HYDROLOGICAL AND FLOODING EFFECTS ON STREAM NUTRIENT LEVELS

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Abstract

Hydrological and Flooding Effects on Stream Nutrient Levels

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Stream solutes are strongly linked to hydrology, and as such, we sought to better understand how hydrology, particularly flooding, influences nitrogen (N) and phosphorus (P) levels. We used a long-term dataset of monthly water quality samples for many Ontario, Canada, catchments to assess the effects of landscape variables, such as land use and physiography, on the export of nutrients during floods, and to characterize overall concentration-discharge patterns. In general, we found that landscape variables could partially explain the export variation in flood waters, but that the importance of specific variables depended on flood characteristics. We also found that overall concentration-discharge relationships for N and P C were positive, but non-linear, with greater concentrations on the rising limb of the hydrograph depending on the nutrient. With these results, we have identified general patterns between nutrients and hydrology, which will be helpful for managing the ecological effects of flooding.

Keywords: flooding, discharge, nutrients, export, land use, topography, C-Q relationships, threshold, hydrograph limb, watershed management

Preface

This thesis is presented in manuscript format, with Chapters 1 and 4 providing a general introduction and conclusion regarding the studies in Chapter 2 and 3, which are being prepared also for publication. Throughout this document, I have used the subject pronoun "we" to acknowledge the contribution of my co-authors.

Chapter 2

D'Amario SC, Metcalfe RA, Xenopoulos MA. 2018. The influence of land cover and landscape variables on the relationships between nutrient export and the magnitude, volume, and duration of floods.

Chapter 3

D'Amario SC, Wilson HF, Metcalfe RA, Xenopoulos MA. 2018. Event-controlled nutrient transport using concentration-discharge relationships.

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And lastly, I'd like to dedicate this thesis to my late grandfathers, Harry Veldhuis for encouraging my curiosity early on in my life, and Alfredo D'Amario, who showed me the value of family and what can be achieved through hard work.

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1.0 General Introduction

Flooding is an important process for aquatic systems as it delivers allochthonous nutrients to streams, which are then carried downstream to lakes and coastal areas, fueling biological processes. Flooding, which occurs as a result of either snowmelt or rain storms in Canada, tends to follow certain patterns, typically with a large pulse in the spring as snow melts, with interspersed storms throughout the year. However, with climate change, it appears that this pattern has been changing. Burn and Whitfield (2016) have noted an increase in frequency and duration in natural catchments in Canada that are affected by both snowmelt and rain, and this and other studies have indicated a trend in warming winters, leading to winter rain-on-snow events and less flooding from snowmelt in the spring (Stewart et al. 2005; Knowles et al. 2006; Berton et al. 2016). This change in hydrologic pattern can have large impacts on nutrient dynamics, changing the timing and intensity of the transport of these solutes. For example, Casson et al. (2012) have reported that winter warming and rain-on-snow events contributed more nitrate to streams in winter months than in previous years, and that this also led to a decline in spring loads. With these hydrologic and solute changes, it is important to understand how nutrients respond to streamflow and flooding.

Regular monitoring of stream water quality can be used to assess how solutes respond to changes in discharge. Ontario's Conservation Authorities generally collect monthly data on select streams, and while more frequent measurements are desirable to examine the response of specific streams to individual flooding events, this lower-resolution data can be used to identify broader patterns and make inferences about the importance of landscape characteristics. Ontario established the Provincial (Stream)

Water Quality Monitoring Network in 1964 (Ministry of the Environment and Climate Change 2015), and while the monitored sites have changed throughout the years, many sites have a significant amount of data from long-term monthly sampling. Using these long-term data, we had two main objectives: 1) to model nutrient export during floods in order to examine the effects of landscape variables on export depending on the magnitude, duration, and volume of a flooding event; and 2) to characterize overall relationships between nutrient concentrations and stream discharge on both rising and falling hydrograph limbs.

Regarding the first objective; a large proportion of nutrient (phosphorus and nitrogen) export occurs during flooding events (e.g., Royer et al. 2006; Banner et al. 2009), and it is therefore important to understand what factors affect the degree to which nutrient export increases with flooding. But floods display a variety of hydrological characteristics, with different durations, magnitudes, and discharge volumes, all of which may interact with the landscape in different ways to influence nutrient export. We expected that the degree to which nutrient export increased with flood duration, magnitude, and discharge volume could be at least partially explained by catchment land cover, topography, and hydroclimate, and that the importance of these landscape variables would differ depending on the flood characteristics (duration, magnitude, discharge volume) being tested.

Regarding the second objective; concentration-discharge (C-Q) relationships are a commonly used tool to assess how landscape and hydroclimate characteristics influence hydrology. Most studies that examine C-Q effects have high-resolution, shorter-term data, and separate solute concentrations depending on whether they were measured on the rising or falling hydrograph limb in order to assess event-specific hysteresis effects. Using longer-term, lower-resolution data, we sought to characterize regional nutrient C-Q patterns across the province to make inferences on the processes controlling stream nutrient levels. We expected that nutrients would generally increase with discharge, and that we would see similar C-Q patterns across nutrients and seasons. We also expected that C-Q relationships would be non-linear, indicating shifts in the types of processes responsible for contributing nutrients to the stream (Moatar et al. 2017).

With both objectives, we sought to identify general patterns and relationships between hydrology and nutrients across Ontario catchments using existing data collected by Conservation Authorities for monitoring purposes. In the chapters that follow, we show that this data can be used to reach general conclusions about how hydrological processes influence nutrient concentrations and export.

2.0 The Influence of Land Cover and Landscape Variables on the Relationships between Nutrient Export and the Magnitude, Volume, and Duration of Floods

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Abstract

Flooding events in streams are complex due to variations in flood characteristics, and the responses of nutrient export to flooding are likely influenced not only by this complexity, but also by catchment topography, hydroclimate, and land use (landscape variables). Here, we linked the export of several nutrients to flood magnitude, volume, and duration. We assessed this for up to 32 rivers in Ontario, Canada by separating streamflow into small and large floods (10% and 1% seasonal discharge exceedance, respectively) using at least 10 years of data. Bayesian Information Criterion (BIC) models were used to select landscape variables that best explained the variation in nutrient export relationships with flood duration, magnitude, and volume, and model strength was determined using multiple linear regression. We found that large, steep catchments had greater total phosphorus (TP), phosphate (PO_4), and total kjeldahl nitrogen (TKN) export with increases in small flood magnitude, while nitrate (NO_3) was only greater in steep catchments. Nutrient export relationships with small flood volume and duration were only weakly explained by landscape variables, except for PO_4, which was strongly explained by many of these variables. Nutrient export relationships with large flood duration and volume tended to be weakly related to landscape variables, or not related at all, except for NO_3. Overall, the influence of landscape variables on nutrient export relationships varied depending on the hydrologic characteristics, suggesting that both the characteristics of a

flood, and the type of catchment in which it occurs, are important for understanding nutrient export during floods.

Introduction

Flooding, which we define here as those events in which discharge exceeds the 10% (Q_{10}; small flood) or 1% (Q_1; large flood) seasonal exceedance, occur naturally in temperate rivers and streams as a result of rain storms or snowmelt. Floods can be characterized by their magnitude, volume, and duration (e.g., Burn and Whitfield 2015); characteristics which can vary considerably between floods and can be defined separately to examine their effects on nutrient concentrations and export. Cumulative nutrient export typically tends to increase with discharge (e.g., Obermann et al. 2009). Even when concentrations are low, a large volume of flood water is capable of transporting a significant proportion of solute loads; indeed, the majority of annual nutrient export occurs during floods (e.g., Andersen et al. 2006; Royer et al. 2006; Banner et al. 2009). It follows that an increase in the magnitude, duration, and/or discharge volume of a flood will also result in higher nutrient export. Indeed, greater nutrient export has been observed with greater storm magnitude (Oeurng et al. 2010; Rodríguez-Blanco et al. 2013a) and with higher daily discharge volume (Outram et al. 2016); storm duration has also been reported to be an important factor (Lloyd et al. 2016). Given that climate change is altering hydrologic patterns, including increased flood frequency and duration in some Canadian catchments (Burn and Whitfield 2016), a better understanding of flood patterns (as described by magnitude, duration, and volume), and their link to nutrients, is needed. This understanding would better position us to tackle future management problems from eutrophication caused by increased nutrients (Hagy et al. 2004; McCullough et al. 2012).

The effect of landscape and climate variables on stream nitrogen (N) and phosphorus (P) has been well studied, particularly the effects of land use and land cover, which have been shown to be related to nutrient levels. For example, nutrients in agricultural and urban streams are typically elevated due to diffuse or point source pollution, respectively (e.g., Aguilera et al. 2012; Lapworth et al. 2013). There have also been many studies that emphasize the influence that hydroclimatic parameters have on N and P export (e.g., Richards et al. 2001; Kortelainen et al. 2006) due to shifts in precipitation patterns and increases in temperatures (e.g., Andersen et al. 2006; Casson et al. 2012). Differences in climatic variables between catchments, then, may at least partially explain nutrient export variability across a region.

While the effects of land use and hydroclimate on nutrient levels are well studied, the influence of topographical features is less well known. One such characteristic is catchment slope. Several studies have characterized hydrologic flow pathway dynamics on sloped land (Tsukamoto and Ohta 1988; McGuire et al. 2005; Li et al. 2006), and these pathways can influence both soil-bound and subsurface nutrient transport (Kortelainen et al. 2006). The effect of other topographical features on nutrient transport have been studied less, such as elevation and stream channel gradient.

Typically, event-based studies linking hydrology to nutrients focus on a relatively small number of streams because of the need for high-resolution data to best capture the storm hydrograph. However, this limits the ability of these studies to assess the influence of a full gradient of landscape variables. To address more fully the interaction between nutrient export and landscape variables, lower-resolution, long-term hydrological data across many sites can be employed; data that is available from monthly water quality monitoring carried out by environmental agencies. For example, Raymond and Saiers (2010) successfully examined dissolved organic carbon (DOC) export using monitoring data collected for 30 sites over as many years by the United States Geological Survey. Here, we used a similar type of dataset from Ontario's Provincial (Stream) Water Quality Monitoring Network (PWQMN; Ministry of the Environment and Climate Change 2015). The objective of this study was to examine the effect of flooding using magnitude, volume, and duration (flood characteristics) on the export of total phosphorus (TP), phosphate (PO_4), total kjeldahl nitrogen (TKN), and nitrate (NO_3) for up to 32 Ontario, Canada streams, and to assess whether landscape variables (topography, hydroclimate, and land use) could explain the variation between sites. Generally, we understand that as flood magnitude, duration, and/or volume increases, there should necessarily be an increase in nutrient export, even if concentrations are low, however the degree to which nutrients increase with flood characteristics varies between sites. We expected that topographic, hydroclimatic, and land use variables would explain a significant proportion of the variation in nutrient export relationships with flood characteristics. Discovering the catchment features that are related to greater nutrient export during floods will help to identify catchments that are more likely to see nutrient contamination with flooding, which should help to focus monitoring and mitigation efforts.

Methods

Site Selection and Landscape Variables

We sourced all water quality data from the PWQMN (Ministry of the Environment and Climate Change 2015), a database consisting of solutes measured by Ontario's 36 conservation authorities under a standard protocol (Ontario Ministry of the Environment 1983) and analyzed at a central location. Discharge data was obtained from Water Survey of Canada gauging stations (Environment and Climate Change Canada 2014). We found that water quality and stream gauging sites were not typically co-located, although they were frequently located close to one another on the same main stream channel; we therefore matched water quality sites to gauging stations by the degree to which their respective upstream catchments overlapped, such that only those that overlapped by at least 75% were retained for analysis. Water quality and gauging station catchments were delineated using the Ontario Flow Assessment Tools III (OFAT III; Ontario Ministry of Natural Resources and Forestry 2015), and the percentage of overlap determined using ArcGIS (ESRI 2016). Further, we excluded those sites with dams located between the water quality site and gauging station (dam locations were determined using the Ontario Dam Inventory; Ontario Ministry of Natural Resources and Forestry 2014). Using these criteria, we assumed that discharge at the gauging stations reflected the actual discharge dynamics at the water quality sites such that discharge could be prorated using the percentage difference between the water quality and gauging station catchment areas. We recognize that this assumption does not take into account landscape features that may be located between the water quality and gauging station sites which may alter flow patterns. For example, riparian wetlands may entrain or release nutrients depending on flow conditions. However, we felt that the use of a 75% catchment overlap would help to minimize these effects. We further reduced the dataset to only include sites which contained at least 20 years of discharge data (to facilitate the calculation of exceedance values, as discussed below) which overlapped with at least 10 years of water quality data. Only sites that contained at least 10% of sample measurements above the 10% seasonal discharge exceedance were included in the study, in order to avoid extrapolation when estimating nutrient export during floods, as described later. In all, 32 sites were selected across Ontario with data records spanning 10 to 50 years between 1964 and 2014 (Figure 2.1). While the data period of record did not necessarily overlap for all sites, other studies have been able to report meaningful results with different data record date ranges (e.g., Raymond and Saiers 2010; Park and Engel 2015).

We calculated landscape variables for each catchment, which included climate, topography, and land use (Table 2.1). Average annual temperature and precipitation were calculated using data from meteorological stations (Environment and Climate Change Canada 2017) using the 1964 to 2014 period of record for each site. Due to this relatively long date range, we could not acquire complete records from a single station per site, as these stations were either not continuously operational for the entire period, or their records contained many missing data. As a result, temperature and precipitation data were averaged daily for all meteorological stations within a 40km buffer of each catchment; this resulted in a record with less than 6% missing data. Temperature data that were still missing were estimated using the linear equation of the missing data site against the mean temperature for all sites, while missing precipitation data was assumed to be zero. Mean annual temperature and annual precipitation were calculated for each site across the entire data record.

We used OFAT III (Ontario Ministry of Natural Resources and Forestry 2015) to calculate topographical variables, which included the average catchment area, slope, and elevation, the length and gradient of the main stream channel, and the catchment shape factor (main channel length squared divided by catchment area). The proportion of each catchment affected by dams was calculated in ArcGIS (ESRI 2016) using upstream catchments delineated in OFAT III (Ontario Ministry of Natural Resources and Forestry 2015) from coordinates obtained from the Ontario Dam Inventory (Ontario Ministry of Natural Resources and Forestry 2014).

While OFAT III does provide land cover data, the “agricultural” land use category is combined with an “undifferentiated rural” category, therefore we determined land cover by overlaying delineated catchments with land use maps from 1966 (Ducks Unlimited Canada 2009), 1990, 2000, and 2010 (AAFC 2015) and 2011-2014 (AAFC 2016), which have more specific agricultural categories. Dominant land use classes were agricultural, forested, urban, and wetland. The various land use map years were used to calculate weighted land use and open water averages, resulting in an overall proportion value for each land cover for the entire period of record (1964 to 2014) for each catchment. While land use changed over time in some of the catchments, Mann-Kendall tests with false discovery rate p-value correction (Benjamini and Hochberg 1995) showed that none of these changes were significant at an alpha level of 0.05 (data not shown).

While we did not run a full analysis on soil data (AAFC 2000) due to the lack of data for several of the sites and the large number of different soil texture types, we briefly assessed the relationship of soil texture with longitude using single linear regressions with data pairs consisting of the longitude and the proportion of area occupied by a given soil texture type for each catchment.

Hydrology

Daily mean discharge for each site (Environment and Climate Change Canada 2014) was used to calculate streamflow exceedances using seasonal standard flow duration curves through the Streamflow Analysis and Assessment Software (SAAS; Metcalfe and Schmidt 2016), with seasons defined as winter (December to February), spring (March to May), summer (June to August), and autumn (September to November). We found that daily discharge records were largely complete, however we filled in some missing data using linear interpolation for up to 3 missing days, and for up to 14 missing days using the linear equation with a highly correlated (r>95%) catchment within the same secondary watershed. Average annual discharge volume was calculated using all the available years within the 1964 to 2014 period of record for each site, and was standardized by dividing by catchment area.

In this study, we defined small floods as events that occurred above each site's 10% seasonal discharge exceedance value (Q_{10}), while large floods were defined as those that occurred above the 1% seasonal discharge exceedance value (Q_1). Seasonal discharge exceedances indicate the amount of time that discharge exceeded a certain value, such that Q_{10} is the discharge value that was exceeded during 10% of the season. We used seasonal exceedances, rather than period of record exceedances, in order to combine floods that would be seasonably high, despite the fact that the flows associated with these exceedances would vary. The range of discharge values across all sites for these thresholds is given in Figure 2.2. We identified peak events over these thresholds for each site and season using the R code (R Core Team 2016) developed by Burn and Whitfield (2015). The magnitude, duration, and volume of discharge above these thresholds was calculated for each flood (Figure 2.3a), such that magnitude was the peak discharge value divided by the threshold discharge value, the duration was the number of consecutive days that discharge remained above the threshold value, and volume was the total volume of discharge that occurred over the threshold, corrected by catchment area. We tested for collinearity in the relationships between flood magnitude, duration, and volume to ensure that all three varied in a separate way from one another. Variance inflation factors (VIF) tests for collinearity using the equation $VIF = \frac{1}{1-R_j^2}$, where $R^2{}_j$ is the correlation coefficient for the variable j. Values greater than 10 are considered highly correlated; our flood characteristics showed non-collinearity (VIF<10).

Nutrient Export

Water quality data for this study consisted of total phosphorus (TP), filtered phosphates (PO_4), total kjeldahl nitrogen (TKN), and nitrate- and nitrite-nitrogen (referred to as simply NO_3 for this study, as nitrite levels were very low) taken from the PWQMN (Ministry of the Environment and Climate Change 2015) as mentioned above. We used LOADEST (Runkel et al. 2004) to estimate daily and annual nutrient exports through the LoadRunner interface (Booth et al. 2007), allowing the program to select the best model (using Akaike Information Criteria) for load estimation. Sites with modelled R^2 values less than 0.80 were excluded from analysis, as these relationships were not considered strong enough to sufficiently estimate export values. This reduced the number of sites to 30 TP, 22 PO_4, 32 TKN, and 30 NO_3 for flood analysis.

Each site's data record spanned at least 10 years and, in most cases, water quality samples were collected approximately monthly (although winter tended to be underrepresented or missing), but this was not the case for all sites and all years. However, given the length of the data record, and the inclusion of only sites in which at least 10% of measurements occurred above Q_{10}, we assumed that LOADEST had enough data to be able to model nutrient export relatively accurately. Although 20-30% would have been more desirable (Park and Engel 2015), high flow samples were not represented to this degree in our dataset. Flood export for each nutrient was calculated as the sum of the daily export for the duration of that flood. We calculated the average proportion of annual export contributed by Q_{10} and Q_1 floods for each site, using only data from sites that included winter measurements. These values were then averaged together to determine the proportion of annual export. Years that did not have a large flood were not included in the site's Q_1 average yearly export calculations; this was not an issue for Q_{10} floods, as there was always at least one of these floods per year at each site.

The slopes of the relationships for each site's nutrient export with flood characteristics (magnitude, volume, and duration) were calculated using linear regression (Figure 2.3b); all export and flood characteristics were ln (natural logarithm) transformed to approximate normal distribution and homoscedasticity (similar variances) of the residuals, and p-values were corrected using the false discovery rate method (Benjamini and Hochberg 1995) such that adjusted p-values less than 0.05 were considered significant. Non-significant relationships were assigned a slope value of zero. Throughout this study, we refer to these relationships as the "nutrient-flood-parameter slopes" (e.g., TP-magnitude slopes). Winter floods were excluded from analysis, as they were underrepresented in the dataset.

Seasonal differences between spring, summer, and autumn nutrient-flood-parameter slopes were assessed using Analysis of Covariance (ANCOVA) with false discovery rate p-value correction (Benjamini and Hochberg 1995). While average nutrient levels did vary with season, we were only interested in the slopes of these relationships, thus the ANCOVA interaction effect was tested. For the most part, seasonal nutrient-flood-parameter slopes did not differ from overall (spring, summer, and autumn data combined) nutrient-flood-parameter slopes, although in two cases there were significant differences for up to about half of the sites (depending on the nutrient and flood characteristic). However, we found that when visually compared, overall nutrient-flood-parameter slopes were near to those for the "different" season. Because of this, and the fact that seasonal differences were not widespread in our data, we felt that an overall nutrient-flood-parameter slope (combining data from all three seasons) would be sufficiently representative of the export relationships. The distribution of Q_{10} and Q_1 floods was relatively even across seasons, with approximately one-third of floods occurring in each (spring, summer, and autumn). At each site, differences between TP-, PO_4-, TKN-, and NO_3-flood-parameter slopes were similarly evaluated using ANCOVA.

Landscape Influence on Nutrient-Hydrology Slopes

We evaluated the influence of topographic, hydroclimatic, and land use variables (which we collectively refer to as landscape variables; Table 2.1) on the relationships of flood nutrient export with flood characteristics across all sites using a combination of the Bayesian Information Criterion (BIC) from the MuMIn package (Barton 2016) and multiple linear regression, both conducted in R (R Core Team 2016). We used BIC to select the best explanatory landscape variables, then multiple linear regression was used to evaluate the explanatory power of those variables. Some variables were ln transformed to fit model assumptions. Collinearity (VIF>10) was detected between the length of the main stream channel and catchment area, thus the former variable (which had the greater VIF value) was removed from the model. Similarly, temperature and agricultural land use were removed as they were negatively collinear with latitude and forest, respectively.

Results

Proportion of Annual Export

We found that a large proportion of nutrient export occurred during floods (Figure 2.4). On average, roughly 44% and 48% of the annual TKN and NO_3 exports for the year (respectively) occurred during Q_{10} floods, which was comparable to the percentage of Q_{10} flood discharge volume (45%). TP and PO_4 exports for floods, however, exceeded this, at an average of 58%. Q_1 floods, which accounted for approximately 11% of annual discharge, contributed a similar percentage of TKN and NO_3 exports, while TP and PO_4 each contributed an average of 23% of annual export.

Nutrient Export – Flood Parameter Relationships

For the three seasons included in the analysis (spring, summer, and autumn), an average of 186±115 Q_{10} floods and 39±28 Q_1 floods were captured at each site, with the number of floods distributed approximately evenly across seasons. The range of discharge values associated with each flood threshold (Q_{10} and Q_1) was greater for Q_1 events than Q_{10}, particularly in the spring (Figure 2.2). Flooding characteristics (magnitude, duration, and volume) were nearly always positively correlated with nutrient export for Q_{10} floods, with only a few non-significant relationships (Table 2.2). Q_1 floods, however, were more variable, and flood parameters were not always significantly correlated with nutrient export, particularly for flood magnitude.

At most sites, the nutrient-magnitude slopes for Q_{10} floods were similar across all nutrients (ANCOVA interaction effects test), although we did find a significant difference between nutrients at a couple sites. The same was true for nutrient-durations slopes as well. Half of the sites, however, had at least one nutrient-volume slope that was different from the others, although there was no apparent pattern as to which nutrient(s) differed across sites (data not shown). We did not conduct similar tests for Q_1 floods given the relatively large number of non-significant relationships.

Landscape Effects

We tested the nutrient-magnitude slopes for Q_{10} floods against our landscape variables and found that they were positively and significantly related to average catchment area and slope for all nutrients except NO_3, which was only related to average catchment slope (Table 2.3, Figure 2.5). These variables explained half the variation of the PO_4- and NO_3-magnitude slopes, and more than 60% of the TP- and TKN-magnitude slopes. Q_{10} nutrient-volume slopes were more variable among the tested nutrients; TP-volume slopes were greater in flatter, more western catchments with low damming impact and little open water. PO_4-volume slopes were similarly affected by these variables (minus damming impact), but were also higher in large, natural, southern, upland catchments with high annual discharge volumes; these explained nearly all of the variation in PO_4-volume slopes. TKN-volume slopes were weakly negatively correlated with latitude, and NO_3-volume slopes could not be explained by our model.

Q_{10} TP--duration slopes were not well explained by our landscape variables, with low R^2 and insignificant p-values, but the relationships were stronger for PO_4 and NO_3 (Table 2.3). Our model indicated that TP-duration slopes were greater in low wetland catchments, while the opposite was true for NO_3-duration slopes, which were also negatively correlated with average annual precipitation. PO_4-duration slopes were more pronounced in flat catchments with low annual discharge and little wetland and urban land cover, according to our model, but landscape variables were not important for TKN. Our BIC model identified north-eastern catchments as having greater Q_1 PO_4-volume slopes (Table 2.4). Q_1 TP-duration slopes were elevated in catchments with low average annual discharge, although this model was not significant, but about half of the Q_1 NO_3-duration slopes were explained by dammed area, geographical location, forest, and open water. Due to the high number of non-significant relationships, we were not able to model landscape variable effects on Q_1 nutrient-magnitude slopes.

Discussion

Floods are inherently complex, varying in magnitude, volume, and duration, therefore stream nutrient export is also necessarily complicated, with nutrients in different types of catchments responding differently to these flooding characteristics. The landscape variables that explained small flood (Q_{10}) nutrient-flood-parameter slopes varied depending on the flood characteristic (magnitude, volume, or duration) as well as the nutrient. Landscape variables were generally not able to explain extreme (Q_1) nutrient-flood-parameter slopes.

Annual Export & Relationships with Flood Characteristics

A high percentage of TP and PO_4 was exported during floods compared to average annual flooding discharge. About 58% and 23% of the annual P export occurred during Q_{10} and Q_1 floods, respectively, however the volume of flood discharge only accounted for 45% and 11%, respectively (Figure 2.4). Flooding contribution of annual TKN and NO_3 export more closely mirrored annual flood discharge volume, at 44-48% for Q_{10} floods and 11-15% for Q_1 floods. The flooding exports occurred over relatively few days in the year (about 10% of the year for Q_{10} floods, 1% of the year for Q_1 floods), which is similar to the findings of other studies (Andersen et al. 2006; Royer et al. 2006; Dalzell et al. 2007; Banner et al. 2009). Because nutrient loading can occur over relatively short time periods, and because P species tend to be elevated in relation to discharge volume, it is important to better understand the factors that control nutrient export.

Seasonal Q_{10} flood characteristics (magnitude, duration, and volume) were nearly always positively correlated with nutrient export (Table 2.2), which we expected given that nutrient export should usually increase with increases in flood water, but the degree of increase was particularly interesting in our study. Sites with a similar seasonal variability of flood magnitudes, for example, may have different export relationships (Figure 2.6). For Q_1 floods, we found non-significant nutrient-magnitude slopes for most sites, and several sites had non-significant nutrient-volume and nutrient-duration slopes as well (Table 2.2). It may be that hydrologic controls on nutrient export are simply less predictable when flow is seasonably high, or perhaps the low number of Q_1 floods captured at each site (39±28), compared to the number of Q_{10} floods (186±115), was not sufficient to identify any significant trend at many of the sites. More likely, however, is that the large range in discharge associated with Q_1 events was simply too great and this, in addition to the smaller sample size, created high variability in the associated flood characteristics (Figure 2.2).

Each site's Q_{10} nutrient-duration and nutrient-magnitude slopes were generally similar between TP, PO_4, TKN, and NO_3. However, we found that at least one nutrient-volume slope differed from the others at more than half of all sites (data not shown). The nutrient(s) that differed appeared to have no pattern among sites; for example, TP slopes might be greater at several sites, but TKN might be greater at others. This lack of pattern across sites suggests the relationships between nutrient export and flood volume were catchment-specific, likely reflecting the inherent variability of the different sources and sinks present in the watershed. We could not similarly assess differences in Q_1 nutrient-flood-parameter relationships due to the high number of non-significant relationships.

Landscape Effects Nutrient-Flood-Parameter Slopes

Q_{10} Nutrient-Magnitude Slopes

Much of the variation in the Q_{10} nutrient-magnitude slopes could be explained by our BIC model of landscape variables for TP, PO_4, TKN, and NO_3. All nutrient-magnitude slopes were greater in larger, steeper catchments, except for NO_3, for which catchment size was not important (Table 2.3, Figure 2.5). The slope of the terrestrial environment in a catchment can greatly influence the hydrology as steeper hills tend to generate more runoff (Rose and Peters 2001; Schaetzl and Anderson 2005; Li et al. 2006) and have shorter water retention times and lower storage capacity (Darboux et al. 2001; McGuire et al. 2005). Sloped surfaces are also more easily eroded, thus runoff can carry more soil particles to streams compared to flatter catchments, and this is an important flow pathway for TP and TKN, which are largely in the particulate form in flood water (Cooke and Cooper 1988; House and Warwick 1998; Lloyd et al. 2016). PO_4 and NO_3 are dissolved nutrients, but have also been reported in overland flow (Miller et al. 2005; Siwek et al. 2013) and may therefore be affected by some of the same processes as TP and TKN, but NO_3 is typically transported via subsurface flows (Bowes et al. 2009; Lloyd et al. 2016). Steep terrain may facilitate the movement of subsurface nutrients as flood magnitude increases because steep slopes are associated with thinner soils (Moore et al. 1993; Pelletier and Rasmussen 2009) which can become quickly saturated, allowing appreciable subsurface flows (Tsukamoto and Ohta 1988). These flows may make their way downhill to the streams relatively rapidly, carrying dissolved nutrients with them.

Another important consideration with catchment slopes are the direction in which these topographical features face. Because we used average catchment slope for the entire watersheds, we were not able to separate hillslopes by their aspect. We do, however, understand that this could have implications for nutrient export during floods, as slope aspect can affect soil moisture and temperature conditions (Western et al. 1999; Kang et al. 2000). This would impact vegetation growth and soil texture, ultimately influencing nutrient export and runoff dynamics. As catchment slope effects are strong for our nutrient-magnitude relationships, it would be interesting to consider catchment slope aspect in future work.

Catchment area, along with catchment slope, was also important to TP-, PO_4-, and TKN-magnitude relationships, perhaps because larger, steep catchments have longer slope lengths, and hence larger sloped area to contribute nutrients. Li et al. (2006), for example, found greater nutrient losses from soils on hills with greater slope lengths and areas.

Q_{10} Nutrient-Volume Slopes

The landscape variables that our BIC model selected as important for Q_{10} nutrient-volume slopes varied between nutrients (Table 2.3). We found that TP-volume slopes were greater in flatter, western catchments that also had few dams and relatively little open water, and these variables explained roughly a third of the variation. Just as steeply sloped areas tend to have thin soils, and limited capacity for storage of flood water and nutrients; flatter land tends to be better able to retain this water, reducing overland flow (Sidle et al. 2000; Rose and Peters 2001). Thus, a high-volume flood may exceed the storage capacity, causing a flushing of TP. Longitude was also important for TP-volume slopes, with more western catchments showing greater relationships, which may reflect differences in soil texture across the province. Soil texture was not included in our models because soil maps were not available for all sites, and because the number and complexity of the various soil texture types. Longitude, however, was correlated with the proportion of some soil types in our catchments, with organic and gravelly sandy loam showing some of the strongest positive correlations (R^2=0.38, p<0.001 and R^2=0.27, p=0.002, respectively). Arheimer and Lidén (2000) reported P was strongly related to soil texture, thus it may also be important here, as P rich soils would supply a large amount of this nutrient with large flood volumes. Damming and open water may be influencing TP-volume slopes in that both variables may act as a P sink (Brown et al. 2011). Water retained in lakes, reservoirs, and behind dams may allow phosphorus to settle out before the water can move downstream, therefore a higher proportion of dams and open water could be associated with lower TP.

PO_4-volume slopes were well explained by a large number of landscape variables (Table 2.3). Like TP-volume slopes, PO_4 was greater in flatter, western catchments with low open water, possibly for similar reasons as those previously discussed. Additionally, catchments with high PO_4-volume slopes were large, southern, natural catchments with high average annual discharge. While PO_4-volume slopes were influenced by the combination of these topographic, hydroclimatic, and land use variables, the positive relationships with wetlands and forest warrant further comment, as forests are usually low in PO_4 (e.g., Kortelainen et al. 2006; Siwek et al. 2013), and wetlands typically act as a PO_4 sink (e.g., Reddy et al. 1999). Forests were negatively collinear with agriculture in our study (r>86%), therefore a positive association with forests can also be interpreted as relatively low PO_4-volume slopes in agricultural catchments. This could point to the influence of tile drainage, which is prevalent in Ontario catchments, on PO_4 export. Studies have shown that tile-drained PO_4 increases with discharge, much as it does in non-drained streamflow (Royer et al. 2006; Gentry et al. 2007). With this facilitated draining, soil stores of PO_4 may become somewhat depleted such that a high-volume event results in low concentrations in runoff. Wetlands are known for complex microtopographic features that can retain waters (Frei et al. 2010) that may spill over in a threshold-like response during high-volume floods, contributing nutrients to the stream; additionally, wetlands that have been previously dry may release a large amount of PO_4 once rewetted (Song et al. 2007), potentially due to the release of stored P into the flood water as a P equilibrium becomes re-established (see the review by Vymazal 2007). We did not include a measure of antecedent soil moisture conditions in our study, though we recognize that this is an important variable. Antecedent conditions have been found to not only influence nutrient levels (Alexander and Smith 2006; Turgeon and Courchesne 2008; Alfonso et al. 2015; Lloyd et al. 2016), but also hydrology (Ivancic and Shaw 2015). For example, (Siwek et al. 2013) reported that high-magnitude precipitation events resulted in greater PO_4 concentrations following drier conditions, which suggests that PO_4 may build up in the soil between events. We expect that consideration of these effects would need to be given to both nutrient export as well as flood characteristics, however we felt that the inclusion of an antecedent moisture parameter would overcomplicate an analysis in which the primary goal was to identify general patterns across the region, though it should certainly be a consideration in future work.

TKN-volume slopes were only weakly explained by catchment latitude, with southern catchments associated with greater relationships (Table 2.3). In our study, latitude was a proxy for temperature (as they were strongly negatively correlated; R^2=0.93, p<0.001), thus the increase in TKN-volume slopes may have been influenced by warmer average annual temperatures. This may be due to increased biological nitrogen processing in catchment with warmer annual temperatures. Ammonification, for example, is more rapid at higher temperatures (Vymazal 2007).

Q_{10} Nutrient-Duration Slopes

Nutrient-duration slopes were relatively weak for TP and NO_3, but were stronger for PO_4 (Table 2.3). We found that TP-duration slopes were greater in catchments with lower wetland coverage, potentially due to the ability of wetlands to retain nutrients (Reddy et al. 1999). On the other hand, NO_3-duration slopes were greater with increased wetlands, along with lower average annual precipitation. The differing wetland effect between the two nutrients may be due to supply. Though P may be flushed from wetlands during high volume floods, as previously discussed, this supply of P may become exhausted with an increase in flood duration. N is more abundant in freshwater systems than P, and therefore NO_3 levels may remain high throughout a flood.

PO_4-duration slopes were greater in flatter catchments with lower average annual discharge and low proportions of urban and wetland cover (Table 2.3). The increase in PO_4-duration slopes with flatter land is in contrast to the PO_4-magnitude slopes, which were greater in steeper catchments. One study of forested catchments did report that flatter sites had higher PO_4 export, but did not postulate as to the reasons for this (Kortelainen et al. 2006). Overland flow is not common in flat catchments (Sidle et al. 2000; Rose and Peters 2001), however a longer flood may eventually saturate soils and begin transporting PO_4 rich water to streams through saturated overland flow, with low mobilization of the particulate material associated with other nutrient forms, such as TP and TKN. For PO_4-duration slopes, we also observed a negative wetland effect. As mentioned previously, wetlands can act as a sink for PO_4 (e.g., Reddy et al. 1999); low wetland cover suggests that PO_4 is delivered directly to the stream during flooding, with low opportunity for interception by wetlands. P from urban areas, conversely, tends to be associated with point-sources, particularly wastewater treatment plants (e.g., Aguilera et al. 2012; Lapworth et al. 2013), which would not be affected by runoff. A long flood may result in an initial flush of nutrients from highly impervious urban land, followed by dilution (Gwenzi et al. 2017), resulting in an overall lower PO_4-duration slope compared to land covers in which P is supplied mainly through diffuse sources. Unlike the other nutrients, TKN-duration slopes could not be explained by the landscape variables in our study.

Strengths of the Models

It is interesting to note that the PO_4 models for flood duration and volume were much stronger than those for the other nutrients, although the R^2 value for PO_4-magnitude slopes were not as strong as TP and TKN. As discussed earlier with nutrient-magnitude slopes, these latter two nutrients are prevalent in the particulate form in floods, while NO_3 is largely subsurface. PO_4 tends to follow a different flow pathway, being transported in overland flow, but in dissolved form rather than particulate. A long, high-volume flood may provide a sufficient amount of time and water for soils to become saturated such that PO_4 stored in “old” soil water to mix with “new” water from snowmelt or precipitation.

The nutrient levels in this stored water likely reflects the landscape in which it is found, therefore floods that cause saturation overland flow may result in stronger landscape effects. In contrast, particulate TP and TKN are not likely to be as mobile as they are in high magnitude floods that may result in Hortonian overland flow (where precipitation or melt water introduction rate exceeds the infiltration capacity of the soils), which may cause the displacement of soil particles to which TP and TKN are often bound.

Q_1 Nutrient-Hydrology Slopes

Due to the high number of non-significant slopes for Q_1 nutrient-magnitude, we ran BIC analysis on nutrient-volume and nutrient-duration slopes only. Our model identified latitude as important for Q_1 PO_4-volume slopes, but landscape variables were not important for any other nutrient-volume slopes (Table 2.4). As with Q_{10} PO_4-volume slopes, Q_1 PO_4-volume slopes were greater in southern catchments and may be caused by larger PO_4 accumulation in soils from more rapid mineralization by microbes at the warmer temperatures typical of these catchments.

Landscape variables were only identified as important in Q_1 nutrient-duration slopes for TP and NO_3. Q_1 TP-duration slopes were weakly related to average annual discharge, while half of the variation in Q_1 NO_3-duration slopes was explained by dammed area, geographical location, land use, and open water (Table 2.4); none of these variables were important for Q_{10} NO_3-duration slopes. These results may highlight the shift in the importance of landscape variables as a small flood increases to a larger one, however it should also be noted that the data used to model nutrient export during floods captured very few Q_1 samples, therefore these export estimates were generally extrapolated by LOADEST and may have been underestimated (Park and Engel 2015).

Future Work

As briefly mentioned earlier, antecedent moisture conditions have been found to be important for nutrient levels during floods (Alexander and Smith 2006; Turgeon and Courchesne 2008; Alfonso et al. 2015; Lloyd et al. 2016). Additionally, the order in which floods occurs can also be important, with subsequent floods seeing reduced nutrient export (Siwek et al. 2013; Outram et al. 2016). The effect of catchment slope aspect is also important for soil conditions (Western et al. 1999; Kang et al. 2000) and therefore nutrient export and hydrology. We did not include measures of antecedent conditions, flood sequence, or slope aspect in our study, but these parameters may help explain some of the variability in nutrient export that could not be explained by our landscape variables, and therefore would be worth examining in future research.

Conclusion

Due to the large contribution of floods to annual nutrient export, it is important to understand how these fluxes vary with the flooding characteristics (magnitude, volume, and duration) and the effect that landscape variables may have on these relationships. Our results show that TP, PO_4, TKN, and NO_3 export relationships with flood magnitude, duration, and volume can be at least partially explained by landscape variables. We found that, in general, catchment area and slope explained roughly half of the small flood (Q_{10}) nutrient-magnitude slopes, but landscape variable effects on nutrient-volume and nutrient-duration slopes were weak or non-existent, except for PO_4. Large flood (Q_1) nutrient-volume and nutrient-duration slopes were relatively weakly related to landscape variables and may be problematic to interpret due to the potential for export underestimation. Our research highlights the importance of considering the hydrologic character of floods when predicting nutrient exports and identifies the characteristics of catchments that are more likely to see more pronounced nutrient export with flooding. This information is useful for identifying watersheds that could potentially see nutrient contamination with the predicted and continued hydrologic changes expected with climate change (Andersen et al. 2006; Burn and Whitfield 2016).

Table 2.1. Summary of catchment topographic, hydroclimatic, and land use variables and their abbreviations.

Landscape Variable	Abbr.	Min	Max	Mean	Median
Longitude (DD)	Long	-89.21	-74.49	-80.14	-79.79
Latitude (DD)	Lat	42.91	48.80	44.39	44.09
Catchment Area (km^2)	Area	45	4277	444	207
Mean Elevation (m asl)	Elev	5	441	260	270
Mean Catchment Slope (%)	Slope	1.12	7.65	3.53	3.23
*Catchment Shape***	Shape	5	44	17	14
Main Channel Length (km)	ChLen	20	274	71	51
Mean Channel Slope (%)	ChSlp	0.06	1.22	0.31	0.22
Catchment Area Affected by Dam (%)	Dam	0	100	32	13
Catchment Agriculture (%)	Agri	0	96	61	77
Catchment Forest (%)	Forest	0	95	25	11
Catchment Urban (%)	Urban	0	79	7	3
Catchment Wetland (%)	Wetland	0	12	1	0.3
Catchment Open Water (%)	OpnWater	0	13	1	0.2
Mean Annual Temperature (°C)	Temp	1.7	8.4	6.7	6.9
Mean Annual Precipitation (mm)	Precip	688	1065	913	900
Mean Annual Discharge (m^3/km^2)	AnnVol	90	5840	2181	1769

**channel length squared divided by catchment area*

Table 2.2. Number of sites that showed non-significant nutrient relationships to hydrologic characteristics (false discovery rate corrected p>0.05). All significant relationships were positive.

Event Threshold	Nutrient	Number of Sites	Duration (days)	Magnitude ($Q_{peak}/Q_{threshold}$)	Volume (m^3/km^2)
Q_{10}	**TP**	30	0	0	0
	PO_4	22	0	1	0
	TKN	32	0	0	0
	NO_3	30	0	1	0
Q_1	**TP**	29	11	24	4
	PO_4	22	7	21	4
	TKN	32	3	21	2
	NO_3	30	6	25	6

Table 2.3. Multiple linear regression coefficients of BIC selected topographic, hydroclimatic, and land use variables for flooding (Q_{10}) nutrient-hydrology (duration, magnitude, and volume) slopes. Nutrient-hydrology slopes that could not be explained by the model are excluded. Variable abbreviations are given in Table 1, and "Ln" denotes a transformation to the natural logarithm.

Landscape Variable	**Duration**			**Magnitude**				**Volume**		
	TP	**PO_4**	**NO_3**	**TP**	**PO_4**	**TKN**	**NO_3**	**TP**	**PO_4**	**TKN**
Long								-0.03	-0.04	
Lat									-0.06	-0.03
Ln Area				0.12	0.27	0.11			0.23	
Elev									6×10^{-4}	
Slope		-0.11		0.26	0.15	0.20	0.21	-0.04	-0.12	
Shape									-0.003	
Ln Dam								-0.21		
Forest									0.55	
Urban		-0.64								
Wetland	-2.74	-8.79	0.144						2.88	
OpnWater								-3.00	-6.9	
Precip			-8×10^{-4}							
AnnVol		-2×10^{-4}							2×10^{-4}	
R^2	0.08	0.35	0.14	0.69	0.50	0.69	0.48	0.37	0.90	0.09
P-value	0.07	<0.05	<0.05	<0.001	<0.001	<0.001	<0.001	<0.01	<0.001	<0.05

Table 2.4. Multiple linear regression coefficients of BIC selected topographic, hydroclimatic, and land use variables for extreme (Q_1) nutrient-hydrology (duration, magnitude, and volume) slopes. Nutrient-hydrology slopes that could not be explained by the model are excluded. Variable abbreviations are given in Table 1, and "Ln" denotes a transformation to the natural logarithm.

Landscape Variable	**Duration TP**	**Duration NO_3**	**Volume PO_4**
Long		-0.10	
Lat		-0.20	-0.13
Ln Dam		1.51	
Forest		1.46	
OpnWater		-9.43	
AnnVol	-1.9×10^{-4}		
R^2	0.10	0.51	0.20
P-value	<0.05	<0.001	<0.05

Figure 2.1. Ontario catchment locations for the 32 sites selected for export analysis.

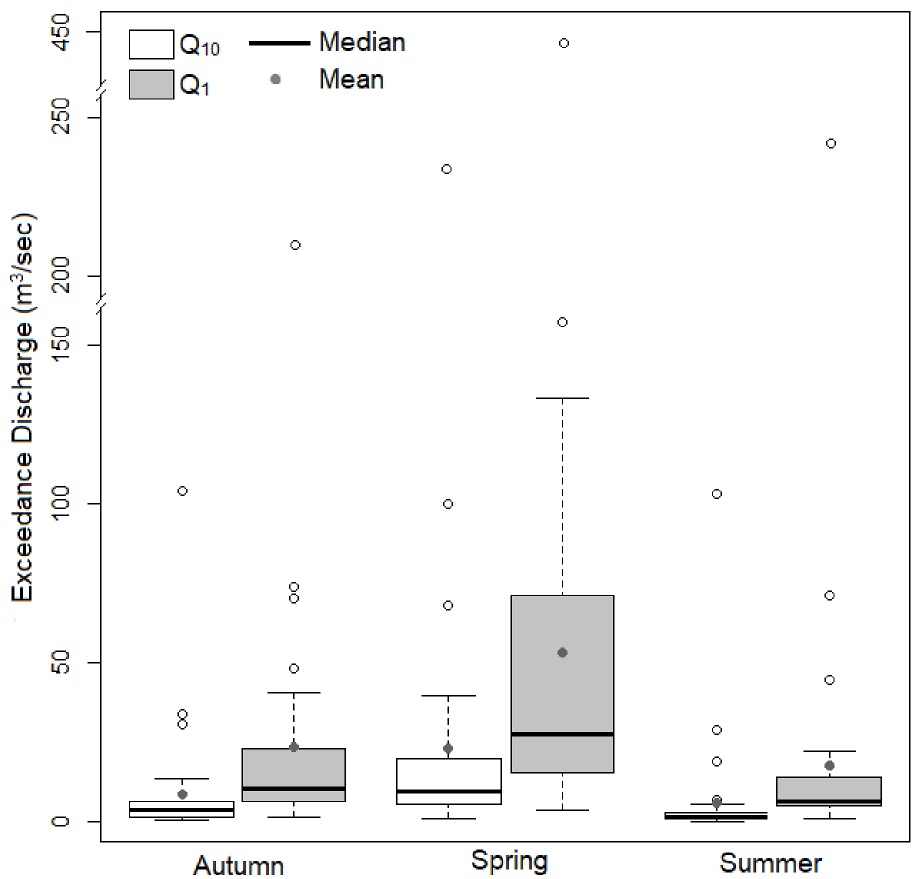

Figure 2.2. Seasonal discharge range associated with the exceedances for small (Q_{10}) and large (Q_1) floods across all sites. Whiskers represent 1.5 times the interquartile range.

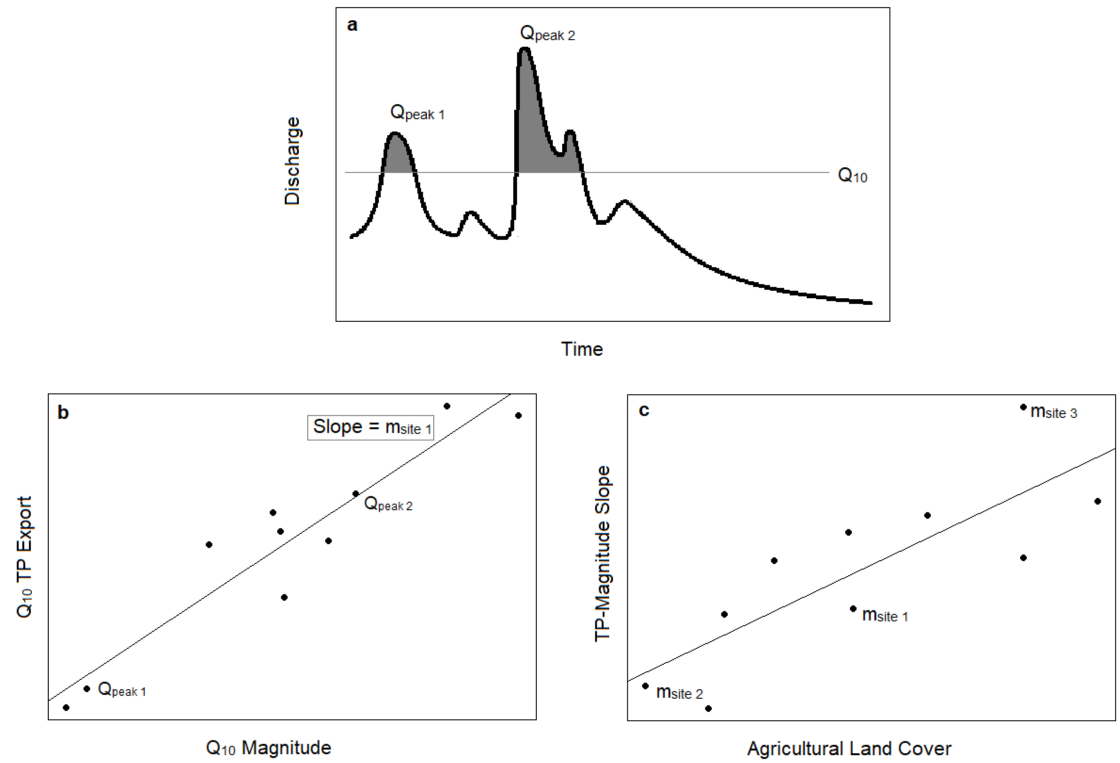

Figure 2.3. Conceptual diagram of the data analysis procedure: a) flood magnitude, duration, and volume were calculated for the areas shown in grey across the entire hydrograph for each site (Q_{10} is shown, but the same procedure applied to Q_1 floods as well); b) the slope (m) of the relationship between nutrient export and magnitude of each peak for each site was calculated; and c) the slopes from all sites were combined and tested against landscape variables (agriculture is shown as an example).

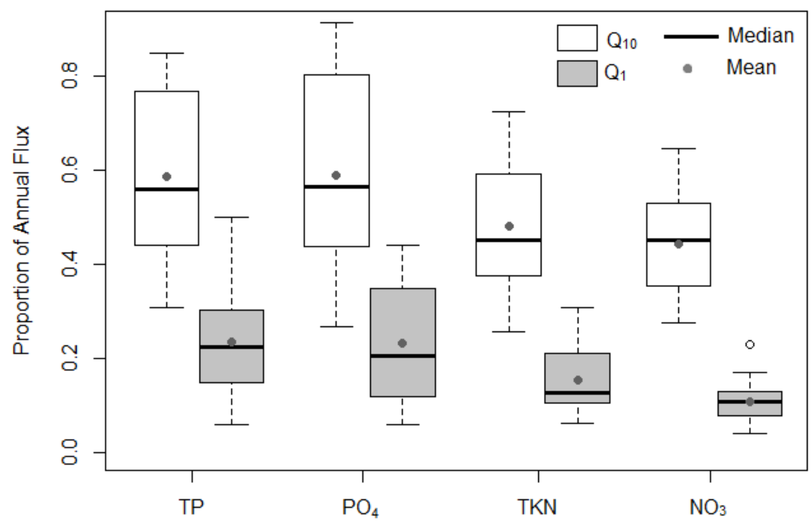

Figure 2.4. Average proportion of annual nutrient export contributed during small (Q_{10}) and large (Q_1) floods. Whiskers represent 1.5 times the interquartile range.

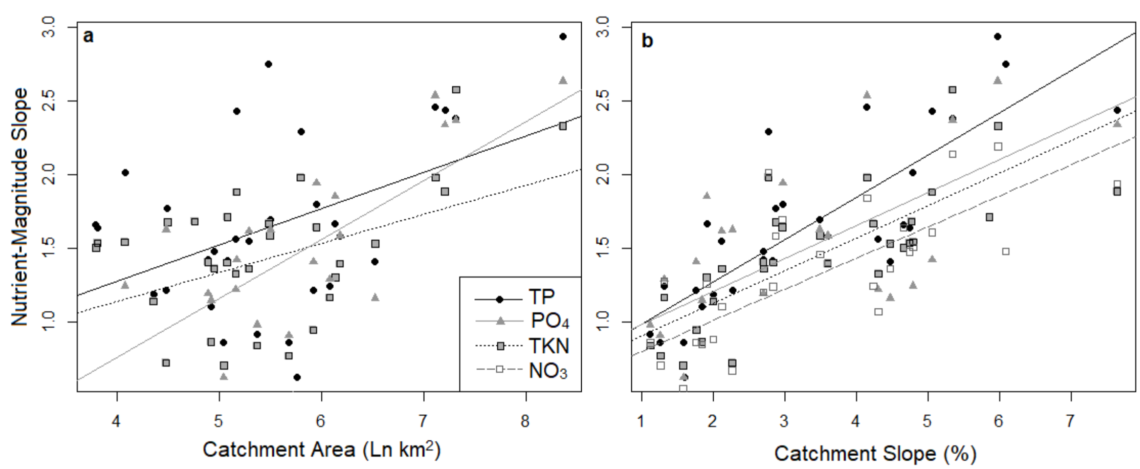

Figure 2.5. Univariate relationships of Q_{10} nutrient-magnitude slopes with a) average catchment slope and b) catchment area.

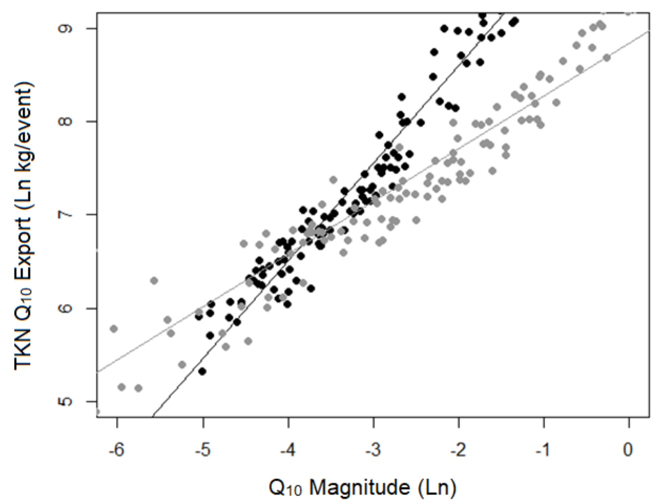

Figure 2.6. Conceptual representation of differing TKN-magnitude slopes for two individual sites.

3.0 Event-Controlled Nutrient Transport Using Concentration-Discharge Relationships

Sarah C. D'Amario, Henry F. Wilson, Robert A. Metcalfe, and Marguerite A. Xenopoulos

Abstract

Concentration-discharge (C-Q) relationships have been widely used to assess the hydrochemical processes that control solutes in streams and can provide important information to watershed managers. Here, using big data, we assessed long-term C-Q relationships for total phosphorus (TP), phosphate (PO_4), total kjeldahl nitrogen (TKN), and nitrate (NO_3) for 63 streams in Ontario, Canada, to better understand the behaviour of nutrients during "rising" and "falling" hydrograph events. We used C-Q plots, Kruskal-Wallis tests, and breakpoint analysis to characterize regional nutrient C-Q relationships and assess seasonal effects, anthropogenic impacts, and differences between hydrograph limbs to gain an understanding of the dominant processes controlling overall C-Q relationships. We found that, with a few exceptions, TP, PO_4, and TKN C-Q dynamics were similar, with nearly flat or gently sloping C-Q relationships up to a discharge threshold, after which C-Q slopes substantially increased with flow on the rising limb. These thresholds, however, were seasonally variable, with summer and winter thresholds occurring at lower flows compared to autumn. Breakpoints during snowmelt were more variable across nutrients. These patterns suggest that seasonal management of high flows in particular would be the most effective way to mitigate contamination from these nutrients. Catchment connectedness is an important consideration as well; higher rising limb concentrations suggest that pools of stored solutes are limited and become easily connected to the stream with increases in flow, causing large increases in solutes. NO_3 C-

Q patterns tended to be different from the other nutrients and were further seasonally complicated by anthropogenic land use. Hydrograph limb effects were either not present or not consistent for NO_3, suggesting that this nutrient may be difficult to successfully manage at a regional level.

Introduction

In riverine ecosystems, solute export, coupled with the catchment's land use and land cover, are used to assess the potential for eutrophication, brownification, or other pollution risks in downstream ecosystems (Evans et al. 2006; Roulet and Moore 2006; Bridgeman et al. 2012; McCullough et al. 2012). Stakeholders and other water managers require this information to implement best management strategies such as the installation of vegetative buffer strips along riparian areas (Loperfido et al. 2014). These mitigation techniques take into account not just the source of solutes, but also the fact that the allochthonous contribution of these solutes is inextricably tied to hydrology (e.g., Banner et al. 2009; Lapworth et al. 2013; Moatar et al. 2017). Because of the link between solutes and hydrology, concentration-discharge (C-Q) relationships are a useful tool, providing valuable information on processes controlling solute availability and connectivity in catchments (Creed et al. 2015; Ali et al. 2017; Moatar et al. 2017), which can be used to inform management decisions. This is especially important in light of the increasing frequency of extreme climatic events (Burn and Whitfield 2016) which will increase hydrological nutrient export (e.g., Andersen et al. 2006; Bosch et al. 2014).

Nutrients typically make their way to stream systems through event-driven transport from the terrestrial environment. Allochthonous transport of solutes in northern cold climates is event-generated, typically driven by floods from snowmelt and storm events (e.g., Hinton et al. 1997; Eimers et al. 2008; Silins et al. 2014). These events can cause soils to become saturated with water, producing subsurface and overland flows. The "new" water mixes with or displaces older soil water in which nutrients have accumulated in both dissolved and particulate form, delivering them to the stream (e.g., Buttle 1994).

As these waters reach the stream, discharge becomes elevated and, depending on solute levels in the soil water and particulates, the resulting stream solute levels will either be chemostatic (where concentrations do not vary much with discharge) or chemodynamic (where concentrations either increase or decrease in synchrony with discharge). Chemostatic behaviour has been observed for nitrate (NO_3) and phosphorus (P) in long-term intensively agricultural catchments (Basu et al. 2011). Negative chemodynamic behaviour occurs due to dilution from incoming subsurface and overland flows, while positive chemodynamic behaviour can be the result of in-stream removal and retention processes during low flows and terrestrial solute export during high flows (Ali et al. 2017; Moatar et al. 2017).

Nutrient C-Q behaviour is variable and depends on catchment- and event-specific factors. Many nutrients, however, exhibit a dominant C-Q pattern for events across a region. total phosphorus (TP), phosphate (PO_4), and total kjeldahl nitrogen (ammonium and organic nitrogen: TKN) tend to show dominant C-Q or hysteresis patterns across study sites, however NO_3 responds to increases in discharge in a less ubiquitous way (Cooke and Cooper 1988; House and Warwick 1998; Butturini et al. 2006; Rodríguez-Blanco et al. 2013b; Long et al. 2014; Lloyd et al. 2016). The greater variability in NO_3 C-Q patterns may be partially because its behaviour depends on groundwater concentrations. Streams fed with NO_3-rich groundwater tend to become diluted when less concentrated event water reaches the stream (Bowes et al. 2009; Lloyd et al. 2016), whereas streams fed with low-NO_3 groundwater may experience increases in concentration with discharge (House and Warwick 1998; Rodríguez-Blanco et al. 2013b; Serrano et al. 2015). The importance of these processes to C-Q relationships may also shift throughout the discharge range. Moatar et al. (2017) reported that nutrient C-Q slopes frequently differ on either side of a discharge threshold, while a prairie study reported models that incorporated a discharge threshold tended to better describe C-Q patterns (Ali et al. 2017). Several other studies have also reported discharge thresholds (e.g., Banner et al. 2009; Murphy et al. 2014). These thresholds indicate a change in the dominant process influencing solute concentrations and may be caused by a change from baseflow to stormflow, for example.

Another important part of chemodynamic relationships are the differences that occur because of increasing (rising hydrograph limb) or decreasing (falling hydrograph limb) discharge. C-Q relationship differences between hydrograph limbs are common and have been extensively reported in the literature (e.g., Whitfield and Schreier 1981; Cooke and Cooper 1988; Raymond and Saiers 2010; Siwek et al. 2013; Lloyd et al. 2016), and can give an indication of how solutes are supplied during events. These and other studies examining hysteresis during a hydrologic event have found a wide range of patterns that can be broadly categorized as clockwise (where the rising limb concentrations are greater than those on the falling limb) and counter-clockwise (greater falling limb concentrations). The former can be an indication of solute sources that are hydrologically connected and relatively close to the stream, while the opposite is suggested of the latter (Creed et al. 2015). A poorly connected catchment has source areas that take a long time or large volume of event water before solutes begin to be transported to the stream. This lag time means that solute concentrations peak at some point after discharge peaks, which results in greater concentrations on the falling limb. Solutes which peak prior to the discharge peak (greater rising limb concentrations) may be well-connected as well as supply limited (Williams 1989), where the solutes stored in the soil water and particulates are quickly exhausted in a "first flush" response.

Most studies use high-resolution data for a single or small number of catchments, and focus on event-specific hysteretic effects (e.g., House and Warwick 1998; Evans et al. 2003; Lloyd et al. 2016), the pattern of which depends on various catchment- and event-specific factors (e.g., Siwek et al. 2013; Feinson et al. 2016). Despite this variability, an overall pattern may emerge when looking at lower-resolution, longer-term datasets that combine multiple sites using a big data approach (Moatar et al. 2017). Raymond and Saiers (2010), for example, examined dissolved organic carbon (DOC) C-Q relationships separated by hydrograph limb from over 5,000 measurements of 30 small, forested sites taken over 31 years. By classifying discharge measurements into "bins," and averaging the discharge and concentrations within each bin, the study was able to determine that DOC concentrations were higher on the rising limb compared to the falling limb. The process of binning the data helps to reduce some of the variability inherent in large water quality datasets, both within and among sites, and allows an overall pattern to be identified. Here, we employed a similar method, but expanded our analysis to include several nutrients, and used catchments of variable sizes and land uses.

Our objective was to characterize the overall C-Q relationships, including threshold behaviour, of several solutes in 63 Ontario, Canada catchments in order to make inferences on the dominant sources and processes controlling nutrient concentrations. As noted by Kirchner (2003), processes influencing hydrology and solute biogeochemistry are common across various catchments, and gaining a simple, general understanding of these processes is more beneficial than a complicated one. Therefore, using data across multiple sites and years, we attempted to gain a regional picture of C-Q patterns and make inferences on what these patterns may mean for nutrient management. Our dataset consisted of up to 14,450 measurements taken from periods of 10 to 50 years between 1964 and 2014. We hypothesized that C-Q relationships of TP, PO_4, TKN, and NO_3 would vary depending on season, hydrograph limb, and land use. We expected that C-Q relationships would generally be positive, but that chemostatic effects might be observed in catchments that were heavily influenced by anthropogenic land uses. We also expected to find similar seasonal patterns across nutrients.

Methods

Site Selection

We obtained total phosphorus (TP), filtered phosphates (PO_4), total kjeldahl nitrogen (organic nitrogen and ammonium; TKN, measured as mg N/L), and nitrate + nitrite (referred to here as simply NO_3 because NO_2 was relatively low, measured as mg N/L) data for 63 sites (Figure 3.1) within the Ontario Provincial (Stream) Water Quality Monitoring Network (PWQMN; Ministry of the Environment and Climate Change 2015). Sites were selected for this study based on proximity to a stream gauging station and the length of the data record. The catchments we studied varied in topography, land use, and hydroclimate (Table 3.1). It is well known that these factors influence stream nutrient levels (e.g., Li et al. 2006; McCullough et al. 2012; Becker et al. 2014), therefore a site-specific standardization was applied to make values comparable across the various types of catchments (more on that below). We did this with the assumption that, though individual C-Q patterns were likely to vary somewhat between catchments and events, a dominant pattern would emerge that would allow us to make inferences on the types of processes influencing solute levels across the discharge range; information that would be applicable to regional water quality management decisions.

Stream gauging stations (Environment and Climate Change Canada 2014) were not usually co-located with water quality sites, thus only gauging stations that were on the same main channel and relatively close to water quality sites were included. Proximity was calculated as the amount of overlap in the water quality and gauging station catchments, with those sites with at least 75% overlap, and no dams located between water quality sites and gauging stations, selected for the study. We did not account for landscape features that may have been located between water quality sites and gauging stations, however we recognize that these may alter flow patterns. For example, nutrients may be intercepted or released by riparian wetlands depending on flow conditions. We used the 75% catchment overlap to try to minimize these effects. Catchments were delineated using the Ontario Flow Assessment Tools III (OFAT III; Ontario Ministry of Natural Resources and Forestry 2015), and dam locations were determined from the Ontario Dam Inventory (Ontario Ministry of Natural Resources and Forestry 2014). Additionally, only those sites with a range of at least 20 years of discharge data overlapped with at least 10 years of water quality data were included in analysis. The record length for water quality data was chosen to ensure a large number of samples could be included for each site. In total, there were 11,100 - 14,450 measurements depending on the nutrient. Discharge records were used to calculate discharge exceedances, as described below. PWQMN water quality samples were collected by Ontario's Conservation Authorities under a standard protocol (Ontario Ministry of the Environment 1983), and analyzed at a central location. Data was collected approximately monthly, although more or less frequent sampling occurred in some years at various sites.

Hydrology

Environment and Climate Change Canada (2014) stream gauging station daily mean discharge data was used to calculate discharge exceedances for each site's period of record using standard flow duration curves in the Streamflow Analysis and Assessment Software (SAAS; Metcalfe and Schmidt 2016). We manually defined seasons using each site's median annual hydrograph for all years in which hydrological data was available during our period of record. While median hydrographs cannot capture interannual variability, they are useful for determining when hydrological seasons typically occur at each site. We estimated the date ranges for each season, rounded to the nearest half-month, for each site, and defined them as snowmelt (large discharge peak occurring in the spring), summer (low flow period), autumn (slightly elevated flow period), and winter (reduced or stabilized flow); see Figure 3.2 for a more detailed explanation of seasonal definitions. This method resulted in uneven season sizes (typically summer was the longest season, and autumn the shortest), however we felt that we obtained a good representation of hydrological seasons. We noted that while the seasonal date ranges and lengths varied from catchment to catchment, sites located within the same secondary catchment generally had similar hydrographical seasonal definitions.

Although discharge records were mostly complete, some missing data was estimated using interpolation (for up to 3 missing days) or using the values derived from the linear equation of a highly correlated site (r >95%) within the same secondary watershed (for up to 14 missing days). SAAS was also used to define rising and falling hydrograph limbs, with rising limb days designated as days in which discharge was increasing, including the day on which discharge peaked, and falling limb days defined as those where discharge was decreasing, including the day with the lowest discharge before flow began increasing again (Figure 3.3). We did not include non-event samples in our analysis due to the low number of measurements taken during baseflow. Samples taken when estimated baseflow (determined using SAAS; Metcalfe and Schmidt 2016) was equivalent to daily mean discharge were considered to be non-events, and were removed from our dataset.

Similar to the method employed by Banner et al. (2009), we converted the mean daily discharge associated with each water quality measurement to the respective discharge exceedance percentage in order to standardize these measurements across all sites. Discharge exceedances refer to the percentage of time that streamflow is greater than or equal to a given discharge. For example, a discharge value associated with a 10% exceedance (Q_{10}) indicates that that discharge value, as well as greater discharge values, are observed only 10% of the time.

Nutrient Concentrations

TP, PO_4, TKN, and NO_3 concentrations were z-scored by season within each site using the equation $Cz = \frac{C - C_{mean}}{C_{stdev}}$, where C_z is the z-scored concentration, C is the measured concentration, C_{mean} and C_{stdev} are the mean and standard deviation for the concentrations, respectively, measured at the given site in the given season. Z-scoring, in this case, converts the concentration data to values that, instead of representing absolute concentration, indicate the number of standard deviations a particular concentration is away from the mean. Thus, large z-scored values are higher concentrations for that site and season, while large negative values are lower compared to seasonal mean concentration levels.

Data Treatment and Analysis

Similar to the method used by Raymond and Saiers (2010), all data was divided into either the rising or falling hydrograph limb and bin-averaged, which we did according to discharge exceedances (Table 3.2). For example, all z-scored TP measurements (across all sites) that occurred on the rising limb when discharge was at Q_{10} (10^{th} discharge exceedance bin) were averaged together to return a single mean TP value. Bins were chosen such that high and low discharge exceedance bins were narrow to better represent high and low flow effects. Most water quality samples were taken in the middle of the discharge exceedance range, with more samples on the falling limb (Figure 3.4). Large datasets will inherently be quite variable (e.g., Bartley et al. 2012), and this method was used to reduce some of this variability in order to assess the overall concentration-discharge patterns.

Our initial assessment of the data showed non-linear tendencies in C-Q relationships, thus breakpoint analysis was run using the “segmented” package (Muggeo 2008) in R (R Core Team 2016). Due to the relatively small number of data points included in each C-Q relationship, there was not enough data to facilitate linear regression or Analysis of Covariance (ANCOVA) tests to compare rising and falling limb slopes with any reasonable degree of power. Instead, we ran Kruskal-Wallis (KW) tests on the complete, unaveraged binned dataset to assess differences between seasons, as well as differences between rising and falling limb concentrations at an alpha level of 0.05 and 0.10, corrected using the Bonferroni method to reduce family-wise type I error. We also investigated land use briefly to assess differences in C-Q relationships at different levels of anthropogenic disturbance. Since land use maps were not available for all years in our data range, we calculated the percentage of each land use type for each site as the weighted average of the available years (1966; Ducks Unlimited Canada, 2009, 1990, 2000, 2010; AAFC 2015, and 2011-2014; AAFC 2016). We defined anthropogenic disturbance as the sum of agriculture and urban land use, and roughly split our sites into high disturbance (where agriculture + urban > 60%, about two thirds of all sites) and low disturbance ($\leq$ 60%, about one third of all sites). KW tests were used to assess differences between disturbance levels at individual bins, similar to the method described above.

Results

The use of concentration-discharge (C-Q) relationships derived from longer-term albeit low frequency water quality sampling allowed us to assess regional patterns between nutrients and hydrology across Ontario, Canada. We expressed C-Q relationships as bin-averaged, seasonally z-scored concentrations against discharge exceedance and, using this standardized dataset, found overall positive C-Q relationships on both the rising and falling limb of the hydrograph. There were, however, variations depending on the hydrological season. Kruskal-Wallis (KW) tests found many significant seasonal differences in concentration levels for TP, PO_4, TKN, and NO_3 in multiple discharge exceedance bin levels (Figure 3.5). As this analysis used the standardized data (which relates each season's nutrients levels to its own mean and standard deviations), we cannot comment on whether absolute concentrations were consistently seasonally higher or lower. We instead used this analysis to justify seasonal separation of our data in further analyses.

We found similar seasonal C-Q patterns for TP, PO_4, and TKN with a few exceptions. Summer, autumn, and winter C-Q slopes for these nutrients tended to be nearly chemostatic or gently positively sloping below discharge thresholds around Q_{60}, Q_{10}, and Q_{40}, respectively (Figure 3.6). In terms of discharge flow values, this can be interpreted as breakpoints occurring at lower flows during the summer and winter compared to autumn, where the breakpoint occurred at high flows. We were unable to detect thresholds for snowmelt TP and TKN on the rising limb, but we did identify a PO_4 threshold around Q_{20}. Falling limb thresholds for this season were variable across nutrients. Above these breakpoints, the C-Q slopes saw a pronounced increase, particularly in autumn, and this was common across all three of these nutrients.

It should be noted that some of the points at the extreme ends of the discharge exceedance ranges for all C-Q relationships were composed of a single sample measurement (identified as a point lacking error bars; Figure 3.6-3.8). We included these points to give full consideration to as much of the discharge range as possible in the interest of making a regional assessment based on the available data. It is likely that, for the most part, the single measurement points tended to follow the observed C-Q patterns and were relatively representative of nutrient levels had we access to more extreme high-flow samples, though we were cautious in their interpretation when they did not follow the C-Q pattern. For example, the summer rising limb TP concentration value for bin 13 ($Q_{0.1}$) is quite a bit higher than the other points (Figure 3.6), which may be uncharacteristic. We therefore did not discuss the threshold associated with this point.

Typically, rising limb C-Q slopes were greater than those on the falling limb for TP, PO_4, and TKN (Figure 3.6). KW tests showed several differences between rising and falling limb concentration levels, largely during snowmelt, however a lack of significant differences at individual discharge exceedance levels does not necessarily preclude differences between slopes. The presence of several significant hydrograph limb differences, and the fact that nearly all TP, PO_4, and TKN C-Q relationships show a similar pattern of pronounced above-threshold rising limb concentration increases with discharge, suggests that above-threshold rising limb levels are indeed greater than those of the falling limb. The snowmelt season is an obvious exception to this pattern, where differences in hydrograph limbs are less distinct or more complicated.

NO_3 C-Q relationships did not tend to follow similar patterns to those displayed by TP, PO_4, and TKN, and were further complicated by anthropogenic land use effects. Anthropogenic disturbance appeared to influence NO_3 C-Q slopes only during snowmelt and summer, with KW tests showing significant differences at individual discharge bin levels on both the rising and falling limb, although the differences were more apparent on the falling limb (Figure 3.7). Differences between rising and falling limb C-Q slopes for these seasons were less apparent compared to the other nutrients. KW tests identified few significant differences between hydrograph limbs in these seasons; in low-disturbance catchments, statistical differences were found at bins 7, 8, and 12 during snowmelt, but only at bin 10 during the summer. In high-disturbance catchments, only summer had significant KW tests for bins 7 and 8, although this latter example's C-Q pattern reflected those observed for other nutrients in this season.

We found neither anthropogenic effects nor hydrograph limb effects for NO_3 C-Q relationships in the autumn and winter. Autumn C-Q slopes increased across the discharge range, while winter C-Q patterns appeared to be chemostatic (Figure 3.8). In both seasons, the falling limb appeared to have a breakpoint around Q_5, however these did not follow any of the other C-Q patterns observed in this study, and they are driven by few points, thus we were not confident that these patterns are representative.

Discussion

C-Q relationships can provide information on the processes controlling stream nutrient concentrations and, using data big data approach from multiple sites, can give an indication of the dominant processes across a region, including thresholds which indicate the point in the discharge range where these processes change. In our study, we were able to estimate regional discharge thresholds by combining long-term data from a large number of hydrologically similar sites. This large dataset allowed us to capture more hydrological points at the higher and lower ends of the discharge range which, at an individual catchment level, tend to be underrepresented when sampling frequency is low. Using this type of data, we found that TP, PO_4, TKN, and NO_3 concentrations typically increased with discharge, but these C-Q relationships were often complicated by threshold effects, hydrograph limb differences and, for NO_3, the seasonal influence of land use disturbance. Our catchments generally showed nearly flat or gently increasing C-Q slopes at lower flows, but a more pronounced concentrating effect above a seasonally variable discharge threshold. TP, PO_4, and TKN C-Q point to evidence of supply limitation and well-connected source pools, however the sources and pathways for NO_3 may be more heterogeneous.

From our analysis of C-Q relationships, we have made inferences about the dominant processes and flow pathways contributing nutrients to streams, which can potentially inform watershed management strategies. From our dataset, TP, PO_4, and TKN management should be largely focussed on high flow above seasonal discharge thresholds. NO_3 may be more difficult to manage on a regional scale, but land use will likely play an important role in catchment-specific mitigation strategies for this nutrient.

TP, PO_4, and TKN

The dominant regional behaviours of TP, PO_4, and TKN were characterized by similar non-linear seasonal C-Q patterns and hydrographic limb effects. Below-threshold C-Q slopes tended to be flat, or gently positively sloping in most seasons for TP, PO_4, and TKN (Figure 3.6), and we attributed this behaviour to in-stream biogeochemical processes, as suggested by the conceptual framework presented by Moatar et al. (2017). These may include processes such as decreases in biological assimilation or the release of sediment-bound nutrients as below-threshold flow increases. As our below-threshold nutrient dynamics are not hydrologically driven (Godsey et al. 2009; Li et al. 2017), management strategies aimed at decreasing low-flow or baseflow concentrations in Ontario streams should focus on reducing ambient in-stream concentrations, potentially through stream channel restoration projects focussed on increasing nutrient retention within the stream. The implementation of these types of strategies would be beneficial only if ambient (low-flow) concentrations are above levels of concern. Even so, it has been suggested that the successful reduction of baseflow nutrient concentrations has little overall impact on annual nutrient loads. Banner et al. (2009), for example, modelled a reduction in baseflow TP concentrations, and found that this reduced annual loads by less than 5%. Further, the effectiveness of stream channel restoration is not certain; Filoso and Palmer (2011), for example, reported that stream channel restorations, which focussed on in-stream processes to reduce nutrients, did not seem to have a significant impact on N concentrations. We did not find below-threshold dilution effects (negative C-Q slopes) in our region, however in these cases, management targeted at below-threshold discharge would be even less effective.

While C-Q thresholds for low-resolution data are rarely reported in the literature, there are a few studies that provide threshold-related results that suggest that flat or decreasing below-threshold C-Q slopes may be relatively common for TP, PO_4, and TKN; Moatar et al. (2017) reported that more than 90% of their French sites exhibited this behaviour for TP and PO_4 below Q_{50}, and other studies have assumed a flat below-threshold C-Q slope as well (Banner et al. 2009; Ali et al. 2017). Therefore, we believe that while individual stream C-Q relationships will vary to a certain degree, regional management strategies aimed at low flows (below-threshold) are likely not the most effective focus for mitigation of TP, PO_4, and TKN when baseflow concentrations are within water quality guidelines. In cases where a regional C-Q analysis shows strongly increasing below-threshold relationships, low-flow mitigation strategies that focus on in-stream processes may be of some benefit.

At high flows (above-threshold), TP, PO_4, and TKN C-Q relationships tended to be chemodynamic on the rising limb, increasing substantially with flow (Figure 3.6), suggesting a shift from in-stream biogeochemical to hydrological controls on nutrient dynamics (Moatar et al. 2017). This indicates that nutrient export from terrestrial sources becomes appreciable at higher flows, and the fact that this occurs primarily on the rising limb suggests that the sources of these nutrients connect relatively easily to the stream as event water increases (Creed et al. 2015). Event water delivered to streams is mainly composed of older water that has been stored in the catchment between events (Buttle 1994); newer event water displaces or mixes with this potentially nutrient-laden stored water, delivering it to the stream. A positive C-Q slope implies that these nutrient pools increase in concentration with increased disconnectedness with the stream; for example, the nutrient pools that only become connected to the stream during extreme high-flow events potentially have higher nutrient levels due to longer periods of accumulation between events. As discharge continues to increase, so too do the connections between nutrient pools and the stream, which further increase nutrient concentrations with discharge. These source pools may be limited, with nutrient concentration reaching its maximum before the discharge peak. We found evidence of this in our dataset, with most seasonal TP, PO_4, and TKN C-Q relationships showing evidence of greater nutrient concentrations on the rising limb of the hydrograph compared to the falling limb (Figure 3.6). This can not only be an indication of source limitation (Williams 1989), but also suggests that the sources become easily and directly connected to the stream as discharge increases (Creed et al. 2015), as previously mentioned.

That the bulk of annual nutrient loads occur during high-discharge events has been well documented (e.g., Andersen et al. 2006; Royer et al. 2006; Banner et al. 2009; Moatar et al. 2017), and the steeper the C-Q slope, the larger this annual proportion is (Banner et al. 2009). Therefore, we are confident that, in our study catchments, streams in which nutrient contamination is a concern would generally benefit most from above-threshold nutrient management that focusses on the reduction of nutrient inputs through hydrological pathways. These might include measures such as improving catchment hydrological connectivity to reduce nutrient build-up between events, and improving riparian vegetation to reduce runoff velocity and increase terrestrial nutrient uptake.

Since high-flow nutrient management is important for most temperate catchments, the next important consideration is defining what is considered “high flow.” We found that the definition of high flow, in terms of discharge thresholds, varied seasonally.

Banner et al. (2009) found TP thresholds between Q_6 and Q_{46}, while Moatar et al. (2017) used Q_{50} as a discharge breakpoint, however these breakpoints may only be relevant during certain times of the year. In our study, for example, autumn breakpoints occurred at much greater flows than the other seasons (Figure 3.6), which indicates that nutrient contamination is not such a large concern in this season except at extremely high flows (above Q_{10}). However, the above-threshold C-Q slope is much steeper than in other seasons, such that flows above Q_{10} will likely have considerably high nutrient export. This highlights the need for seasonally-based nutrient management.

Also of seasonal importance is the contributions of nutrients species through snowmelt. TP and TKN rising limb C-Q relationships do not show evidence of a discharge breakpoint, while the processes affecting PO_4 shifted at about Q_{20}. While all three of these nutrients are associated with overland flow (e.g., Cooke and Cooper 1988; House and Warwick 1998; Siwek et al. 2013; Lloyd et al. 2016), TP and TKN are composed of both dissolved and particulate fractions, while PO_4 is exclusively dissolved, thus the difference between the threshold behaviour (or lack thereof) of these nutrients may be due in part to nutrient form. A higher level of flow may be required, for example, to sufficiently mix with the older water in which PO_4 is stored before this nutrient spills into the stream in appreciable amounts, while TP and TKN may be more readily mobile. Regardless of the transport mechanism, these results suggest that while TP, PO_4, and TKN may benefit from similar seasonal watershed management during most of the year, snowmelt mitigation strategies may require a nutrient-specific approach.

NO_3

We found that NO_3 C-Q patterns differed from the other nutrients, with fewer threshold effects and added complexity from anthropogenic disturbance. This difference is not surprizing as, unlike the other nutrients, NO_3 is largely associated with groundwater and subsurface flow pathways (e.g., Bowes et al. 2009; Lloyd et al. 2016). No sufficient hydrograph limb influences were found for autumn and winter NO_3 C-Q slopes (Figure 3.7), which suggests that this nutrient is transport limited (Williams 1989). This would mean that NO_3 supply is not exhausted during events, which we would expect in more anthropogenically-influenced catchments due to fertilization and wastewater, however autumn and winter did not show these anthropogenic effects. We think it is more likely that there is instead heterogeneity of hysteresis behaviour across our catchments and events. Most studies focussing on hysteresis behaviour find that there is a dominant pattern type (clockwise or counter-clockwise) for TP, PO_4, and TKN across sites and events, however NO_3 rarely shows this same preference (Cooke and Cooper 1988; House and Warwick 1998; Butturini et al. 2006; Rodríguez-Blanco et al. 2013b; Lloyd et al. 2016; Long et al. 2017). Because of this, we suspected that, in autumn and winter at least, hysteretic NO_3 patterns were highly variable, which prevented us from postulating on the dominant regional supply pathway of this nutrient. Snowmelt and summer seasons, in contrast, showed a few hydrograph limb differences. These, however, tended to be found in the middle of the discharge range (Q_{60} to Q_{40}), with no consistent pattern between the seasons. There were also few similarities with the C-Q patterns found for other nutrients. Therefore, hysteresis heterogeneity likely extends across all seasons for NO_3. If similar rising and falling limb concentrations are indeed representative of regional NO_3 patterns, steps to reduce terrestrial source inputs may need to be taken, including projects such as creating riparian wetlands in areas of concern. However, if there is no dominant C-Q pattern across the province, it would be difficult to form a regional management plan for this nutrient, and a more catchment-specific approach may be required.

We found that the effect of anthropogenic disturbance, though present, was difficult to interpret. While there were many significant NO_3 differences between low and high anthropogenic land uses, rising limb C-Q slopes appear to be relatively similar, for the most part (Figure 3.8). When event water receded (falling limb), however, we did observe a more pronounced reduction in concentration in high disturbance catchments as discharge decreased. This more rapid decrease in NO_3 may indicate that this nutrient is primarily sourced from the terrestrial environment, with relatively low baseflow concentrations compared to more natural catchments. This was not unexpected, as agriculture and urban land uses are both associated with elevated NO_3 levels and different nutrient dynamics (e.g., Aguilera et al. 2012; Lapworth et al. 2013), however we were expecting to also find some evidence of chemostatic C-Q patterns in high-disturbance catchments. Nutrient C-Q relationships in intensive agricultural areas, for example, have shown chemostatic responses to flow across most of the discharge range due to “legacy” nutrients built up in the soils through years of fertilization (Basu et al. 2011). Because our study catchments tended to contain more agricultural than urban land (Table 3.1), we thought that this might influence our C-Q relationships. Additionally, NO_3 chemostasis has been reported in urban catchments as well, where chemostatic effects may be caused by a combination of high groundwater and high stormwater NO_3 (Long et al. 2014). The tendency of urban stormwater in highly impervious catchments to completely bypass riparian areas through stormwater drainage (Hogan and Walbridge 2007) may contribute to this effect. Interestingly, a study of intensive agricultural catchments in Manitoba, Canada did not find chemostasis at their sites, and suggested that the presence of legacy nutrients alone was not sufficient to result in discharge-invariant nutrient dynamics, particularly in catchments with seasonally variable hydrologic pathways (Ali et al. 2017). The lack of anthropogenic C-Q responses may also be due to the fact that our catchments, though largely agricultural, were also mixed, containing a mosaic of other land covers.

We observed below-threshold near-chemostasis in many cases for TP, PO_4, and TKN, however the management strategies for nutrients that show this discharge-invariance across the entire discharge range would require different management strategies. In the case of NO_3, for example, stream channel restoration aimed at improving denitrification rates would work poorly at high flows because absolute NO_3 losses to denitrification would be low compared to the volume of discharge water (Royer et al. 2004; Smith et al. 2006). Chemostasis tends to occur in catchments that have high ambient concentrations (Moatar et al. 2017); catchment management in these cases should therefore focus on terrestrial-based projects, such as working to reduce legacy nutrient stores and redirecting urban stormflow to riparian wetlands.

Conclusion

The identification of regional seasonal thresholds and slope patterns in C-Q relationships may be an important first step for water quality managers as it gives an indication of broad, regional patterns which can help to focus mitigation efforts. By examining overall C-Q patterns, inferences can be made about the dominant processes influencing solute concentrations, and at what point in the discharge range these tend to switch. We found that TP, PO_4, and TKN C-Q slopes generally increased substantially after a discharge exceedance threshold that varied seasonally, suggesting that management efforts should primarily focus on flows above these thresholds, and may require different strategies depending on season. NO_3 management may need to consider anthropogenic impacts during snowmelt and summer. Considering the connectedness of the catchments is also important, and nutrient control measures may benefit from either reducing the concentrations in solute pools that are only connected to the stream during high-flow events, or by improving the connection of these pools in the catchment to inhibit solute build-up between events.

In this study, we have used C-Q relationships as a diagnostic tool to help identify the dominant processes controlling nutrients in streams, but this procedure can be extended to other regions with low-frequency, long-term water quality data for the same purpose. While individual catchment processes will be variable across sites and events, identifying the dominant patterns will help watershed managers form regional policies to control nutrients.

Table 3.1. Summary of catchment landscape variables for the Ontario catchments.

Landscape Variable	**Minimum**	**Maximum**	**Mean**	**Median**
Longitude (DD)	-89.21	-74.49	-80.24	-79.83
Latitude (DD)	42.16	49.61	44.54	44.17
Catchment Area (km^2)	32	8532	501	210
Mean Elevation (m asl)	5	475	260	271
Mean Catchment Slope (%)	0.41	7.65	3.42	2.99
Main Channel Length (km)	15	380	72	54
Mean Channel Slope (%)	0.04	1.22	0.28	0.17
Catchment Area Affected by Dam (%)	0	100	32	10
Catchment Agriculture (%)	0	96	61	70
Catchment Forest (%)	0	96	22	10
Catchment Urban (%)	0	79	11	3
Catchment Wetland (%)	0	13	2	1
Catchment Open Water (%)	0	13	1	0.1
Mean Annual Temperature (°C)	1.28	9.72	6.53	6.80
Mean Annual Precipitation (mm)	688	1095	913	896
Mean Annual Discharge (m^3/km^2)	43	13357	2751	1657

Table 3.2. Discharge exceedance ranges contained within each exceedance bin.

Bin Number	**Bin Percentage**	**Exceedance Range (%)**
1	99.99	<99.9 to 99.99
2	99.9	<99 to 99.9
3	99	<95 to 99
4	95	<90 to 95
5	90	<80 to 90
6	80	<60 to 80
7	60	<40 to 60
8	40	<20 to 40
9	20	<10 to 20
10	10	<5 to 10
11	5	<1 to 5
12	1	<0.1 to 1
13	0.1	<0.01 to 0.1
14	0.01	>0.01

Figure 3.1. Ontario, Canada catchments used in regional concentration-discharge analysis.

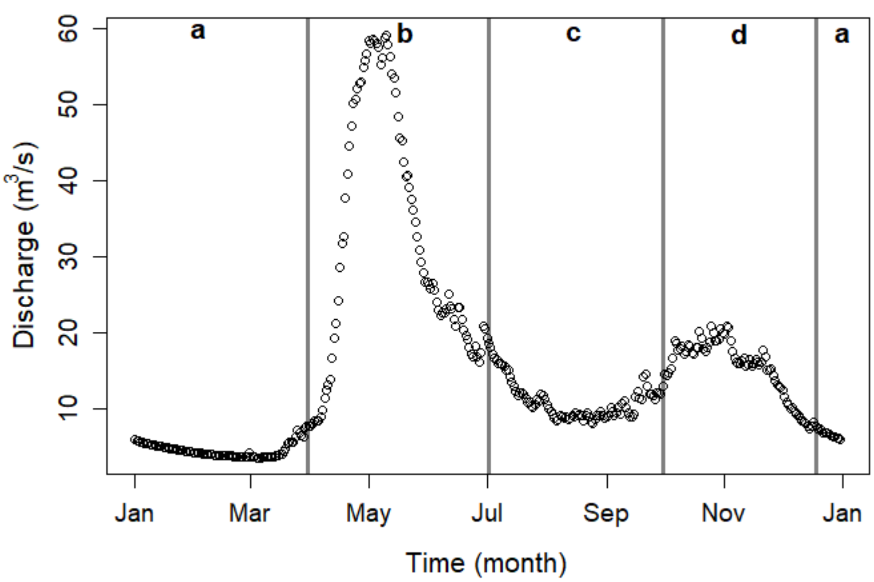

Figure 3.2. Example of hydrologic seasonal boundary definitions, with a) winter as the low flow period during the cold season, b) snowmelt as the point where discharge increases rapidly over time following winter, c) summer as the point where discharge begins to drop less dramatically following snowmelt, and d) the period of increased flows between summer and winter.

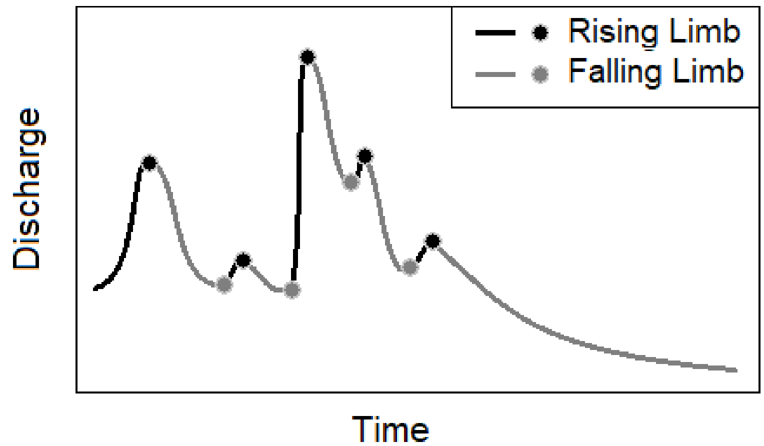

Figure 3.3. Conceptual diagram of differentiation between rising and falling hydrograph limbs used in this study. Discharge peaks were considered to be part of the rising limb, while discharge lows were considered part of the falling limb. Non-events, where mean daily discharge was equivalent to baseflow discharge (not shown) were not included in analysis.

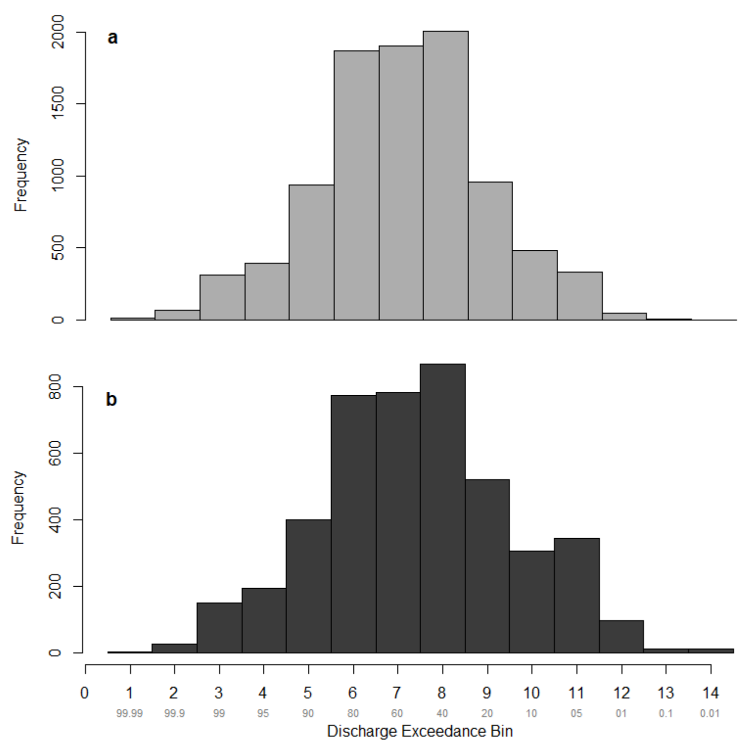

Figure 3.4. Number of data associated with each discharge exceedance bin for the a) falling limb and b) rising limb of the hydrograph. TP had the most samples (shown). PO_4, TKN, and NO_3 had slightly fewer samples, however data distribution was similar.

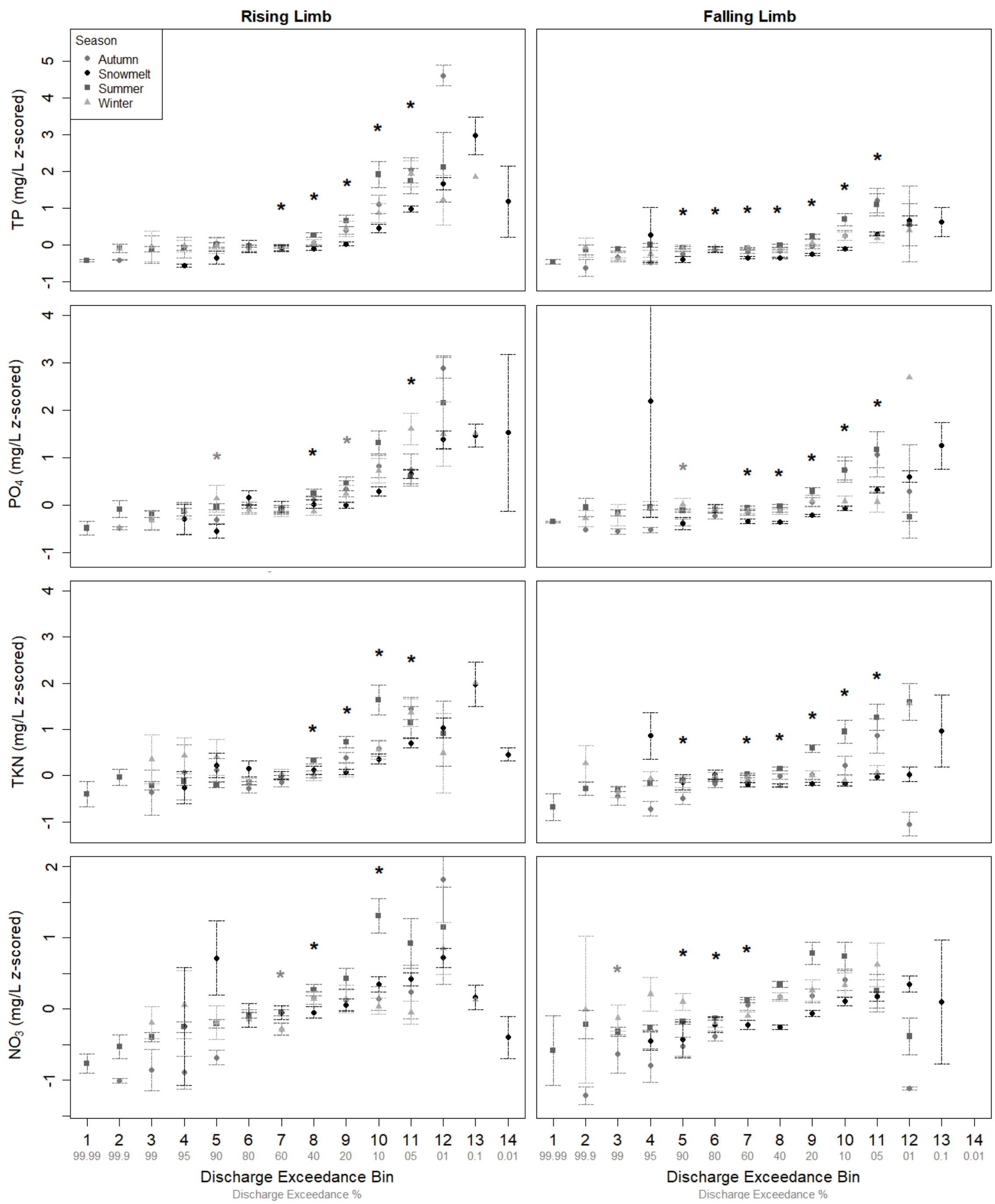

Figure 3.5. Seasonal C-Q relationships all nutrients on the rising (left) and falling (right) hydrograph limb. Asterisks denote significant differences between at least 2 seasons (Kruskal-Wallis tests) at a corrected alpha level of 0.05 (black) and 0.1 (grey) for individual discharge exceedance bins. Error bars represent standard errors. Points lacking error bars represent single measurements rather than averages.

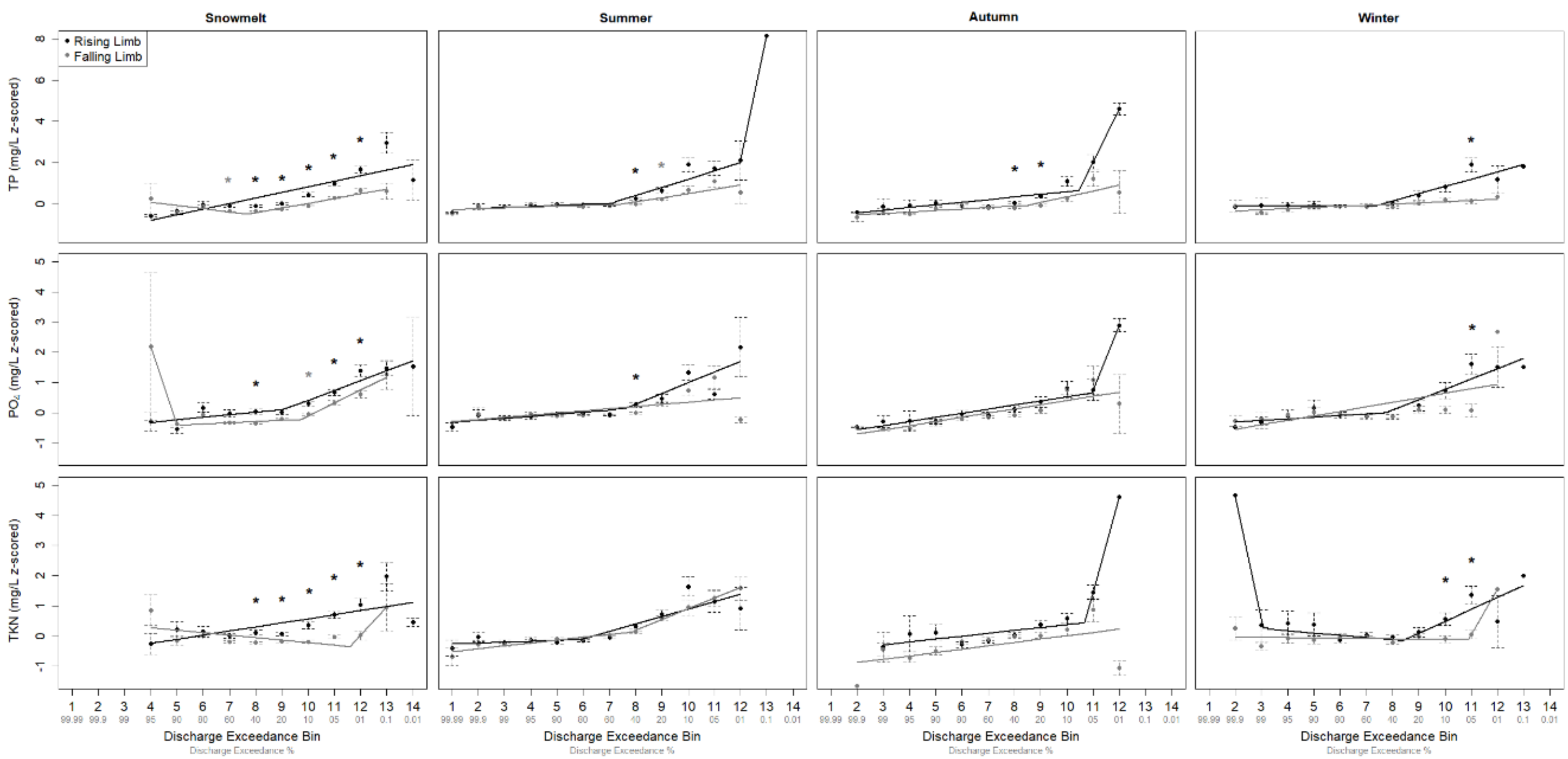

Figure 3.6. Regional concentration-discharge relationships for TP (top row), PO_4 (middle row), and TKN (bottom row) on both the rising (black) and falling (grey) hydrograph limb during each season (grouped by column, as labelled). Asterisks denote significant differences at a corrected alpha level of 0.05 (black) and 0.1 (grey) for individual discharge exceedance bins (Kruskal-Wallis tests). Error bars represent standard errors. Points lacking error bars represent single measurements rather than averages.

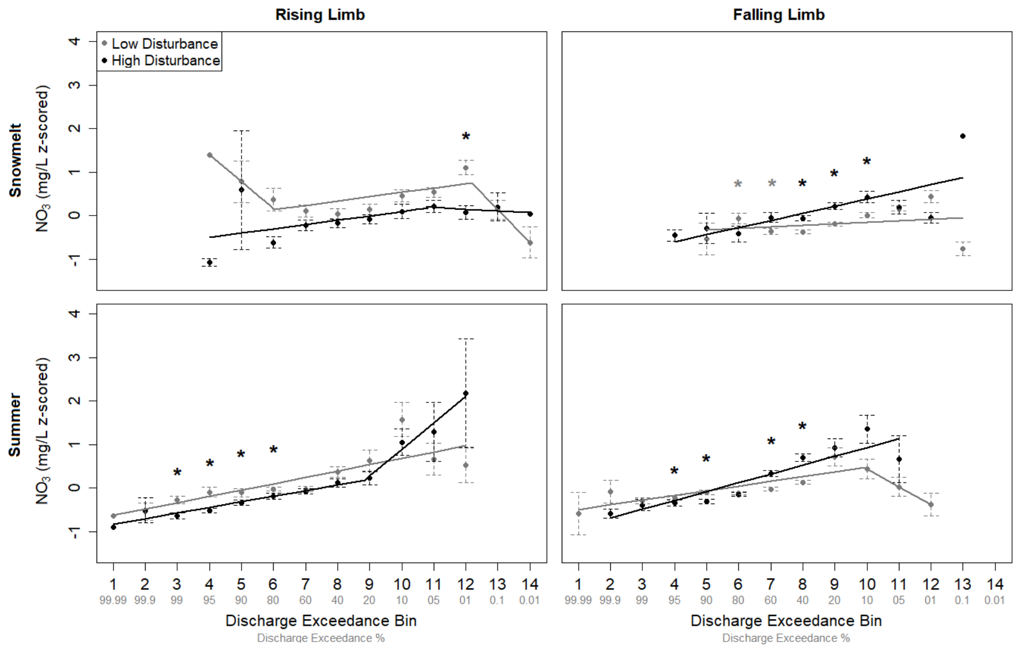

Figure 3.7. Regional NO_3 C-Q relationships for snowmelt (top row) and summer (bottom row) on the rising (left) and falling (right) hydrograph limb for catchments with low (grey) and high (black) anthropogenic disturbance (agricultural plus urban land use). Asterisks denote significant Kruskal-Wallis tests at a corrected alpha level of 0.05 (black) and 0.1 (grey) for individual discharge exceedance bins. Error bars represent standard errors. Points lacking error bars represent single measurements rather than averages.

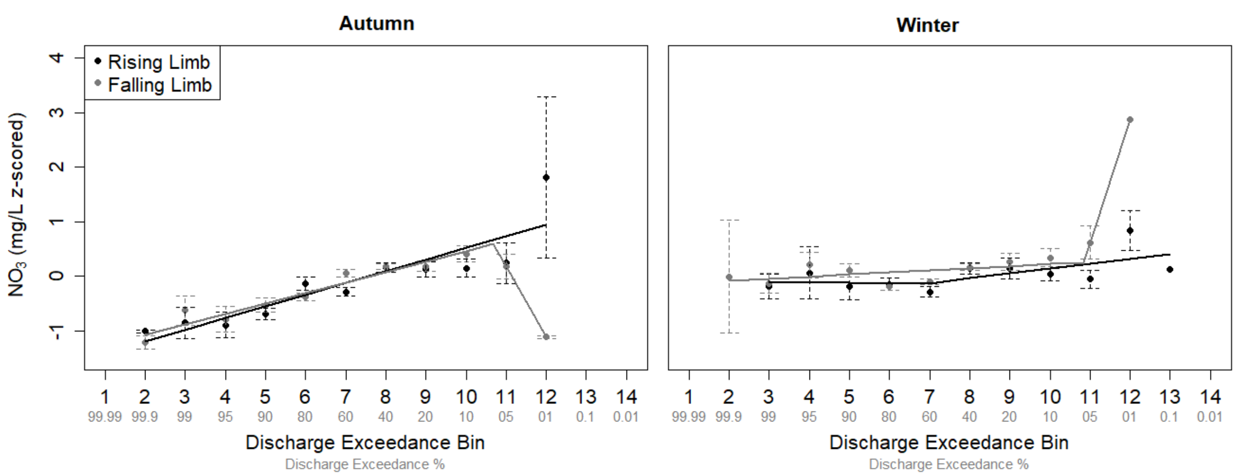

Figure 3.8. Regional NO_3 C-Q relationships for autumn (left) and winter (right) on both the rising (black) and falling (grey) hydrograph Error bars represent standard errors. Points lacking error bars represent single measurements rather than averages.

4.0 General Conclusion

In this thesis, we used long-term, low-resolution data for sites across Ontario to 1) assess how landscape variables influenced nutrient and carbon export during floods; and 2) characterize nutrient concentration-discharge (C-Q) relationships. Our findings show that landscape variables could partially explain the degree to which solute export increased with floods, depending on the hydrologic characteristic (duration, magnitude, or volume) and nutrient being tested. We also found that C-Q relationships were non-linear, but generally positive, with differences between rising and falling hydrograph limb relationships only observed for some solutes.

Floods are complex hydrological events, which differ in hydrologic characteristics (duration, magnitude, and volume) across catchments and events. In chapter one, we found that landscape variables were able to explain some of the relationships between nutrient export and these characteristics during Q_{10} floods. Large, steep catchments had higher nutrient export with increasing Q_{10} magnitude, suggesting that these streams are at the highest risk for nutrient contamination given a high-magnitude flood. Nutrient export relationships with duration and volume were not as strongly explained in the study, except for phosphate, which was influenced by a large number of landscape variables, suggesting that phosphate export is highly complex during floods. Q_1 flood export relationships with hydrologic characteristics were generally not well explained by landscape variables.

With this information we can begin to untangle how the landscape, along with other factors, influence nutrients. Physiographic variables have not received as much attention in the literature as land use and hydroclimate when it comes to flooding exports, but given their importance to hydrologic connectivity, they should be included in remediation and mitigation plans. Steeply sloped catchments, for example, may see the greatest benefit from mitigation, or should perhaps be subject to a greater degree of riparian protection. Our results also indicate the landscape effects on flooding export depend on the hydrologic characteristics of the flood, thus different export dynamics can be expected for different types of floods. There is already some indication that this is the case, as different precipitation and event types have been linked to different nutrient levels (Siwek et al. 2013; Bauwe et al. 2015). Our study has provided evidence that flooding discharge characteristics may also influence nutrients in certain landscapes.

C-Q dynamics were also addressed in this thesis, and we found that most nutrients had near-chemostatic or gently sloping C-Q relationships below a discharge threshold that varied seasonally, whereas there was a pronounced increase after this breakpoint, particularly on the rising limb. Rising limb concentrations were higher than those on the falling limb, which suggested supply-limitation and well-connected source pools. Nitrate C-Q relationships did not tend to follow the same pattern as other nutrients, and were also seasonally influenced by land use. Additionally, this nutrient did not show a difference in concentrations between limbs, either because these solutes are transport-limited, or because C-Q behaviour is heterogeneous between events and catchments. These results suggest that seasonal high-flow management at a regional scale would be beneficial for most nutrients in areas of concern, but different strategies would be required for nitrate.

In these studies, we have successfully used long-term, low-resolution data to identify general patterns and relationships between hydrology and nutrients, which enhances our understanding of discharge and flood effects on nutrients and provide valuable information which will be helpful for managing the ecological effects of flooding.

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