.2	0	3.8	0.5	6.5	31.6	4	2	0.6	0.1
	75%	7.2	56.3	7.3	0.6	0.8	0.3	0.3	5.2	5	0.9	7.8	40	12	7.3	7.2	0.3
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range	2013	2002	2013	2013	2013	2013	2013	2012	2013	2013	2013	2013	2013	2013	2013	2013
n	78	56	93	103	103	91	114	72	114	107	103	77	69	52	47	49	
LYS MI SH	Median	5.5	15.8	1.2	0.2	0.1	0.5	0.2	0.8	1	8.5	3.9	7.1	267.4	16.4	47	2.9
	25%	5.2	12.2	1	0.1	0.1	0.2	0.2	0.4	0.7	6.8	2.7	6.2	207.4	13	29.4	1.8
	75%	5.7	21.8	1.6	0.2	0.2	0.8	0.5	1.2	1.9	10.4	5.2	8.6	345	20	66.4	4.9
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2003-	1992-	2003-	2003-	2008-
	Range	2016	2002	2015	2015	2015	2015	2016	2016	2016	2016	2015	2015	2015	2015	2015	2015
n	56	19	61	66	63	63	76	72	75	74	61	57	51	50	56	49	

Station		pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)	
LYS MI MI	Median	6.4	15.5	2.1	0.2	0.2	0.1	0.3	0.4	2.4	3.9	5.4	18.4	81.3	8.3	15.4	1.4	
	25%	6.2	15.4	1.9	0.2	0.2	0.1	0.2	0.2	1.8	2.2	4.5	15.3	30	4.8	8.8	1	
	75%	6.5	19.5	2.4	0.2	0.3	0.2	0.3	2	2.6	4.4	6	20.1	90.5	10.1	37.1	1.6	
	Date	1992-	1993-	199 -	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2003-	1992-	2003-	2003-	2008-
	Range n	2011 9	1998 5	2011 12	2011 13	2011 13	2011 13	2011 15	2011 15	2011 15	2011 13	2011 12	2011 10	2011 9	2011 8	2011 9	2011 7	
LYS MI DP	Median	6.6	24.2	3	0.2	0.3	0.1	0.3	0.3	2.7	1.6	5.3	20.9	30.7	2.7	3.1	0.5	
	25%	6.3	19.3	2.6	0.2	0.3	0	0.2	0.2	2.1	1.3	4.8	19.5	26.4	1.9	1.8	0.4	
	75%	6.7	25.7	3.3	0.2	0.4	0.1	0.3	1.1	3.3	1.7	6.2	25.4	35.1	6.9	6.5	0.8	
	Date	1992-	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008	
	Range n	2015 23	1999 17	2015 29	2015 32	2015 32	2015 26	2015 34	2015 30	2015 34	2015 30	2015 30	2015 25	2015 22	2015 18	2015 25	2015 18	
LYS UP SH	Median	5.5	16.1	0.9	0.2	0.1	1	0.2	1	1.4	9.6	3.5	6.2	340.4	5.7	83.6	4.4	
	25%	5.3	12	0.7	0.2	0.1	0.7	0.2	0.5	0.8	5.5	1.9	4.8	219	5.1	65	1.9	
	75%	6	28.2	1.3	0.3	0.2	1.4	0.4	1.9	2	11.9	5.2	8.1	437.8	7.7	110	7.8	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-	
	Range n	2016 82	2002 40	2015 89	2015 99	2015 98	2015 99	2016 119	2016 114	2016 120	2016 106	2015 92	2015 71	2015 72	2015 58	2015 72	2015 58	
LYS UP MI	Median	6.4	15.2	1.2	0.3	0.2	0.1	0.3	0.2	2.8	1	4.9	10.1	24.1	6.5	1.7	1.6	
	25%	6	12.8	1.1	0.2	0.2	0.1	0.2	0.1	2.6	0.8	4.7	8.4	17.7	4	0.9	1.6	
	75%	6.6	19.8	1.5	0.3	0.3	0.2	0.4	2.7	3.2	1.4	6.1	10.6	31.9	9.6	2.9	2	
	Date	1992-	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-	
	Range n	2011 15	1999 15	2011 23	2011 26	2011 25	2011 22	2011 27	2011 24	2011 27	2011 23	2011 23	2011 14	2011 15	2011 8	2011 12	2011 8	
LYS UP DP	Median	6.6	24.3	2.6	0.3	0.6	0.2	0.3	0.2	3.3	0.5	5.7	13.9	5.7	1.1	3.7	0.4	
	25%	6.4	18.6	2.4	0.3	0.5	0.2	0.2	0.1	2.8	0.4	5.4	12.3	3.3	0.9	1.2	0.2	
	75%	7	27.1	2.9	0.3	0.6	0.3	0.3	4.8	3.7	0.6	6.1	15.8	24.8	1.4	7.8	0.6	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-	
	Range n	2016 53	1999 35	2015 68	2015 72	2015 72	2015 70	2016 80	2016 48	2016 80	2016 68	2015 70	2015 56	2015 45	2015 37	2015 37	2015 35	

Station		pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-1	Median	7.6	216.5	28.8	6.3	4.7	2.1	0.4	1.3	9.7	1.6	11.1		69.9			
	25%	7.5	209.8	27.9	4.9	4.6	2.1	0.4	1.3	8.6	1.3	10.7		64.1			
	75%	7.7	223.3	29.7	7.7	4.8	2.1	0.4	1.3	10.8	1.9	11.6		75.7			
	Date																
	Range	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992		1992			
BW-2	n	2	2	2	2	2	2	2	1	2	2	2		2			
	Median	8	373	43.3	4	3.3	2.6	0.6	0.2	9.8	3.6	10.8		74.7			
	25%	7.9	373	36	3.9	2.8	2.2	0.5	0.2	9.2	2.8	10.6		64.5			
	75%	8.1	373	50.5	4.2	3.8	2.9	0.6	0.3	10.5	4.3	11		85			
	Date																
BW-3	Range	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992		1992			
	n	2	1	2	2	2	2	2	2	2	2	2		2			
	Median	7.58	232	36.7	3.64	1.52	2.15	0.39	1.49	9.09	2.91	7.62	198.9	48.03		1.5	
	25%	7.45	232	31.84	2.4	0.94	1.74	0.39	0.99	7.17	2.25	7.2	198.9	46.95		1.5	
	75%	7.71	232	43.37	3.67	1.68	2.34	0.51	6.62	9.46	4.84	7.72	198.9	49.11		1.5	
BW-4	Date			1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-					
	Range	1992	1992	2003	2003	2003	2003	2003	2003	2003	2003	2003	2003	1992		2003	
	n	2	1	3	3	3	3	3	3	3	3	3	1	2		1	
	Median	8.18	187.9	33.26	1.58	0.93	1.65	0.42	6.36	9.26	0.04	9.44	151.9	54.5		3.7	
	25%	8.18	181.8	33.23	1.55	0.88	1.63	0.38	3.64	9.19	0.04	9.34	151.9	54.5		3.7	
BW-5	75%	8.18	193.8	33.28	1.6	0.98	1.68	0.45	9.07	9.32	0.05	9.54	151.9	54.5		3.7	
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-					
	Range	1992	1996	2003	2003	2003	2003	2003	2003	2003	2003	2003	2003	1992		2003	
	n	1	6	2	2	2	2	2	2	2	2	2	1	1		1	
	Median	7.54	150	24.14	0.9	0.88	1.45	0.46	6.04	9.18	0.58	8.22	110.4	36.97			
BW-5	25%	7.54	150	24.05	0.87	0.88	1.44	0.45	3.2	9.13	0.35	8.18	110.4	36.97			
	75%	7.54	150	24.22	0.92	0.88	1.46	0.48	8.89	9.22	0.81	8.26	110.4	36.97			
	Date			1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-					
	Range	1992	1992	2003	2003	2003	2003	2003	2003	2003	2003	2003	2003	1992			
	n	1	1	2	2	2	2	2	2	2	2	2	1	1			

Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-6	Median	8	213	38.7	2.5	1	1.6	0.3	11.2	8.7	0.4	9.1	185.1	70.4		25
	25%	8	169	38	2.4	1	1.5	0.3	4.5	8.6	0.3	8.7	179.6	70.4		25
	75%	8	219.5	39.4	2.5	1	1.7	0.4	12.2	9.4	0.4	9.7	186.9	70.4		25
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1993-	1992-	2002-	1992-		
	Range	1993	1993	2004	2004	2004	2004	2004	2004	2004	2004	2004	2004	1993		2003
	n	3	3	9	9	9	9	9	9	9	4	9	6	2		1
BW-7	Median		176.5	30.8	1.6	1	1.4	0.4	6.7	9.4	0.6	7.3	130.7	77.4		
	25%		175.2	30.3	1.6	1	1.4	0.4	4.5	9	0.6	7.2	130.7	77.4		
	75%		176.8	31.3	1.6	1	1.4	0.4	9	9.8	0.6	7.4	130.7	77.4		
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-		1992-				
	Range		1996	2003	2003	2003	2003	2003	2003	2003	1992	2003	2003	1992		
	n		6	2	2	2	2	2	2	2	1	1	1	1		
BW-8	Median	7.7	128	21.3	1.3	0.6	1.2	0.3	2	7.6	0.5	6.4	92.5	44		
	25%	7.7	120.5	20	1.2	0.6	1.1	0.3	1.4	7.1	0.2	6.2	92.5	38.3		
	75%	7.8	137.5	22.5	1.3	0.7	1.2	0.3	2.3	8.2	0.5	7.1	92.5	88.2		
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-		1992-		
	Range	1993	1993	2003	2003	2003	2003	2003	2003	2003	1993	2003	2003	1993		
	n	5	4	6	6	6	6	6	6	6	5	6	1	5		
BW-9	Median	8.1	232	39.7	1.8	0.9	2	0.5	2.8	10.2	0.4	7.6	153.5	45.5		
	25%	8	228.5	39.4	1.7	0.9	1.9	0.4	2.4	10.1	0.3	7.5	153.5	36.8		
	75%	8.1	235.5	40.3	1.9	0.9	2.1	0.5	7.9	10.4	0.5	8.2	153.5	54.2		
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-		1992-		
	Range	1993	1993	2003	2003	2003	2003	2003	2003	2003	1993	2003	2003	1993		
	n	2	2	3	3	3	3	3	3	3	2	3	1	2		
BW-10	Median		122.5	20.9	1.2	0.5	1.1	0.3	1.3	6.5	1.9	5.5	86.5	58.3		15.4
	25%		113.1	17.2	1	0.5	1.1	0.2	0.5	5.5	1.7	5.3	74.6	58.3		14
	75%		137.5	28.6	1.7	0.7	1.2	0.3	1.5	7.2	2.1	7	104.5	58.3		21.5
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-
	Range		1999	2003	2003	2003	2003	2003	2003	2003	2000	2003	2003	1992		2003
	n		11	8	8	8	7	15	12	15	15	8	7	1		7

Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-11	Median	97.5	15.5	0.7	0.6	0.8	0.3	1.5	5.5	0.4	5.8	72.6	51.3		15.9	
	25%	80.5	13.3	0.6	0.5	0.7	0.3	0.6	5.1	0.4	5.6	65.9	51.3		10.7	
	75%	111.5	20	1	0.7	1.2	0.3	3.4	6.3	0.5	6.9	78.8	51.3		27.6	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	1999-			1999-	
	Range	1999	2003	2003	2003	2003	2003	2003	2003	2000	2003	2003	1992		2003	
	n	6	8	8	8	7	15	15	15	12	8	7	1		7	
BW-12	Median	145	22.4	1.1	0.7	1.2	0.3	1.6	9	0.4	6.3	98.6	99.6		25.6	
	25%	141.9	22.3	1	0.6	1.2	0.3	0.4	8.6	0.4	6	96.6	99.6		16.8	
	75%	149.4	24.8	1.1	0.7	1.4	0.4	2.5	9.2	0.6	6.4	100.8	99.6		34	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-	
	Range	1999	2003	2003	2003	2003	2003	2003	2003	2000	2003	2003	1992		1999	
	n	11	7	7	7	7	15	15	15	19	7	6	1		5	
BW-14	Median	93.9	11.2	0.6	0.5	0.7	0.3	1.7	5.4	0.7	5.6	55.4			13.7	
	25%	80.7	9.4	0.5	0.4	0.7	0.2	0.5	5.2	0.5	5	41.5			10.8	
	75%	107.8	12.3	0.6	0.5	0.8	0.4	2.1	5.7	0.9	5.8	63.3			20.9	
	Date	1996-	1999-	1999-	1999-		1999-	1999-	1999-	1996-	1999-	1999-			1999-	
	Range	1999	2000	2000	2000	1999	2000	2000	2000	2000	2000	2000			2000	
	n	10	6	6	6	5	12	12	12	18	6	6			6	
BW-15	Median	7.8	108	16.4	0.9	0.6	1.1	0.3	1.7	6.6	0.5	5.5	68.8	87.8	12.6	
	25%	7.8	88	13.6	0.6	0.5	0.9	0.2	0.9	5.7	0.4	5.3	62.6	84	8.7	
	75%	7.8	132	21.1	1.2	0.7	1.4	0.3	3	7.1	0.5	6.6	89.4	91.7	15.6	
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-		1999-	
	Range	1993	1999	2004	2004	2004	2004	2004	2004	2003	2004	2004	1993		2004	
	n	1	7	13	13	13	11	19	19	19	17	13	11	2	8	
BW-16	Median		112	18.7	0.7	0.4	0.8	0.3	0.8	5.1	0.4	4.3	103.8		11.8	
	25%		104	16.2	0.6	0.3	0.8	0.2	0.6	4.9	0.4	4	90.8		10.7	
	75%		125	20.6	3.9	0.5	0.8	0.4	2.3	6	0.5	6	111		15.8	
	Date			1999-	1999-	1999-		1999-	1999-	1999-	1999-	1999-	1999-		1999-	
	Range		1999	2000	2000	2000	1999	2000	2000	2000	2000	2000	2000		2000	
	n		5	7	7	7	5	13	12	13	12	7	7		5	

Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-17	Median	198	32.5	1.1	0.7	1.9	0.3	0.5	9.9	0.9	7		132.5			
	25%	198	32.5	1.1	0.7	1.9	0.3	0.5	9.9	0.9	7		132.5			
	75%	198	32.5	1.1	0.7	1.9	0.3	0.5	9.9	0.9	7		132.5			
	Date															
	Range n	1992 1	1992 1	1992 1	1992 1	1992 1	1992 1	1992 1	1992 1	1992 1	1992 1		1992 1			
BW-18	Median	133.5	27.6	1.1	0.6	1.3	0.4	0.9	8.3	0.5	5	120	62.6		9.2	
	25%	130.3	20.4	0.8	0.5	1	0.3	0.2	7.8	0.4	4.9	101.5	62.6		6.5	
	75%	157	29.8	1.2	0.7	1.5	0.4	10.5	9	0.5	6.4	139.6	62.6		16.1	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-	
	Range n	1999 6	2004 14	2004 14	2004 14	2004 12	2004 19	2004 17	2004 19	2003 15	2004 14	2004 13	1992 1		2000 6	
BW-19	Median	146	25.3	1	0.6	1.2	0.3	0.6	7.6	0.5	5.2	112.4	61.5		4	
	25%	141.5	23.3	0.8	0.5	1	0.3	0.2	7.1	0.5	5.1	105.6	61.5		2	
	75%	193	28.4	1.2	0.7	1.3	0.4	9.1	7.8	0.6	5.7	127.5	61.5		8.7	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-	
	Range n	1999 7	2004 15	2004 15	2004 15	2004 14	2004 21	2004 21	2004 21	2003 16	2004 15	2004 14	1992 1		2004 9	
BW-21	Median	143.7	24.4	1.2	0.6	1	0.4	1	7.2	0.5	5	102.8	67.5		6.2	
	25%	138.8	21.9	1	0.6	0.9	0.4	0.5	6.2	0.4	4.8	98.1	67.5		2.7	
	75%	147.1	28.8	1.4	0.7	1.4	0.4	1.5	8.3	0.6	5.9	113.1	67.5		12.5	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-	
	Range n	1999 11	2003 11	2003 11	2003 11	2003 9	2003 17	2003 17	2003 17	2003 13	2003 11	2003 10	1992 1		2003 8	
BW-22	Median	135	22.7	0.8	0.5	1.2	0.4	0.1	8	0.5	5.2	90.5			8	
	25%	128.5	21	0.7	0.5	1.1	0.3	0	7.7	0.5	4.9	88.1			8	
	75%	168	26.9	0.9	0.6	1.3	0.4	0.4	8.5	0.8	5.5	109.7			8	
	Date	1996-	1999-	1999-	1999-	1999-	1999-	1999-	1999-	1996-	1999-	1999-				
	Range n	1999 9	2003 5	2003 5	2003 5	2003 5	2003 13	2003 13	2003 13	2000 16	2003 5	2003 5			1999 1	

Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-23	Median	180	25.4	1	0.6	0.9	0.4	7.2	8.7	1.1	5.3	84	61.3			
	25%	180	20.9	0.8	0.5	0.6	0.3	4.6	7.1	0.9	4.7	74.2	61.3			
	75%	180	26.4	1.1	0.6	1.2	0.4	9.2	9.2	1.4	5.5	93.9	61.3			
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-					
	Range	1992	2003	2003	2003	2003	2003	2003	2003	2003	2003	2003	1992			
BW-24	n	1	3	3	3	3	3	3	3	2	3	2	1			
	Median	144	24.1	1.4	0.6	0.9	0.3	0.4	7	0.8	6.1		38			
	25%	144	24.1	1.4	0.6	0.9	0.3	0.4	7	0.8	6.1		38			
	75%	144	24.1	1.4	0.6	0.9	0.3	0.4	7	0.8	6.1		38			
	Date															
BW-25	Range	1992	1992	1992	1992	1992	1992	1992	1992	1992	1992		1992			
	n	1	1	1	1	1	1	1	1	1	1		1			
	Median	7.46	7.5	163.9	26.4	1.2	0.8	1.8	0.5	4.2	9.1	0.5	7.3			
	25%	7.46	7.5	159.3	25	1.2	0.8	1.8	0.4	3	8.9	0.5	7.2			
	75%	7.46	7.5	168.8	27.8	1.2	0.9	1.8	0.5	5.4	9.2	0.5	7.5			
BW-26	Date		1992-													
	Range	1992	1996	1992	1992	1992	1992	1992	1992	1992	1992		1992			
	n	1	7	2	2	2	2	2	2	2	2		2			
	Median		146.5	23.7	1.7	0.6	1.3	0.3	0.8	8.4	0.6	6.4	97.3	56.7		13.8
	25%		101.1	17.9	1.1	0.6	1.1	0.3	0.5	7.2	0.5	5.4	73.3	56.7		11
BW-27	75%		194.4	32.7	2	0.8	2.1	0.4	1.9	10	0.9	6.8	141.2	56.7		18.2
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-				1999-
	Range		1999	2004	2004	2004	2004	2004	2004	2004	2004	2004	1992			2000
	n		10	12	12	12	9	18	18	18	16	12	11	1		7
	Median	7.7	91.9	17.3	1.2	1.1	0.8	0.3	0.1	5.9	0.8	11	31	90.9		37.6
BW-27	25%	7.6	54.6	9.4	0.7	0.9	0.7	0.3	0	4.2	0.5	9.3	23.8	66.9		32.8
	75%	7.8	107.3	27.4	1.6	1.9	0.9	0.3	0.3	6.5	1.5	17.2	51.6	150		57.3
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-			1999-
	Range	1993	1999	2000	2000	2000	1999	2000	2000	2000	2000	2000	1993			2000
	n	4	18	22	22	22	10	18	13	18	26	22	7	5		7

	Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-27A	Median	7.8	128.1	21.5	1.1	1.1	1	0.3	0.2	6.6	0.4	9.7	95.7	7.9	4.3	6.2	0.4
	25%	7.5	121.7	20.5	1.1	1	0.9	0.3	0.1	6	0.3	9.1	86.8	3.4	3.8	1.6	0.2
	75%	7.9	134.1	22.6	1.2	1.2	1.1	0.3	8.1	7.1	0.5	10.3	101.2	42.4	5.3	22.4	0.6
	Date	1992-	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range n	2013 40	2000 28	2013 49	2013 57	2013 57	2013 55	2013 61	2013 52	2013 61	2013 56	2013 55	2013 39	2013 29	2013 20	2013 27	2013 20
BW-29	Median		92.9	22.3	0.7	0.5	1	0.4	9.2	7.5	1.6	5.5	83	45.3			1.4
	25%		82.4	17.5	0.6	0.5	0.7	0.3	8.7	7.1	1.5	4.6	67.1	45.3			1.4
	75%		99.3	26.9	0.9	0.6	1.4	0.4	11.5	9	1.7	6.5	118	45.3			1.4
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2003-				
	Range n		1996 6	2004 6	2004 6	2004 6	2004 6	2004 6	2004 6	2004 6	2003 2	2004 6	2004 5	2004 1	1992 1		2003 1
BW-32	Median		207	28.3	0.8	0.6	1.6	0.4	11.4	9.3	0.5	6	108	46.7			127
	25%		207	26.5	0.8	0.6	1.5	0.4	11.2	8.8	0.4	5.7	104.8	46.7			64.9
	75%		207	29.3	0.8	0.7	1.9	0.4	12	9.7	0.7	6.6	112.3	46.7			189
	Date			1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2002-				2003-
	Range n		1992 1	2004 7	2004 7	2004 7	2004 7	2004 7	2004 7	2004 7	2003 3	2004 7	2004 6	1992 1			2004 2
BW-34	Median		125.6	22.4	0.9	0.5	0.9	0.3	0.1	6.1	0.5	5.2	92.7				8.4
	25%		107.8	18.4	0.6	0.4	0.7	0.2	0.1	5.6	0.4	4.7	78.8				4.4
	75%		139.4	39.4	1.4	1	1	0.4	0.3	6.4	0.7	9.2	104.6				11
	Date		1996-	1996-	1996-	1996-	1999-	1999-	1999-	1999-	1996-	1996-	1999-				1999-
	Range n		1999 16	2004 22	2004 22	2004 22	2004 12	2004 21	2004 19	2004 21	2003 25	2004 22	2004 14				2003 8
BW-36	Median	6.7	29.8	3.7	0.6	0.8	0.3	0.3	0.1	4.8	0.7	8.5	23	10.8	1.3	22.8	2.2
	25%	6.6	26.3	2.5	0.5	0.7	0.3	0.2	0.1	4.4	0.6	6.8	17.8	8.3	1	6.2	1.5
	75%	6.8	39	4.9	1	1.1	0.3	0.3	6	5.9	1	13.5	32.1	11.7	1.6	57.1	2.6
	Date	2008-	1996-	1996-	1996-	1996-	1999-	1999-	1999-	1999-	1996-	1996-	1999-	2008-	2008-	1999-	2008-
	Range n	2012 8	1999 13	2012 29	2012 29	2012 29	2012 18	2012 25	2011 16	2012 25	2012 30	2012 29	2012 21	2012 9	2012 9	2012 19	2012 9

Station		pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-37	Median	7.5	146	28.1	1.2	0.8	1.4	0.3	0.6	7.3	0.4	6.7	128.7	1.7	9.4	5	0.2
	25%	7.4	119.7	26.9	1.2	0.7	1.2	0.3	0.4	6.6	0.4	6.4	117.3	1.1	9	1.2	0.1
	75%	7.8	154.7	29.3	1.3	0.8	1.5	0.4	10.5	8.2	0.5	7.1	137.4	4.4	10.8	11.4	0.2
	Date	1998-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	1999-	1992-	2008-	1999-	2008-
	Range n	2013 21	2000 19	2013 41	2013 41	2013 41	2013 40	2013 50	2013 48	2013 50	2013 41	2013 41	2013 40	2012 16	2013 20	2013 28	2013 19
BW-38	Median		132	21.1	1.4	0.8	0.9	0.3	0.1	6	0.4	8	88.8	83.6		29.3	
	25%		125.8	16.7	1.1	0.7	0.8	0.2	0.1	5.8	0.3	7.8	77.7	83.6		25	
	75%		139.8	24.3	1.6	0.9	1.1	0.3	1.2	6.5	0.5	8.7	101	83.6		35.5	
	Date		1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-			1999-	
	Range n		1999 6	2003 12	2003 12	2003 12	2003 10	2003 18	2003 18	2003 18	2003 15	2003 12	2003 11	1992 1		2003 8	
BW-39	Median	7.8	84.1	15.6	1	1.2	0.6	0.3	0.1	5.2	0.4	12	82.9	9.4	3.2	4.8	
	25%	7.4	80.1	14.5	0.9	1.1	0.6	0.3	0.1	4.6	0.3	11.5	77.5	5.5	3	1	
	75%	8	88.2	17	1.1	1.4	0.7	0.4	0.5	6.1	0.5	12.8	87.7	32	3.5	19.5	
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-		1999-	
	Range n	1993 2	1999 7	2000 10	2000 10	2000 10	1999 8	2000 15	2000 7	2000 15	2000 15	2000 10	2000 7	1993 3		2000 7	
BW-39A	Median	7.8	84.1	15.6	1	1.2	0.6	0.3	0.1	5.2	0.4	12	82.9	9.4	3.2	4.8	0.2
	25%	7.4	80.1	14.5	0.9	1.1	0.6	0.3	0.1	4.6	0.3	11.5	77.5	5.5	3	1	0.1
	75%	8	88.2	17	1.1	1.4	0.7	0.4	0.5	6.1	0.5	12.8	87.7	32	3.5	19.5	0.4
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range n	2016 126	2002 69	2015 149	2015 158	2015 159	2015 147	2017 176	2017 145	2017 176	2017 166	2015 157	2015 122	2015 105	2015 87	2015 98	2015 79
BW-40	Median	7.7	106.4	20.5	1.6	1.3	0.8	0.3	0.2	5.3	0.4	14.1	66	48.6		10.6	
	25%	7.6	98.5	15	1.1	0.9	0.7	0.3	0.2	4.8	0.3	10	64.8	25.2		6	
	75%	7.9	120.9	26.6	2.4	1.9	1	0.4	0.3	5.5	0.7	19.2	68.9	79.6		13.9	
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1993-	1992-	1999-	1992-		1999-	
	Range n	1993 7	1999 23	2000 25	2000 25	2000 25	1999 13	2000 22	2000 22	2000 22	2000 29	2000 25	2000 7	1993 7		2000 7	

	Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
BW-40A	Median	7.5	97.3	16.5	1	1.1	0.6	0.3	0.2	5.6	0.5	10.1	57.6	2.3	3.3	2.7	0.1
	25%	7.1	84.2	10.2	0.8	1	0.4	0.3	0.1	4.7	0.4	9.2	50.5	1.1	3	1.9	0.1
	75%	7.9	119	25.8	1.2	1.2	0.9	0.3	7.2	5.9	0.7	11.4	79.2	31.8	4.4	6.4	0.1
	Date	1992-	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range	2013	2000	2013	2013	2013	2013	2013	2011	2013	2013	2013	2013	2013	2013	2012	2013
T-1	n	36	34	59	67	67	55	60	50	61	67	65	39	29	20	25	19
	Median	7.9	161.3	28.4	1.6	1.2	2	0.3	0.5	9.4	0.4	9.2	124.3	5.5	5.5	8.2	0.1
	25%	7.7	156	27	1.5	1.1	1.8	0.3	0.3	8.1	0.3	8.5	114.8	2.9	4.9	2	0
	75%	8	165.3	29.6	1.7	1.3	2	0.4	6.2	9.7	0.6	10	131.7	21.7	7.9	18.8	0.1
	Date	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
T-2	Range	2012	2000	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012
	n	35	33	56	65	65	54	62	62	62	64	63	40	27	19	28	16
	Median	7.9	172	31.4	1.5	1.1	1.4	0.3	0.4	7.5	0.5	9.3	123.1	4.5	5.9	3	0.1
	25%	7.7	167.7	29.3	1.5	1	1.3	0.3	0.3	6.2	0.4	8.3	117.7	2.2	5.3	1	0.1
	75%	8	176.9	34.6	1.7	1.2	1.6	0.4	1	8	0.7	10.2	129.9	20.2	8.8	14.4	0.1
T-3	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range	2012	2000	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012	2012
	n	33	35	52	61	61	49	57	57	58	63	59	35	25	18	25	17
	Median	7.6	164.3	27.7	1.3	0.8	1.1	0.3	0.3	5.7	0.8	7.9	113	7.1	7.4	7.2	0.7
	25%	7.2	150	23.4	1.2	0.7	1	0.3	0.2	5.2	0.6	7.2	101	3.1	6.4	4.2	0.3
T-4	75%	7.9	172.6	31.6	1.6	1	1.3	0.4	0.6	7.2	1.1	9.2	127.1	23.1	8.9	14.8	1.2
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1999-	1992-	2008-	1999-	2008-
	Range	2016	2000	2015	2015	2015	2015	2016	2016	2016	2016	2015	2015	2015	2015	2015	2015
	n	52	37	65	73	74	64	78	77	79	84	72	47	34	28	36	28
	Median	8.1	202	29.9	3.1	1.7	2.9	0.3	21.7	16.8	1.3	7.9	257	62.3		2	
T-4	25%	8	196.5	29.3	3.1	1.6	2.9	0.3	21	16.2	0.8	7.7	253	51		1.4	
	75%	8.2	208	30.5	3.2	1.8	3.1	0.3	22	17	1.6	8.1	260.5	117.6		3	
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2003-	1992-		2003-	
	Range	1993	1996	2004	2004	2004	2004	2004	2004	2004	2003	2004	2004	1993		2004	
	n	4	9	30	30	30	30	30	29	30	6	30	25	5		15	

Station	pH	SC ($\mu\text{S cm}^{-1}$)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Cl ⁻ (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	DOC (mg L ⁻¹)	Si (mg L ⁻¹)	Sr ($\mu\text{g L}^{-1}$)	Al ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Fe ($\mu\text{g L}^{-1}$)	Mn ($\mu\text{g L}^{-1}$)
T-5	Median	8.1	197.7	30.6	3.2	2	2.3	0.4	11.1	15.3	0.6	8.7	203.5	50.6		23.6
	25%	8	191.3	27.9	3.1	1.9	2.1	0.3	0.4	13.8	0.3	8	195.3	47.3		23.6
	75%	8.2	203	31.6	3.2	2.1	2.5	0.4	21.3	16.4	0.9	9.6	205.8	51.9		23.6
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1993-	1992-	1992-	1992-	2003-	1992-		
	Range	1993	1996	2004	2004	2004	2004	2004	2004	2004	2003	2004	2004	1993		2003
	n	4	9	8	7	8	8	8	6	8	6	7	3	4		1
T-6	Median	8	143.1	13.6	0.8	0.5	0.7	0.3	7.3	6.3	2.1	4.3	57.5	43		17.5
	25%	7.8	135.6	12.2	0.6	0.4	0.6	0.3	4.5	5.7	1.8	4	55.2	31.7		14
	75%	8	214	21.2	1.8	1.4	1.1	0.4	8.1	8.9	2.8	5	65.1	70.4		28.1
	Date	1993-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	1992-	2003-	1992-		2003-
	Range	1993	1996	2004	2004	2004	2004	2004	2004	2004	2003	2004	2004	1993		2004
	n	8	13	33	33	33	33	33	33	33	9	33	24	8		24

Supplemental Table 2.A.2. Annual total precipitation and average air temperature for the water years 1992-2015.

Water Year	Annual precipitation (mm)	Average Temperature (°C)
1992	1169	4
1993	1278	4
1994	1213	5
1995	1057	6
1996	1543	4
1997	1385	4
1998	1435	5
1999	1233	6
2000	1205	5
2001	1043	4
2002	1373	5
2003	1174	4
2004	1432	4
2005	1225	5
2006	1685	5
2007	1412	5
2008	1633	5
2009	1337	4
2010	1349	6
2011	1675	5
2012	1177	6
2013	1443	5
2014	1161	4
2015	1353	4

Supplemental Table 2.A.3. Median solute concentrations in stream water during the four periods during water years 1992-2015.

Species	Dormant	Rising limb	Falling limb	Growing
SC (µs)	110.2	89.3	83.3	130.3
Ca ²⁺ (mg L ⁻¹)	22.6	17.1	16.8	23.0
Mg ²⁺ (mg L ⁻¹)	1.1	0.8	0.8	1.0
Na ⁺ (mg L ⁻¹)	0.7	0.5	0.5	0.7
K ⁺ (mg L ⁻¹)	1.1	0.9	0.9	1.2
Cl ⁻ (mg L ⁻¹)	0.3	0.3	0.3	0.3
NO ₃ ⁻ (mg L ⁻¹)	0.6	1.6	0.8	0.6
SO ₄ ²⁻ (mg L ⁻¹)	6.8	6.1	5.7	5.8
DOC (mg L ⁻¹)	1.3	1.9	1.7	2.0
Si (mg L ⁻¹)	5.3	4.8	5.0	5.4
Sr (µg L ⁻¹)	91.4	63.7	64.2	89.7
Al (µg L ⁻¹)	13.4	13.7	12.7	16.4
Ba (µg L ⁻¹)	7.8	5.5	7.2	8.5
Fe (µg L ⁻¹)	7.9	6.2	4.9	10.9
Mn (µg L ⁻¹)	2.1	0.8	0.8	1.3

Supplemental Table 2.A.4. Median solute concentrations at the 5th and 95th quantiles of streamflow from 1992 to 2015

Species	5th Quartile	95th Quartile
SC (μs)	149.2	82.1
Ca^{2+} (mg L^{-1})	31.2	15.0
Mg^{2+} (mg L^{-1})	1.5	0.7
Na^{+} (mg L^{-1})	1.0	0.5
K^{+} (mg L^{-1})	1.6	0.9
Cl^{-} (mg L^{-1})	0.3	0.3
NO_3^{-} (mg L^{-1})	0.5	0.9
SO_4^{2-} (mg L^{-1})	9.1	4.3
DOC (mg L^{-1})	1.3	3.6
Si (mg L^{-1})	5.8	4.5
Sr ($\mu\text{g L}^{-1}$)	131.1	62.9
Al ($\mu\text{g L}^{-1}$)	56.9	21.1
Ba ($\mu\text{g L}^{-1}$)	11.1	6.0
Fe ($\mu\text{g L}^{-1}$)	8.7	17.1
Mn ($\mu\text{g L}^{-1}$)	22.0	1.3

Supplemental Table 2.A.5. Median solute concentrations in soil lysimeters and groundwater wells deeper than 1 meter

	Season	SC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	DOC	Si	Sr	Al	Ba	Fe	Mn	
		(μS cm ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(mg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	(μg L ⁻¹)	
09	LYS SH	dormant	47.8	1.7	0.3	0.3	0.4	0.4	1.0	2.1	6.5	6.2	9.9	220.3	7.0	53.9	2.8
		rising limb	27.0	2.3	0.4	0.2	0.4	0.3	0.7	2.8	3.5	5.5	9.5	81.2	7.3	29.6	1.7
		falling limb	23.5	1.0	0.2	0.1	0.2	0.2	0.3	1.6	3.0	2.8	6.6	169.8	7.9	36.7	1.1
		growing	21.6	1.4	0.3	0.1	0.8	0.2	0.6	1.4	10.2	5.2	7.8	307.9	6.3	67.3	2.6
	LYS MI	dormant	17.9	1.6	0.2	0.2	0.2	0.4	3.0	2.6	4.2	4.7	10.4	57.3	4.7	8.8	1.8
		rising limb	15.4	2.1	0.4	0.2	0.1	0.3	2.7	3.4	1.0	6.7		18.9			
		falling limb	12.3	1.4	0.2	0.2	0.1	0.2	0.3	2.6	1.4	5.0	11.2	28.0	8.8	1.7	1.6
		growing	27.0	1.4	0.2	0.2	0.1	0.2	0.1	2.7	1.0	5.4	12.0	39.2	4.8	8.1	1.5
	LYS DP	dormant	50.4	5.7	0.4	0.8	0.2	0.3	0.2	3.9	0.7	6.7	29.9	5.2	1.9	1.9	0.2
		rising limb	27.1	5.0	0.5	0.7	0.3	0.3	0.2	4.0	0.5	6.6	30.0	26.2	2.2	9.9	0.1
		falling limb	25.0	2.7	0.3	0.5	0.2	0.3	0.2	3.2	0.9	5.5	19.3	24.2	2.0	4.4	0.4
		growing	49.1	3.3	0.3	0.6	0.2	0.2	0.1	3.6	0.8	6.4	30.2	5.7	2.6	1.6	0.3
	WELLS	dormant	114.1	19.3	1.1	1.1	0.8	0.3	0.3	5.9	0.5	10.2	87.2	5.4	4.0	2.5	0.1
		rising limb	121.8	24.4	1.4	1.1	1.0	0.3	0.4	6.6	0.4	9.8	94.0	66.9	3.0	11.5	0.1
		falling limb	121.0	19.4	1.0	0.9	0.8	0.3	0.3	6.3	0.5	8.1	85.8	8.0	4.8	15.5	0.2
		growing	144.0	23.6	1.2	1.1	1.2	0.3	1.4	7.0	0.5	9.6	100.0	17.9	3.6	3.6	0.1

Supplemental Table 2.A.6. Median solute concentrations across soil lysimeters and groundwater well types

Species	Lysimeter	Riparian well	Hillslope hollow well	Hillslope well	Hillslope bench well
SC (μs)	29.2	165.3	125.0	93.4	141.0
Ca ²⁺ (mg L ⁻¹)	2.7	29.0	22.4	16.7	22.3
Mg ²⁺ (mg L ⁻¹)	0.3	1.5	0.9	1.0	1.1
Na ⁺ (mg L ⁻¹)	0.5	1.0	0.6	1.1	0.6
K ⁺ (mg L ⁻¹)	0.2	1.5	1.0	0.7	1.2
Cl ⁻ (mg L ⁻¹)	0.3	0.3	0.3	0.3	0.3
NO ₃ ⁻ (mg L ⁻¹)	0.5	0.6	0.7	0.2	1.4
SO ₄ ²⁻ (mg L ⁻¹)	3.0	7.7	6.7	5.7	7.6
DOC (mg L ⁻¹)	1.5	0.5	0.5	0.5	0.5
Si (mg L ⁻¹)	5.9	8.0	5.3	11.0	5.8
Sr (μg L ⁻¹)	16.5	123.5	97.8	82.8	97.0
Al (μg L ⁻¹)	37.5	7.3	80.1	11.0	61.2
Ba (μg L ⁻¹)	5.0	8.0		3.2	
Fe (μg L ⁻¹)	19.6	6.9	9.3	7.9	15.2
Mn (μg L ⁻¹)	0.8	0.2		0.2	

2.11 APPENDIX 2.B SUPPLEMENTAL FIGURES

62

Supplemental Figure 2.B.1. Timeseries of precipitation, air temperature, selected solute (Ca²⁺, Cl⁻, NO₃⁻, DOC) concentrations in streamflow, and stream discharge from water years: 1992-2015. The shaded grey areas indicate the snowmelt period.

Supplemental Figure 2.B.2 Solute concentrations in streamflow during the rising (blue) and falling (green) limbs of the snowmelt period using data from all water years (1992-2015), showing a mild hysteresis for NO_3^- and a slight hysteresis for DOC.

3 Chapter 3: Synoptic Diagnosis of Catchment Hydrologic and Biogeochemical Processes and Climate and Land Use Change Effects in the Great Lakes Basin

3.1 Abstract

The goal of this study was to investigate the hydrologic and biogeochemical cycles present in 138 catchments to better understand how land-use, snow abundance, and surficial geology control stream chemistry using C - Q relationships ($C=aQ^b$) throughout the US portion of the Great Lakes Basin (GLB). Multi-decadal C - Q relationships for specific conductance and 15 solutes (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , P , NH_4^+ , NO_3^- , NO_2^- , Al , Fe , Mn , Si , and Sr) were created using data downloaded from the USGS website and the Water Quality Portal. Specific conductance (SC) was measured daily over varying periods in the past 5 decades by the US Geological Survey (USGS) at 98 locations while data for the other 15 solutes was collected less frequently, ranging from 1 to 11 samples per year over multiple years to decades at 67 different catchments. SC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , Si , and Sr concentrations often diluted ($b < -0.1$) during high flows, becoming the dominant pattern for 46% - 97% of the sampled sites measuring each solute. P , NH_4^+ , NO_3^- , NO_2^- , Al , and Fe concentrations often exhibited a flushing response ($b > 0.1$), increasing with flow for 70% - 100% of the sampled sites. The enrichment patterns indicate that those solutes likely have higher concentrations in shallow flowpaths that are activated during high flow conditions while dilution patterns indicate that those have higher concentrations in deeper flowpaths. No measured solute was predominately chemostatic throughout the studied catchments and solutes were instead frequently chemodynamic. Land use and precipitation characteristics were frequently correlated to the strength (R^2) and slope (b -coefficient) of the C - Q relationships. These results indicate that land cover and precipitation patterns are potential factors impacting the intensity and the pattern of solute export by rerouting dominant flowpaths and changing biogeochemical processes. Primarily, as urban areas expand and the precipitation regimes shift away from snow dominated systems to rain dominated systems, the C - Q power-law relationship may weaken, and the buffering capacity of nutrients and other contaminants may be reduced.

3.2 INTRODUCTION

Shifting precipitation patterns resulting from climate change coupled with rapid land-use changes highlight the importance of water protection and sustainable use, requiring that we understand processes controlling water quality and streamflow generation. Natural hydrologic processes vary spatially and temporally, making each watershed unique with differing hydrologic controls on inputs and outputs (Meybeck & Moatar, 2012; Williams et al., 2018). This natural heterogeneity often makes it difficult to apply findings between watersheds, and this heterogeneity can be further influenced by human activities. Anthropogenic modifications to land use and atmospheric carbon dioxide concentrations are quickly shifting hydrologic processes (flowpaths, stormflow, infiltration, etc.) (Hung, James, Carbone, 2018; Rose, 2003) and climate variables (precipitation, evapotranspiration, evaporation, storm event frequency and duration) (Bieroza, Heathwaite, Bechmann, Kyllmar, Jordan, 2018; Williams et al., 2018), making it even more critical to understand potential water quality vulnerabilities.

Under warmer conditions, northern latitudes see more rapid changes to snow precipitation patterns than lower latitudes. Northern latitudes will continue to see earlier onset of snowmelt compared to historic trends (D'Orgeville, Peltier, Erler, & Gula, 2014; Demaria et al., 2016). Catchments that are currently snow-dominated areas will shift to rain-dominated systems as temperatures rise and snow cover decreases (D'Orgeville, Peltier, Erler, & Gula, 2014; Demaria et al., 2016). Snow cover extent has significantly decreased over the last 100 years especially during the spring snowmelt season (Derksen & Brown, 2012). Additionally, Demaria et al. (2016) project that future winter precipitation will increase while snow water equivalent (SWE) will decrease in the northeastern and upper Midwestern United States, including the Great Lakes Basin. Several models predict that the number of days with snowpack and the snow depth will decrease while snowfall intensity will increase (Demaria et al., 2016). Peak streamflows are predicted to increase 5% to 25% over historical patterns in the Great Lakes Region. The center of volume or the hydrograph centroid, the day on which 50% of annual streamflow has occurred, is estimated to happen 22 to 27 days earlier (Demaria et al., 2016).

In addition to changes in climate, anthropogenic changes in land-use through expanding agriculture and urbanization can alter certain hydrologic, geomorphic, ecologic, aquatic, and water quality features (Hung et al. 2018; Liu, Wang, & Li, 2013; Zambrano, Pacheco-Muñoz, & Fernández, 2017). Urbanization increases impervious surfaces while decreasing forest cover, reducing infiltration capacities and often increasing risks of flooding (Zambrano et al., 2017). Changes in landscape characteristics coupled with changing meteorological inputs increase runoff and severity and frequency of flood events, subsequently impacting water quality (Liu et al., 2013; Zambrano et al., 2017). Additionally, the expansive croplands in the Great Lakes area have extensive tile drainage networks that change hydrological flowpaths while the accompanied fertilizer additions change solute availability (Guo et al. 2017). These changes fuel rising water quality concerns as the human population increases, and approximately 50% of the global population is living in communities faced with complex water quality issues (Liu et al., 2013).

To address these concerns, researchers and natural resource managers require a more comprehensive understanding of streamflow generation and factors that affect the variation of stream chemistry. One method used to study catchment-wide hydrologic and biogeochemical processes is to analyze concentration-discharge (C - Q) relationships, which measure how concentrations of a solute of interest respond to variations in stream discharge (Bieroza et al., 2018). Although studies have investigated C - Q relationships for decades (Evans & Davies, 1998; Godsey et al., 2009), there are still unanswered questions regarding the factors controlling C - Q behavior across sites with varying climate, geology, and land use processes (Bieroza et al., 2018; Moater et al., 2017). Few studies have investigated the impact of urbanization, snow dominance, and surficial geology on C - Q relationships over a large scale. Additionally, most studies have focused on C - Q patterns in montane systems with very little research conducted in the Midwestern US and especially the Great Lakes region. The objective of this study is to narrow that knowledge gap by investigating the how urbanization, snow dominance, and surficial geology affect the magnitude and

temporal variance of C - Q relationships, with a particular focus on catchments within the Great Lakes Basin.

The Great Lakes region includes land areas in the province of Ontario, Canada and eight US states – Minnesota, Wisconsin, Michigan, Indiana, Illinois, Ohio, Pennsylvania, and New York. However, since the same stream chemistry and landform data is not collected in Canada, only the United States portion of the Great Lakes Basin is included in this study. Water is an important resource within the Great Lakes region since the area contains 84% of North America's fresh water and 21% of the world's surface fresh water, and its population relies heavily on the Great Lakes for transportation, drinking water, recreation, and power regeneration (Pathak, Kalra, & Ahmad, 2017). The 764,000 km² area has over 35 million inhabitants and contributes one fifth of the gross national product of the US and one half of that of Canada (D'Orgeville et al., 2014; Quinn, 1981). The region also contains a gradient of urban development from intensely urbanized areas around the large urban centers of Detroit, Chicago, Cleveland, Green Bay, and Milwaukee to catchments covered by cropland to those dominated by forests, creating an ideal landscape to study C - Q relations. The area was glaciated resulting in varying types and depth of surficial deposits with generally shallower deposits in the northern areas and deeper deposits throughout the lower basin. There is also a gradient of snow inputs that is primarily controlled by latitude and lake proximity (Eichenlaub, 1970). These variations in climate and landscape create ideal conditions to study variation in C - Q relationships.

The objective of this study was to answer related questions by first investigating how C - Q patterns respond with variation in snow abundance and urbanization amount as a proxy of future urbanization. This objective was pursued by investigating multi-decadal C - Q relationships throughout watersheds within the United States portion of Great Lakes Basin using stream chemistry and discharge data from public stream chemistry datasets. High frequency specific conductance and discharge measurements and low-frequency, long-term water chemistry dataset for 15 additional solutes was used to create C - Q relationships at decadal timescales. The questions posed are

Q1. What factors control C - Q relations in the Great Lakes Basin?

Q2. How might expected reductions in snowfall and increases in urbanization impact future water quality and abundance?

3.3 SITE DESCRIPTION

The Great Lakes Basin can be divided into a southern, lowland region that includes the Erie and Michigan basins and most of the Huron and Ontario basins and a northern, upland region composed of the Superior and Georgian Bay basins. The northern region is underlain by granite, gneiss, and metavolcanics and metasedimentary rocks of Precambrian age, while the southern region has deeper sedimentary rocks of Paleozoic age (Larson & Schaetzl, 2001). In general, southern lowland areas of the basin have shallow rolling hills that are continuously covered by glacial deposits ranging from 50 to >350 meters thick, while northern areas are rugged and rocky with glacial sediments that are thin and discontinuous (Larson & Schaetzl, 2001; Wilcox, Thompson, Booth, & Nicholas, 2007)

Overall, about 35% of the land is managed for agriculture, 52% is forested and often used for timber production, and 7% is urbanized with varying intensities, the highest being around the larger urban centers of Detroit, MI, Milwaukee, WI, and Chicago, IL (Wilcox et al., 2007). Due to the longer growing season and more favorable soil types, more land is used for agriculture in the lower basin while most land in higher latitudes is managed for timber production by private, commercial, or government stakeholders.

Annual average precipitation and air temperature varies throughout the four sub-basins: Superior Basin (80.9 cm and 2.93°C), Michigan-Huron (84.5 cm and 6.49°C), Erie (91.9 cm and 9.19°C), and Ontario (92.3 cm and 7.41°C) (Croley and Lewis, 2006). Winter precipitation occurs as snow throughout the northern basin with snowfall amount and timing varying with latitude, cyclone frequency, moisture, lake proximity, and altitude (Eichenlaub, 1970). The mean seasonal snowfall within the Great Lakes Basin is on average between 10% to 50% of the total regional winter precipitation (Eichenlaub, 1970; Wright, Posselt, & Steiner, 2013).

3.4 METHODOLOGY

3.4.1 Data Sources and Preparation

The United States Geological Survey (USGS) maintains a sampling network with stream gauges measuring multiple water quality parameters throughout the nation as part of the National Water Information System (waterdata.usgs.gov/nwis). Most stations include measurements of stream discharge and specific conductance (SC), with fewer water quality parameters from other stations. Ninety-eight monitoring sites were selected within the GLB with daily mean measurements for stream discharge and SC, and the locations were throughout the Great Lakes Basin in various cover types (Figure 3.1). The data for the other 15 chemical solutes were downloaded using the Water Quality Portal from the National Water Quality Monitoring Council, a collaboration between the Environmental Protection Agency (EPA) and USGS (www.waterqualitydata.us/). These 15 solutes included eight major geogenic solutes: Calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), sulfate (SO_4^{2-}), strontium (Sr), and silica (hereafter referred to as Si). Additionally, there were four biogenic solutes: phosphorus (P), ammonia and ammonium (hereafter referred to as NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) and three trace elements: aluminum (Al), iron (Fe), and manganese (Mn). These data were collected at low frequency over multiple decades (1950 – 2020) for annual/seasonal water quality monitoring and compiled from multiple state or federal agencies. There were 67 sites with stream water chemistry data available within the GLB, of which 27 were also included in the 98 sites with SC and discharge data, yielding a total of 138 gauge/monitoring stations. Solute were not measured at all sites.

Most of the 138 sites were located within Michigan and Wisconsin (MI = 53; WI = 39) and 1 to 16 in the surrounding states (IN = 3, IN/IL=1, IN/MI=1, IN/OH=2, MI/OH=1, MI/WI=1, MN = 5, NY = 15, OH = 16, PA = 1), which roughly reflected the contributing areas composing the Great Lakes Basin (Table 3.A.1). The sampling frequency varied between the solutes. SC had much higher sampling frequency with daily measurements over 1 to 20 years with a median of 4 and a mean of 5 years. The other solutes had lower sampling frequency that ranged from 1 to 356 samples per year with a mean of 8.9 samples

per year over 1 to 53 water years with a mean of 15 years. Mean stream discharge varied from $0.029 \text{ m}^3\text{s}^{-1}$ to $5,832.1 \text{ m}^3 \text{ s}^{-1}$ with a mean of $61.7 \text{ m}^3 \text{ s}^{-1}$ and a standard deviation of $496.1 \text{ m}^3\text{s}^{-1}$. Watershed area ranged from 3.77 km^2 to 163.85 km^2 with a mean of 75.91 km^2 and a standard deviation of 31.56 km^2 .

HUC 8 12-digit watershed boundaries from USGS were used for the watershed boundaries for all 138 sites. Seven watersheds had 2 or more sampling locations. These watersheds were delineated into smaller watersheds to contain only one gauge using the ArcGIS “watershed tool” and 10m DEMs, using the USGS stream gauge locations as pour points. The hydrologic interpretation of a pour point is that it is the outlet of the newly created catchment. Those split watersheds were considered nested and all contributing area to each USGS stream gauge was considered in following calculations (Table 3.A.2). If discharge was not measured where the chemical concentrations were sampled ($n=9$), the discharge measured at the nearest USGS stream gauge was used, which ranged between approximately 3 m to 11.64 km from the water chemistry sampling location.

If there were multiple measurements in a day for a chemical species, only the first observation was selected. Multiple daily entries were not used because there was only mean daily stream discharge data available. This deleted 40,273 entries from 28,015 days out of final 124,972. Most of the duplicates were analytical duplicates where 2 to 6 samples were collected at the same time with a mean of 2. Only 6,498 days had entries that were deleted because multiple samples were collected on the same day but not at the same time. The number of samples deleted on days with multiple samples ranged from 1 to 14 samples per day with a mean of 2.4 and a standard deviation of 1. A median of 4 entries were deleted from $C-Q$ relationships with multiple, non-analytical duplicates. The mean standard deviations of the concentrations of these duplicates ranged from 7.0×10^{-4} to 6.25×10^2 with aluminum, iron, and manganese having the highest standard deviations. The mean standard deviation of duplicates from the other 12 solutes (removing Al, Fe, and Mn) was 2.7 and ranged from 7.0×10^{-4} to 13.7.

3.4.2 Concentration-Discharge Analysis

All concentration-discharge (C - Q) analysis was calculated on $\log_{10}$ - $\log_{10}$ scales across multi-annual timescales for all solutes using the equation: $\log(C) = \log(a) + b \cdot \log(Q)$ (Hofmeister et al., 2019; Zimmer et al., 2019), where C is the solute concentration, Q is stream discharge, and a and b are constants with a as a coefficient with units of concentration and b as an exponent (Hofmeister et al., 2019; Liu et al., 2017; Zimmer et al., 2019). The b -coefficients were classified as chemostatic when concentration varied little with changes in stream discharge ($-0.1 \leq b \leq 0.1$) or chemodynamic when the concentration varied significantly with stream discharge ($|b| > 0.1$) (Godsey et al., 2009; Herndon et al., 2015). Chemodynamic patterns were further classified into dilution when b was negative and mobilization when b was positive (Figure 3.2). Whether the best-fit slope was significantly different from a reference slope of zero was determined using Student's t -test. The strength of the C - Q relationship was measured by the coefficient of determination (R^2) and a relationship was considered significant if the p -value was less than 0.05. The physical meaning of a -coefficient is unit-flow stream concentration.

The coefficient of variation CV_C/CV_Q is another measure of chemostasis v. chemodynamics that is used in addition to slope b to provide a more robust assessment of what is occurring in the catchment. For each site, CV_C/CV_Q was calculated to further measure C - Q relationships, following Thompson et al., (2011), using the equation:

$$\frac{CV_C}{CV_Q} = \frac{\mu_Q \sigma_C}{\mu_C \sigma_Q}$$

Here μ is the mean and σ is the standard deviation of the solute concentration (C) and the stream discharge (Q) (Zimmer et al., 2019). Chemostatic behavior is $CV_C/CV_Q < 1$ and chemodynamic behavior is > 1 but the sign of the b -coefficient must be considered to determine whether the chemodynamic pattern is flushing or dilution. $CV_C/CV_Q > 1$ indicates there is greater variability in the solute concentrations and that discharge is not the sole influencing factor, and solute concentrations could be influenced by other abiotic and biotic factors such as in-stream processes, biotic processes, plant uptake,

anthropogenic additions, and colloidal transport or formation which greatly control concentrations of nutrients and trace metals (Mulholland & Hill, 1997).

3.4.3 Correlation Between *C-Q* Coefficients and Catchment Characteristics

Spearman's Rank Correlation was used to understand how *C-Q* regression coefficients are related to associated environmental and catchment conditions. Spearman's Rank Correlation was selected because the correlations between the *C-Q* coefficients and the catchment characteristics are not necessarily expected to be linear. Spearman's Rank Correlation works with monotonic relationships and linear relationships by using rank-ordered variables rather than raw data values, making it more appropriate than Pearson Correlation which only applies to linear relationships.

The *b*-coefficients and R^2 values from the multi-annual *C-Q* relationships were correlated against 9 independent variables: the watershed area, the weighted mean depth of overlaying glacial deposits, the 30-year-average precipitation, the average yearly accumulated SWE (in), the percent of total precipitation delivered as snow, the baseflow index (BFI) at the point where discharge was measured, the percent of urbanized area within the catchment, the percent of cropland area within the catchment, and the percent of forested area within the catchment.

Each of the catchment characteristics were determined using information from public datasets (Figure 3.3). The 30-water year average precipitation were created using precipitation values from 1981 to 2010 downloaded from PRISM (prism.oregonstate.edu/). Weighted mean depths of glacial deposits were derived from a GIS layer created by USGS (pubs.usgs.gov/ds/656). For this study, only the information on the thickness of Quaternary sediments was utilized, and an area-weighted mean thickness of sediment was calculated for each watershed using the area covered by the sediments and the estimated thickness. The snow water equivalent (SWE) was calculated using SWE data from National Snowfall Analysis created by the National Operational Hydrologic Remote Sensing Center (NOHRSC) (www.nohrsc.noaa.gov). Annual accumulated SWE was calculated for each of the catchments for the available data years

(2004-2019) and averaged. BFI describes the ratio of base flow to total stream flow as a percent and was recorded from a geospatial layer that estimated the BFI throughout ungauged streams in the US by extrapolating the BFI values calculated at USGS stream gauges using an automated hydrograph separation computer program called the BFI program (Wahl & Wahl, 1988; Wahl & Wahl, 1995) (water.usgs.gov/GIS/metadata/usgswrd/XML/bfi48_grd.xml). Land-use data was derived from the 2016 version of the 30-meter pixel National Land Cover Database 2016 (NLCD) (www.mrlc.gov/data), using all intensities of developed area described by NLCD (Developed-Open Space, Developed-Low intensity, Developed-Medium intensity, Developed-High intensity). The proportion of cropland and forested areas was similarly calculated using pixels that were described as cropland (“Cultivated Crops”) and forested (“Evergreen Forest”, “Deciduous Forest”, and “Mixed Forest”).

3.5 RESULTS

3.5.1 Solute Concentration-Discharge Patterns

The percent of catchments with significant C - Q relationships ($p < 0.05$) varied among solutes ranging from 38% for NO_3^- and NH_4^+ to 97% for SC (Table 3.1). Cations (e.g., Ca^{2+} , Mg^{2+} , Na^+) had higher percentage of catchments ($> 81\%$) with significant relationships than biogenic solutes and trace elements ($< 52\%$ except for P). Mean R^2 values ranged from 0.10 to 0.53 among those catchments with significant C - Q power-law relationships, with standard deviations of 0.07 to 0.28. The major cations had the highest mean values, e.g., 0.53 and 0.52 for Mg^{2+} and Na^+ , respectively (Table 3.1; Figure 3.4). The b -coefficient also varied among solutes and catchments, with mean values ranging from -0.28 for Na^+ to 1.11 for Fe (Table 3.1). Dilution ($b < -0.1$) was the most common pattern for SC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , Si, and Sr (Figure 3.5). Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , and Sr were nearly always diluted with 90% or more catchments following this pattern. Meanwhile, 15% to 44% of catchments showed chemostatic behavior ($-0.10 < b < 0.1$) for SC, Ca^{2+} , K^+ , Si. The remaining solutes, P, NH_4^+ , NO_3^- , NO_2^- , Al, Fe, and Mn, were predominantly enriched with an increase in streamflow. SC, K^+ , Cl^- , P, NO_2^- , Fe, and

Si displayed all three *C-Q* patterns, but no solute was persistently dominated by chemostatic *C-Q* behavior (Figures 3.5 and 3.6). It is worth noting that 22% of catchments (7 catchments) had a significant dilution pattern for NO_3^- . Most solutes that were dominated by dilution had mean CV_C/CV_Q values that were < 1 , while those exhibiting flushing patterns were often ~ 1 or > 1 (Figure 3.7).

3.5.2 Catchment Characteristics and Concentration-Discharge Patterns

3.5.2.1 R^2 and Catchment Characteristics

The depth of the glacial deposit was negatively correlated with SC R^2 ($\rho = -0.3$), but positively for NO_3^- and Fe ($\rho = 0.3$; Figure 3.8a). The R^2 of power-law relation for Mn was positively correlated with the 30 water year mean annual precipitation ($\rho = 0.3$). Mean SWE, snow proportion, and BFI were positively correlated with the R^2 values for SC ($\rho = 0.2$ to 0.5), no significant correlation with Ca^{2+} , Mg^{2+} , and Na^+ , but negatively correlated with some of the rest of the solutes, mainly nutrients and trace elements ($\rho = -0.3$ to -0.4). The R^2 values of SC, Ca^{2+} , Mg^{2+} , and Na^+ , and Cl^- were negatively correlated to percent of urban area ($\rho = -0.3$ to -0.7). Meanwhile, the percent of cropland was positively correlated with the R^2 values of Na^+ , Cl^- , SO_4^{2-} , nutrients (P, NH_4^+ , and NO_3^-), Fe and Sr ($\rho = 0.3$ to 0.6), but negatively with that of Si ($\rho = -0.3$). The percent of forested area and R^2 values had only three significant correlations, a positive one with SC ($\rho = 0.6$) and a negative one with SO_4^{2-} ($\rho = -0.3$) and NH_4^+ ($\rho = -0.4$).

3.5.2.2 Correlation Between *b*-Coefficients from all Sites and Catchment Characteristics

The depth of glacial deposit was positively correlated with the *b*-coefficients from SC ($\rho = 0.3$) and NH_4^+ ($\rho = 0.6$), while the 30-water year normal of precipitation was positively correlated with those from Ca^{2+} , Fe, Mn, and Si ($\rho = 0.4 - 0.7$) (Figure 3.8b). Mean SWE, percent of precipitation as snow, and BFI were negatively correlated with the *b*-coefficients of SC, Ca^{2+} , Mg^{2+} and Si ($\rho = -0.3$ to -0.8). Urban area and cropland were positively correlated with the *b*-coefficients from SC, Ca^{2+} , Mg^{2+} ($\rho = 0.3$ to 0.5), while

cropland was also positively correlated with the b -coefficients of NO_3^- , and Si ($\rho = 0.4$). Forested area was negatively correlated with the b -coefficients from SC, Ca^{2+} , Mg^{2+} ($\rho = -0.4$ to -0.5) and positively correlated with P ($\rho = 0.3$).

3.6 DISCUSSION

By combining information from multiple public datasets, I analyzed stream chemistry data from 138 diverse catchments across the GLB to identify which physical and environmental catchment characteristics were correlated with specific C - Q attributes and strengths. In the multi-annual C - Q relationships, solute behavior was predominantly chemodynamic among the sites, as geogenic solutes were diluted and biogeochemically reactive and anthropogenically-enriched solutes were often enriched with an increase in streamflow. The opposite chemodynamic patterns between the geogenic and biogenic solutes are likely caused by contrasting distributions of solutes from shallow soil water to deeper groundwater (Chen et al., 2020; Herndon et al., 2015) and the mixing from two or more endmembers with distinct solute concentrations (Evans & Davies, 1998). Results from Spearman's Rank-Order Correlation indicate that land-use and precipitation characteristics, especially urbanization, agriculture, forestation, and snow abundance, are frequently significantly correlated to the b -coefficients and R^2 values from the C - Q power-law relationships, emphasizing the influences of anthropogenic modifications on streamflow generation processes and flowpath dynamics.

The combination of R^2 values and b -coefficients from the C - Q power-law relations reveals relevant information on many aspects of hydrologic and hydrochemical processes at the catchment scale (Figure 3.2), as described in the method section. In the following sections, a holistic view is applied to provide perspective on some hydrologic and biogeochemical processes useful for managing water resources and evaluating climate and land use change effects that can be inferred from C - Q relationships. Examples are given to demonstrate how to use R^2 values and b -coefficients to gain insights into hydrologic and hydrochemical characteristics of a catchment. Limited by data availability, however, every application cannot be mentioned in this study. The demonstration below includes (1) strong

and consistent dilution patterns of major ions in forested catchments, (2) disconnection of hydrologic flowpaths accompanied by transport of pollutants in urban areas, and (3) persistent flushing of nutrients, specially NO_3^- , in agriculture areas.

3.6.1 Insight into Contrasting Solute Distributions

From the sign and magnitude of the b -coefficient, one can infer multiple active hydrologic processes and solute distribution throughout the catchment (Figure 3.2). The observed C - Q relations revealed most geogenic major ions (Mg^{2+} , Na^+ , Cl^- , and Sr) were dominated by dilution with few catchments exhibiting chemostatic behavior and nearly zero indicating flushing behavior (Figure 3.5). Meanwhile, nutrients and multiple trace elements, namely P , NH_4^+ , Al , and Fe , exhibited consistent flushing behavior with very few chemostatic or dilution sites (Figure 3.5). This contrasting pattern in b -coefficients is created from dissimilar solute concentrations in the shallow and deep soil layers, which creates distinct solute concentrations between the contributing stream end-members (Chen et al., 2020; Evans & Davies, 1998; Herndon et al., 2015). The dominant dilution pattern of geogenic major ions indicates that, throughout the GLB, these solutes likely have higher concentrations in deeper soil water than in shallow water and are mainly exported through groundwater contributions while nutrients are mainly located in shallow soil water and exported through subsurface flowpaths or contributions from surface overland flow. Additionally, the export patterns of Mg , Na , Cl , SO_4^{2-} , P , NH_4^+ , Al , and Fe were consistent with 90% of studied catchments exhibiting the same C - Q pattern, indicating that the relative vertical distribution of each solute is similar throughout the Great Lakes region. Meanwhile, there was much more variation in the C - Q behaviors of SC , Na^+ , Cl^- , K^+ , P , NH_4^+ , NO_3^- , NO_2^- , Fe , Si , and Mn , suggesting that the solute distribution and processes controlling export of those solutes change throughout the GLB.

Additionally, major ions and nutrients had contrasting CV_C/CV_Q values with the former having low values (<1) and the latter having higher mean values (~ 1 or >1) (Figure 3.7; Table 3.1). When interpreted, this pattern indicates that the variation in nutrient concentrations is similar to the amount of variation in discharge while there is much less

variation in geogenic solute concentrations compared to variation in discharge, indicating major ions are chemostatic or near-chemostatic while nutrients and trace elements are chemodynamic or near chemodynamic. This interpretation is not always a good determinate of C - Q behavior. For example, Ca^{2+} and Mg^{2+} have CV_C/CV_Q values that are less than 1 even when the b -coefficients are relatively small ($-0.2 < b < -0.6$), but both have high R^2 values indicating a strong C - Q power-law relationship (Figure 3.7). Additionally, Ca^{2+} , Mg^{2+} , and Na^+ are often conservative, indicating that changes in concentrations (b -coefficients) are a product of mixing between contributing endmembers even when b is less than 1 (Liu et al., 2004; Liu et al., 2020; Sebestyen et al., 2008). Meanwhile, major nutrients had lower median R^2 values compared to major ions (major nutrients R^2 : 0.1 – 0.27; major ions R^2 : 0.36 – 0.52) and are not conservative but have other processes controlling concentrations. Thus, although the CV_C/CV_Q values for nutrients were close to 1, CV_C/CV_Q values are not an accurate indicator of how concentration and discharge are coupled since the observed variation in concentrations could match that of discharge but due to other active processes independent of discharge. However, comparing CV_C/CV_Q values could be useful in identifying locations or moments where or when there is variable solute export.

3.6.2 Importance of Snow Abundance on Hydrologic Processes

The role of snowmelt on solute transport and generation is particularly relevant as studies observe decreasing snowpack and extent with earlier snowmelt (Derksen & Brown, 2012; Dyer & Mote, 2006; Hidalgo et al., 2009). Snow abundance and baseflow index were correlated with R^2 , indicating increasing snow abundance deteriorates the C - Q relationships for biogenic solutes while enhancing those of SC. This deteriorating effect may be due to the conservative nature of geogenic solutes compared to the non-conservative behavior of nutrients and trace elements. Conservative transport of major ions creates a clean, less complicated relationship between solute transport and discharge since there are fewer processes modifying solute availability and transport. Nutrients and trace elements, however, do not behave conservatively and transport is modified by additional

processes (ie, colloidal formation and transport, biotic uptake, and microbial transformations), which deteriorate the C - Q relationship. Additionally, nutrients and trace elements may have variable solute stores throughout the catchment or limited solute sources that deplete or become hydrologically connected during the snowmelt event. If changes in solute concentrations are uncoupled with changes in stream discharge, this would deteriorate the C - Q relationships for those solutes. An example would be if a solute begins a storm or melt event with enrichment but as the event progresses becomes depleted and cannot match the initial response, changing export patterns mid-event and weakening R^2 .

Snow abundance and baseflow index had similar effects on solute export. Both were positively correlated with the b -coefficient of major ions and Si (Figure 3.8b). Snowpack releases large amounts of meltwater during spring snowmelt and, as that new water flows through the subsurface, it accumulates solutes from chemical weathering reactions. This release of new water that is low in ionic concentrations strongly dilutes concentrations of major ions and Si that are highest in groundwater, leading to more negative b -coefficients for geogenic solutes in areas with high snow abundance. Under future conditions when there is less snow precipitation but continued snow cover, one can expect less dilution of major ions and subsequently higher b -coefficients since there is less new water released during snowmelt. However, less snowmelt accompanied by freezing conditions can create deeper ground frost which can impede infiltration and result in more runoff (Shanley et al., 2002). Thus, there is uncertainty in how hydrologic processes and solute export will respond to climate change with the predicted responses dependent on winter temperatures.

3.6.3 Land-Use Impacts on Solute Transport and Hydrologic Flowpaths

3.6.3.1 Prevalent Transport Dynamics in Forested Catchments

Comparing C - Q behavior of solutes located in deep flowpaths to those in shallow flowpaths reveals how flowpaths and solute availability change with land-use. C - Q behavior measured in forested areas should represent natural solute export processes since the critical zone in forested areas remains more intact compared to other land-uses. This study found forested catchments had SC - Q relationships with higher R^2 values while the R^2 from relationships with SO_4^{2-} and NH_4^+ were negatively correlated to forested area (Figure 3.8). Additionally, catchments with more forested area had stronger dilution of SC , Ca^{2+} , and Mg^{2+} and increased enrichment of P (Figure 3.8). In forested systems, shallow subsurface are extremely formative in stream water chemistry, creating rapid dilution of base cations and less dilution or greater enrichment of solutes primarily found in shallow flowpaths such as P (Hung et al., 2018). Stronger SC - Q patterns are likely due to SC predominately measuring Ca^{2+} , Mg^{2+} , and Na^+ concentrations which often behave conservatively and have strong C - Q relationships. Meanwhile, SO_4^{2-} and NH_4^+ are influenced by plant and microbial uptake whose influence would be greatest in forested areas where solute source pools are limited and demand is high (Hofmeister et al., 2019; Moater et al., 2017). These biological processes would contribute to decreasing C - Q R^2 values.

Unlike C - Q patterns often observed in urban and agriculture areas, C - Q patterns for nutrients can be diluted in forested catchments as seen in a study on C - Q patterns of a headwater stream in northern Michigan (Hofmeister et al., 2019). Hofmeister et al. (2019) observed dilution C - Q patterns for NO_3^- , PO_4^{3-} , and SO_4^{2-} which they attributed to restricted solute availability by biological activity and large inputs of snowmelt and precipitation diluting concentrations. Thus, transport from uplands may be supply limited. During events, the subsurface flow low in NO_3^- dilutes the higher NO_3^- stream concentrations, creating the observed dilution pattern. The spatial distribution of NO_3^- b -coefficients

throughout the GLB also supports this idea of limited NO_3^- with frequent NO_3^- - Q dilution or chemostatic behavior in the northern basin where catchments are forested. However, nearly 80% of the studied catchments measuring NO_3^- showed enrichment, indicating that NO_3^- is no longer source limited in most areas in the GLB.

3.6.3.2 *Prevalent Transport Dynamics in Urbanized Catchments*

Catchments with more urbanized area had weaker C - Q relationships for major ions (SC , Ca^{2+} , and Mg^{2+}), indicating a decoupling of normally strong C - Q relationships (Figure 3.8a; Figure 3.9). Urban area was positively correlated to the b -coefficients of SC , Ca^{2+} , and Mg^{2+} leading to more chemostatic patterns. In 2005, researchers at the University of Wisconsin Milwaukee studied stormwater pollutant concentrations and loadings in the Milwaukee Metropolitan Sewage District, (including five USGS sites: 4087000, 4087142, 4087170, 40869416, and 40871488). They found that stormwater had high concentrations of Ca^{2+} and Mg^{2+} from soil erosion, which would push C - Q relationships toward chemostasis in urban areas (University of Milwaukee, 2005). They also found that total Kjeldahl nitrogen (TKN) and total suspended solids exceeded the EPA standards and attributed these high concentrations to runoff of fertilizer applied on crops and lawns. Runoff can inconsistently transport pollutants, fertilizers, or roads salts and decouple changes in concentrations with discharge, especially if these additions are only present during specific events or seasons. Old, leaking sewage pipes above or within the water table are other potential factors that deteriorate the R^2 values of Na^+ and Cl^- as they contaminate groundwater (Rose, Karwan, & Godsey, 2018). Additional factors complicating C - Q relationships involve rerouting groundwater water and disruption of geochemical weathering from impervious surfaces.

3.6.3.3 *Prevalent Transport Dynamics in Areas with Agriculture*

Many nutrients and trace elements had C - Q relationships with higher R^2 values in catchments with cropland. A key factor controlling the strength of the C - Q relationship is the contrast of solute concentrations between the contributing endmembers, with higher

contrasting concentrations creating stronger C - Q relationships (Chen et al. 2020; Herndon et al. 2015). Fertilizer application on cropland elevates nutrient solute concentrations in surface soils, creating solute rich dominant shallow flowpaths and extenuating distinction in solute concentration between endmembers. This distinction between endmember concentrations simultaneously increase the C - Q R^2 value and $|b|$ coefficient when those endmembers mix during events.

Catchments with more cropland also had stronger enrichment for NO_3^- with over 75% of the study sites exhibiting enrichment, but cropland is accompanied by more chemostatic relations for SC, Ca^{2+} , and Mg^{2+} (Figure 3.5, Figure 3.8b; Figure 3.10). Rapid flushing of NO_3^- rich shallow near-stream groundwater or soil water create stronger enrichment behavior (Bowes et al., 2015; Chen, Wu, & Hong, 2012; Jaing et al, 2010; Outram, Cooper, Sunnenberg, Hiscock, & Lovett, 2016). Flushing is enhanced when groundwater tables rise into nutrient-rich soil layers and mobilize solutes into nearby streams along natural flowpaths or subsurface tile drainage (Williams et al., 2018). Tile drainage is a common agricultural practice in the Midwest with 20.6 million hectares of land drained by surface and subsurface tile drainage networks in the states creating the Great Lakes Basin (Fausey, Brown, Belcher, & Kanwar, 1995). Jiang, Frankenberger, Bowling, & Sun (2014) studied nitrate export from catchments near Lake Erie dominated by agriculture (including USGS site: 4193500). They found nitrate generally increased and the enrichment was especially clear in areas with tile drainage, supporting the findings of Williams et al. (2018) who found that larger drainage networks created higher solute concentrations. Antecedent conditions also control the magnitude of NO_3^- export with more export occurring when groundwater levels are already high and soil is saturated, allowing for faster and more contributions from shallow soils (Outram et al., 2016). Tile drainage can delay the response of the groundwater table and transport which might complicate the hydrologic response of SC, Ca^{2+} , Mg^{2+} , and Si and create the observed chemostatic behaviors. Nitrification of nitrogen fertilizers can create nitric acid (HNO_3) which accelerates chemical weathering and raise concentrations of SC, Ca^{2+} , Mg^{2+} , and Si in

shallow soils and decreasing the disparity between solute concentrations in shallow flowpaths compared to deeper ones.

3.6.3.4 Nutrient Export and Water Quality Concerns

Nutrient export is a pressing water quality issue especially in the Great Lakes Basin as export characteristics are rapidly changing due to intensified agriculture and fossil fuel combustion more than doubling the amount of reactive nitrogen in the environment (Gruber & Galloway, 2008) and quadrupling phosphorus loading (Elser & Bennett, 2011). Most sites in the GLB with NO_3^- values had enrichment patterns, indicating that most of NO_3^- was flushed from shallow soil water, which contrasted the dilution patterns in the northern basin that indicate source limited conditions (Basu et al., 2010; Hofmeister et al., 2019; Salmon, Walter, Hedin, & Brown, 2001; Thomas, Abbott, Troccaz, Baudry, & Pinay, 2016). The predominant enrichment pattern for NO_3^- across the GLB indicates that surface soil water contains high NO_3^- concentrations in legacy stores that are enhanced by N atmospheric deposition and fertilizer application. However, there were three catchments with dilution patterns in highly urbanized or agricultural areas (USGS: 04161820, 04208000, 04149000) with high R^2 values ($R^2 = 0.48 - 0.58$), which could be indicative of NO_3^- contaminated groundwater steadily supplying concentrations of NO_3^- during low flows and diluting during high flow.

Groundwater contamination is particularly concerning since the Great Lakes are partially fed by groundwater and susceptible to contamination, especially Lake Erie which is surrounded by the most contaminant-prone land with a high percentage of agriculture and urban area compared to the other four Great Lakes (Culbertson, Martin, Aloysuis, Ludsins, 2016). Bowes et al. (2015) observed NO_3^- diluting in a rural catchment in Southern England and determined the primary cause for dilution was that the river received the majority of NO_3^- input from groundwater. Knights et al. (2017) also observed particularly high concentrations in nitrate at Cedar Point, a peninsula in northern Ohio into Lake Erie. It was difficult to determine how much NO_3^- from groundwater discharged into the lake since concentrations were lower in the lakebed porewater, but the decrease could have been

from mixing between groundwater and lake water and/or denitrification (Knights et al., 2017). The three observed flushing patterns in the GLB could be a sign of the growing issue of NO_3^- groundwater contamination that will become increasingly important if left unaddressed and nitrogen fertilizers are continually applied.

Groundwater contamination is not the only future concern and high stream nutrient loading is a continued threat despite recent decreases as loads are predicted to increase due to increased precipitation and stream discharge under future warming scenarios (Culbertson et al., 2016). If fertilizer application does not remain the same and instead matches increased P plant uptake, then TP loading will increase under both climate change scenarios and exacerbate eutrophication (Culbertson et al., 2016). These pressing issues highlight the importance of studying $C-Q$ patterns, especially since controlling factors are changing so rapidly through land-use and climate changes.

3.7 CONCLUSION

The relationships between environmental and physical catchment characteristics and solute export behavior were investigated using concentration-discharge analysis and Spearman's Rank Order Correlation Analysis. Results indicate that the long-term export patterns of Mg, Na, Cl, SO_4^{2-} , P, NH_4^+ , Al, Fe, and Sr are relatively consistent across the Great Lakes Basin despite changes in land-use and precipitation patterns. CV_C/CV_Q values do not accurately summarize the concentration-discharge pattern and can under-represent endmember mixing, resulting in misclassifying solute export as chemostatic rather than chemodynamic. Among the studied environmental factors, snow abundance, potentially through greater snowmelt, increased the dilution of solutes and strengthened the concentration-discharge power-law relationship. Fertilizer additions and rapid subsurface flow increased the b -coefficients from certain solutes and increased the power-law relationship by exaggerating the gradient of solute concentrations throughout the soil profile. Urbanization circumvents shallow flowpaths increasing some major ions b -coefficients and deteriorating the concentration-discharge relationship by decoupling the response in concentration to discharge through inconstant additions and flowpaths. The

observed impacts of cropland and urbanization on solute concentrations might change with the proximity of the cropland to the sampling location, with more prominent effects when the cropland and urban areas are close to the sampling location. This could be an interesting research question for future studies and would provide useful information for land managers prescribing best management practices. Lastly, forested areas have strong dilution of major ions and less negative or positive b -coefficients for NO_3^- and P. These results indicate that snow abundance and land-use are key factors influencing concentration-discharge patterns and that certain patterns can be expected in those environments, which permits characterization of solute export patterns across similar catchments.

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3.9 TABLES AND FIGURES

3.9.1 Tables

Table 3.1. Mean values of multi-annual C - Q relationships by solute

Species	Sig/Total	Mean R^2 (sd)	Mean b (sd)	Mean CV_C/CV_Q (sd)
SC (us)	95/98	0.44 (0.28)	-0.15 (0.13)	0.21 (0.11)
Ca ²⁺ (mg L ⁻¹)	55/65	0.36 (0.26)	-0.15 (0.11)	0.18 (0.08)
Mg ²⁺ (mg L ⁻¹)	59/65	0.53 (0.23)	-0.19 (0.08)	0.19 (0.07)
Na ⁺ (mg L ⁻¹)	48/59	0.52 (0.23)	-0.28 (0.17)	0.37 (0.22)
K ⁺ (mg L ⁻¹)	27/57	0.22 (0.14)	-0.04 (0.18)	0.42 (0.66)
Cl ⁻ (mg L ⁻¹)	55/64	0.32 (0.20)	-0.23 (0.26)	0.46 (0.57)
NO ₃ ⁻ (mg L ⁻¹)	32/48	0.27 (0.19)	0.31 (0.54)	0.71 (0.63)
NH ₄ ⁺ (mg L ⁻¹)	15/40	0.10 (0.07)	0.21 (0.20)	1.09 (0.36)
NO ₂ ⁻ (mg L ⁻¹)	24/57	0.18 (0.10)	0.15 (0.33)	0.91 (0.44)
P (mg L ⁻¹)	44/65	0.24 (0.20)	0.32 (0.24)	0.80 (0.34)
SO ₄ ²⁻ (mg L ⁻¹)	51/57	0.32 (0.22)	-0.19 (0.11)	0.31 (0.17)
Si (mg L ⁻¹)	26/38	0.18 (0.12)	0.06 (0.34)	0.41 (0.26)
Sr (μg L ⁻¹)	36/42	0.59 (0.28)	-0.27 (0.13)	0.41 (0.55)
Al (μg L ⁻¹)	27/45	0.40 (0.20)	0.54 (0.25)	1.23 (1.41)
Fe (μg L ⁻¹)	34/53	0.27 (0.22)	1.11 (2.92)	2.27 (3.63)
Mn (μg L ⁻¹)	24/53	0.19 (0.20)	0.18 (0.81)	1.47 (1.49)

3.9.2 Figures

Figure 3.1. Map showing study catchments throughout the US portion of the Great Lakes Basin.

Diagnosis of Hydrologic & Biogeochemical Characteristics Using C-Q Power-Law

Figure 3.2. A flow chart used for diagnosing catchment hydrologic and biogeochemical characteristics/behaviors based on Concentration-Discharge (C-Q) relationships. Note that some behaviors may exist at various power-law strengths (those crossing the dashed boxes).

Figure 3.3. Distribution of catchment characteristics among the 138 study sites with the dashed vertical line indicating the median value.

Figure 3.4. Frequency of R^2 values from the significant ($p < 0.05$) multi-annual $C-Q$ relationships created for 16 solutes. The vertical dashed line indicates the median of the R^2 values

Figure 3.5. Prevalence of dilution, chemostatic, and enrichment C - Q patterns among the sites with significant ($p < 0.05$) multi-annual power-law relationships for 16 solutes.

Figure 3.6. Frequency of b -coefficients from the significant ($p < 0.05$) multi-annual C - Q relationships created for 16 solutes. The vertical dashed line indicates the median while the shaded red area indicated the chemostatic range ($b \leq \pm 0.1$).

Figure 3.7. Relationship between $C-Q$ $|b|$ -coefficients and CV_c/CV_q from the significant ($p < 0.05$) multi-annual $C-Q$ relationships for 16 analytes

Figure 3.8. ρ from Spearman Rank Correlation Analysis for significant relationships ($p < 0.05$) between the R^2 and b -coefficients from the C - Q relationships and catchment characteristics among SC and the 15 solutes. (a) illustrates the correlations between the catchment characteristics and the R^2 values from all significant C - Q relationships. (b) illustrates the correlations between the catchment characteristics and the b -coefficients from all significant C - Q relationships. Blue indicates positive correlation while green indicates negative correlation. Note that the results of solutes that do not have a significant relationship with any factors were not shown.

Figure 3.9. Spatial distribution of *SC-Q* *b*-coefficients and R^2 values with SWE (a) and land cover (b) on background.

Figure 3.10. Spatial distribution of NO_3^- - Q b -coefficients and R^2 values with SWE (a) and land cover (b) on background.

3.10 APPENDIX 3.A: SUPPLEMENTAL TABLES

Supplemental Table 3.A.1. Site locations for the 138 locations used for this study. * indicates that the site measured water chemistry parameters and not specific conductance. ** indicates that the site measured specific conductance and additional water chemistry parameters. Sites without a * are sites that only measures specific conductance and stream discharge.

Site No	Site ID	STATES	Latitude	Longitude	Elevation (ft)
4014500**	USGS-04014500**	MN	47.33742	-91.20072	755
4015475	USGS-04015475	MN	47.527146	-92.12267	1483
4024000**	USGS-04024000**	MN	46.70328	-92.4188	1158
4024090	USGS-04024090	MN	46.517444	-92.48214	984
4024093	USGS-04024093	MN	46.5155	-92.46269	928
4024430*	USGS-04024430*	WI	46.63333	-92.09389	659
4026561	USGS-04026561	WI	46.394722	-90.59	1266
4027000**	USGS-04027000**	WI	46.48661	-90.6963	735
4040000**	USGS-04040000**	MI	46.720774	-89.20709	856
4043097	USGS-04043097	MI	46.734655	-88.44319	702
4043126	USGS-04043126	MI	46.721043	-88.33013	1401
4043140	USGS-04043140	MI	46.751043	-88.3618	1004
4043150	USGS-04043150	MI	46.804097	-88.31707	797
4043238	USGS-04043238	MI	46.782222	-87.8775	1106
4043244	USGS-04043244	MI	46.785759	-87.85235	1033
4043275	USGS-04043275	MI	46.713539	-87.84069	1532
4044724*	21MICH-030077*	MI	46.34078	-86.85015	853
4045500*	USGS-04045500*	MI	46.574583	-85.26964	748
4059000**	USGS-04059000**	MI	45.908917	-87.21353	801
4059500**	USGS-04059500**	MI	45.754967	-87.20208	702
4063700**	USGS-04063700**	WI	45.76361	-88.46361	1460
4067500**	USGS-04067500**	MI,WI	45.32583	-87.66333	666
4072150**	USGS-04072150**	WI	44.53339	-88.12969	659
4074538*	SOKAOGON_WQX-SC2@55*	WI	45.4883	-88.96372	1572
4074548*	SOKAOGON_WQX-SC3@M*	WI	45.47941	-88.99789	1575
4080798	USGS-04080798	WI	44.524444	-89.33778	1112
4081000	USGS-04081000	WI	44.329167	-88.99583	804
4085108	USGS-04085108	WI	44.371944	-88.09222	656
4085427**	USGS-04085427**	WI	44.10617	-87.71603	676
4085813	USGS-04085813	WI	43.63833	-87.89842	840
4085845	USGS-04085845	WI	43.696662	-87.82092	715
4086149	USGS-04086149	WI	43.527219	-88.22232	961
4086200	USGS-04086200	WI	43.550274	-88.18843	961
4086265	USGS-04086265	WI	43.425	-88.08093	886
4086340	USGS-04086340	WI	43.482776	-88.06093	853
4086360	USGS-04086360	WI	43.472777	-87.98981	860
4086500	USGS-04086500	WI	43.323056	-87.97861	853
4086600*	WI_MMDS-RI-01S*	WI	43.28028	-87.9425	725

4087000**	WI_MMSD-RI-04S & USGS-04087000**	WI	43.10001	-87.90897	679
4087030	USGS-04087030	WI	43.172778	-88.10389	781
4087050	USGS-04087050	WI	43.206674	-88.03842	758
4087070	USGS-04087070	WI	43.123611	-88.04361	738
4087088	USGS-04087088	WI	43.054722	-88.04611	741
4087119	USGS-04087119	WI	43.043833	-88.00511	696
4087120	USGS-04087120**	WI	43.04556	-87.99972	696
4087142**	WI_MMSD-RI-11M & USGS-04087142**	WI	43.0339	-87.93425	627
4087170	USGS-04087170	WI	43.024444	-87.89833	627
4087204**	WI_MMSD-OC-05S & USGS-04087204**	WI	42.925	-87.87	673
4087214*	WI_MMSD-RR-04S*	WI	42.945	-88.01417	778
4087220*	WI_MMSD-RR-05S*	WI	42.87361	-87.99583	725
4087233	USGS-04087233	WI	42.815556	-87.99472	728
4087240	USGS-04087240	WI	42.751389	-87.82361	682
4087242	USGS-04087242	WI	42.733909	-87.78452	620
4092750**	INSTOR_WQX-1899 & USGS-04092750**	IL,IN	41.649202	-87.46865	587
4095090**	INSTOR_WQX-1918 & USGS-04095090**	IN	41.622259	-87.17587	600
4095300*	INSTOR_WQX-1924*	IN	41.716707	-86.85975	620
4099000*	USGS-04099000*	IN,MI	41.800883	-85.7561	784
4101500**	USGS-04101500**	MI	41.829214	-86.25973	702
4107850	USGS-04107850	MI	42.482256	-85.79836	728
4108500*	USGS-04108500*	MI	42.593641	-85.9842	650
4108660**	21MICH_WQX-030077 & USGS-04108660**	MI	42.65086	-86.1067	705
4116000*	USGS-04116000*	MI	42.971977	-85.06917	745
4119400	USGS-04119400	MI	43.024188	-86.02644	610
4121650	USGS-04121650	MI	43.693634	-85.46754	948
4121970	USGS-04121970	MI	43.434746	-85.66532	860
4122500*	USGS-04122500*	MI	43.945006	-86.27869	686
4126802	USGS-04126802	MI	44.903329	-85.96231	689
4126970	USGS-04126970	MI	44.65667	-85.43673	892
4135000*	USGS-04135000*	MI	45.093901	-83.49998	653
4137500**	21MICH-350061 & USGS- 04137500**	MI	44.4364	-83.43386	636
4142000**	USGS-04142000**	MI	44.07252	-84.01999	741
4144032	USGS-04144032	MI	42.881698	-83.98468	833
4145000*	USGS-04145000*	MI	43.254748	-84.10553	600
4149000*	USGS-04149000*	MI	43.308359	-83.95358	591
4157005	USGS-04157005	MI	43.42197	-83.95192	597
4159492	USGS-04159492	MI	43.15086	-82.62465	728
4160398	USGS-04160398	MI	42.858642	-82.53797	623
4160625	USGS-04160625	MI	42.768366	-82.51214	584
4160800	USGS-04160800	MI	42.720031	-83.35355	994
4160900	USGS-04160900	MI	42.660309	-83.39022	961
4161000	USGS-04161000	MI	42.633366	-83.22438	856
4161540	USGS-04161540	MI	42.688366	-83.14299	823
4161820**	USGS-04161820**	MI	42.614478	-83.02659	643
4163030	USGS-04163030	MI	42.537813	-83.00576	610

4164000	USGS-04164000	MI	42.577812	-82.95159	600
4164980	USGS-04164980	MI	42.642811	-82.93326	594
4165500	USGS-04165500	MI	42.59587	-82.90881	600
4165557	USGS-04165557	MI	42.561424	-82.8452	574
4165559**	21MICH-500233 & USGS-04165559**	MI	42.596423	-82.82603	581
4166100	USGS-04166100	MI	42.447536	-83.29743	656
4166500	USGS-04166500	MI	42.373092	-83.25465	617
4167150	USGS-04167150	MI	42.330593	-83.24798	610
4168400	USGS-04168400	MI	42.308371	-83.25271	607
4170000	USGS-04170000	MI	42.578921	-83.62661	958
4174500	USGS-04174500	MI	42.286982	-83.73383	860
4174518	USGS-04174518	MI	42.264761	-83.68827	833
4176500**	USGS-04176500**	MI	41.9606	-83.53105	633
4178000*	21OHIO_WQX-510220*	IN,OH	41.38561	-84.80163	830
4183038	USGS-04183038	IN	41.183083	-84.86969	738
4183500	USGS-04183500	IN,OH	41.198939	-84.7444	725
4184500*	21OHIO_WQX-500330*	MI,OH	41.6595	-84.24911	728
4185000*	21OHIO_WQX-300020*	OH	41.5045	-84.42967	712
4186500*	USGS-04186500*	OH	40.94866	-84.26606	732
4188496	USGS-04188496	OH	40.97922	-83.65327	801
4189000*	21OHIO_WQX-500040*	OH	41.05589	-83.68799	778
4193500*	USGS-04193500*	OH	41.50005	-83.71271	640
4195820*	21OHIO_WQX-S02P08*	OH	41.49116	-83.22465	594
4196500*	21OHIO_WQX-500860*	OH	40.85061	-83.25631	843
4196800*	21OHIO_WQX-500850*	OH	40.92283	-83.34881	804
4197100*	21OHIO_WQX-U03S02*	OH	41.02228	-83.10964	833
4198000*	USGS-04198000*	OH	41.30783	-83.15881	656
4199000**	21OHIO_WQX-501030 & USGS-04199000**	OH	41.30089	-82.60823	643
4199155*	21OHIO_WQX-K01G31*	OH	41.34838	-82.51378	666
4199500**	21OHIO_WQX-501260 & USGS-04199500**	OH	41.38199	-82.31683	712
4200500	USGS-04200500	OH	41.380324	-82.10459	719
4208000**	USGS-04208000**	OH	41.39533	-81.62985	732
4212100	USGS-04212100	OH	41.718934	-81.22788	686
4213152	USGS-04213152	PA	42.073889	-80.23472	577
4213500**	USGS-04213500**	NY	42.46333	-78.93417	948
4214500*	USGS-04214500*	NY	42.85472	-78.755	620
4216000	21NYDECA-01031002	NY	42.87778	-78.91639	571
4217000*	USGS-04217000*	NY	42.9975	-78.18861	899
4226000	USGS-04226000	NY	42.682472	-77.82869	728
4231600	USGS-04231600	NY	43.141722	-77.61631	541
4232040*	USGS-04232040*	NY	43.05417	-77.49083	518
4232046*	USGS-04232046*	NY	43.10611	-77.46194	459
4232047*	USGS-04232047*	NY	43.12111	-77.47639	459
4232050*	USGS-04232050*	NY	43.12803	-77.527	446
4249000**	USGS-04249000**	NY	43.45167	-76.50528	302
4250750*	USGS-04250750*	NY	43.81333	-76.07472	545
4260500*	USGS-04260500*	NY	43.98556	-75.92472	423
4263000*	USGS-04263000*	NY	44.59944	-75.37889	315
4268000*	USGS-04268000*	NY	44.83889	-74.97889	269
40851325	USGS-040851325	WI	44.501111	-87.93611	663

40851385	USGS-040851385	WI	44.528611	-88.01	584
40869416	USGS-040869416	WI	43.097222	-87.96722	676
40871488	USGS-040871488	WI	42.989722	-87.95194	663
41482663	USGS-041482663	MI	42.941944	-83.84611	784

Supplemental Table 3.A.2. The order of the 7 sets of nested catchments that were split from the respected HUC 8 watersheds

Nested order	Site No	Site ID	State	Latitude	Longitude	Elevation (ft)
1	4024090	USGS-04024090	MN	46.51744	-92.48214	984
2	4024093	USGS-04024093	MN	46.5155	-92.46269	928
1	4043140	USGS-04043140	MI	46.75104	-88.3618	1004
2	4043150	USGS-04043150	MI	46.8041	-88.31707	797
1	4087000**	WI_MMSD-RI-04S & USGS-04087000**	WI	43.10001	-87.90897	679
2	4087170	USGS-04087170	WI	43.02444	-87.89833	627
1	4087050	USGS-04087050	WI	43.20667	-88.03842	758
2	4087070	USGS-04087070	WI	43.12361	-88.04361	738
1	4087119	USGS-04087119	WI	43.04383	-88.00511	696
2	4087120	USGS-04087120**	WI	43.04556	-87.99972	696
3	4087142**	WI_MMSD-RI-11M & USGS-04087142**	WI	43.0339	-87.93425	627
1	4087240	USGS-04087240	WI	42.75139	-87.82361	682
2	4087242	USGS-04087242	WI	42.73391	-87.78452	620
1	4161820**	USGS-04161820**	MI	42.61448	-83.02659	643
2	4164000	USGS-04164000	MI	42.57781	-82.95159	600
3	4165500	USGS-04165500	MI	42.59587	-82.90881	600
4	4165559**	21MICH-500233 & USGS-04165559**	MI	42.59642	-82.82603	581

4 Conclusion

Concentration-Discharge analysis continues to be a promising analytical method to understand and monitor solute export processes. These studies illustrated some of the hydrogeochemical and hydrological controls on multi-annual and annual concentration-discharge patterns within Northeastern and North Midwestern United States and throughout catchments with different land-covers.

In combination with End-Member Mixing Analysis, concentration-discharge analysis yielded more confident and detailed results at the Sleepers Watershed (Chapter 2). A key factor that controlled the concentration-discharge b -coefficient was vertical solute concentrations throughout the soil profile and consequently the contributing end-members. The change in concentration with depth determined whether the coefficient would be positive or negative with a decrease in depth creating the former and an increase with depth creating the latter. Conservative solute transport was determined pivotal in creating consistent annual concentration-discharge patterns. The end-member contributions changed over seasons with larger fractions flowing from subsurface runoff during the snowmelt period, creating larger $|b|$ -coefficients. The results indicate that with decreasing snow abundance this flushing period will become shorter and likely lower the amount of dilution or enrichment occurring.

The sites in the Great Lakes Basin offered valuable insight into catchment scale changes in hydrologic inputs and processes over times, such as, solute availability and dominant hydrological pathways (Chapter 3). Most solutes displayed significant ($p < 0.05$) chemodynamic behavior, indicating that stream discharge is a significant driving factor in controlling stream chemistry. Snow abundance also had a positive correlation with concentration-discharge strength of SC but a negative correlation with nutrients and trace elements, forecasting weaker concentration-discharge relationships for major ions under future climate conditions. Land-use, especially cropland and urbanization, is correlated with concentration-discharge strength and direction and intensity of solute export, related to fertilizer additions and drainage networks facilitating rapid subsurface flow. A major

finding was that urbanization deteriorates the concentration-discharge relationship, likely due to anthropogenic solute additions and disruption of natural flowpaths, decoupling the concentration response from change in discharge.

The low frequency sampling resolution of the data used to study change in stream water chemistry in the Great Lakes Basin presents some limitations to the interpretation of the study results by limiting the interpretation to general long-term patterns (Chapter 3). The results exclude many of the likely present temporal variations in stream chemistry, and the observed trends should be viewed as overall patterns in stream water chemistry. The impact of land-use was studied using the percent of watershed area without considering proximity to the sampling location. Future related research could investigate how proximity of cropland, urban areas, or forested areas to the sampling locations controls the impact those land-cover types have on stream concentrations. Another potential future study could investigate if there are thresholds that, once crossed, the studied land-uses have a significantly stronger impact on stream chemistry. These future studies could provide valuable information for sustainable development and land-use that minimizes the negative effects of necessary structures and practices.

Results from these studies improve our understanding of current hydrologic processes relating to streamflow generation and solute export while highlighting this importance of solute vertical distribution and land-use. Climate scientists predict an average rise of 1.5 to 4.5°C globally accompanied with changes in seasonal distribution, intensity, and duration of precipitation (Mortsch & Quinn, 1996; D'Orgeville et al., 2014). High temperature changes in winter will affect freeze thaw frequencies, ice formation, and the heat balance of water bodies (D'Orgeville et al., 2014; Mortsch & Quinn, 1996). These changes will modify biogeochemical and biotic processes, impacting solute availability, and negatively impact the concentration-discharge behaviors positively associated with snow abundance. Additionally, streamflow at higher latitudes is expected to increase by 10-40% over the next 100 years, which could lead to a proportional increase in solute loadings while maintaining similar concentrations in streams with chemostatic behavior (IPCC, Core Writing Team, 2007). By better understanding current hydrologic and biogeochemical

processes and how these are modified by existing climate and land-use change, scientists and land managers can predict how ecosystems might change under further modified conditions.

4.1 REFERENCES

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