# The role of wetland coverage within the near-stream zone in predicting of seasonal stream export chemistry from forested headwater catchments

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**Abstract**

Stream chemistry is often used to infer catchment-scale biogeochemical processes. However, biogeochemical cycling in the near-stream zone or hydrologically-connected areas may exert a stronger influence on stream chemistry compared with cycling processes occurring in more distal parts of the catchment, particularly in dry seasons and in dry years. In this study, we tested the hypotheses that near-stream wetland proportion is a better predictor of seasonal (winter, spring, summer and fall) stream chemistry compared with whole-catchment averages and that these relationships are stronger in dryer periods with lower hydrologic connectivity. We evaluated relationships between catchment wetland proportion and 16-year average seasonal flow-weighted concentrations of both biogeochemically-active nutrients, dissolved organic carbon (DOC), nitrate ($NO_3$-N), total phosphorus (TP), as well as weathering products, calcium (Ca), magnesium (Mg), at ten headwater (< 200 ha) forested catchments in south-central Ontario, Canada. Wetland proportion across the entire catchment was the best predictor of DOC and TP in all seasons and years, whereas predictions of $NO_3$-N concentrations improved when only the proportion of wetland within the near-stream zone was considered. This was particularly the case during dry years and dry seasons such as summer. In contrast, Ca and Mg showed no relationship with catchment wetland proportion at any scale or in any season. In forested headwater catchments, variable hydrologic connectivity of source areas to streams alters the role of the near-stream zone environment, particularly during dry periods. The results also suggest that extent of riparian zone control may vary under changing patterns of hydrological connectivity. Predictions of biogeochemically-active nutrients, particularly $NO_3$-N, can be improved by including near-stream zone catchment morphology in landscape models.

Keywords: Canadian Shield; forested wetlands; nitrate; total phosphorus; dissolved organic carbon; wetlands

## 1. Introduction

Topography is an important control on hydrologic connectivity in forested landscapes, influencing runoff, flowpaths and water drainage, which in turn govern stream chemistry in two important ways. First, rates of catchment biogeochemical processes that are sensitive to soil moisture, temperature and redox conditions will fluctuate as areas of the landscape wet up or dry out (Lohse *et al.*, 2009). Second, transport of the products of these reactions is mediated by the connection of catchment source areas to the stream via the movement of water (Kirchner *et al.*, 1992). Predicting stream chemistry based on catchment characteristics is useful as it provides insight into controls on terrestrial biogeochemical processes and allows extrapolation of the trends observed at small, long-term study catchments to ungauged catchments and the broader landscape (Smart *et al.*, 2001; Laudon *et al.*, 2012). Understanding the influence of the distribution of landscape units on stream chemistry can allow for targeted sampling of key biogeochemical processes. For example, mineralization and nitrification rates in upland forest soils may be important to quantify for terrestrial nitrogen (N) budgets, but are unlikely to influence stream nitrate ($NO_3$-N) concentrations unless those upland source areas are hydrologically connected to the stream (Ross *et al.*, 2012; Casson *et al.*, 2014). Understanding the role of the near-stream zone for modifying water quality is also critical from a management perspective, as it can inform decisions around buffer zone sizing and stream-set back requirements for development and forest harvesting projects (Lee *et al.*, 2004).

Hydrological transfer from catchment source areas to the stream is the predominant source of solutes in many headwater forested streams (Vannote *et al.*, 1980). Thus, connectivity of these source areas to the stream may control variability in stream chemistry (Zimmer *et al.*, 2013). Transport of these solutes can be seen as a combination of "conservative export", driven by the movement of water and "reactive export", where changes in concentrations are driven by biogeochemical processes (Petrone *et al.*, 2007; Basu *et al.*, 2010). Some solutes, such as weathering products including calcium (Ca) and magnesium (Mg), often behave as chemostats, where concentrations are relatively invariable through time, even under different flow conditions (Godsey *et al.*, 2009). For other solutes such as carbon (C), N, or phosphorus (P), where biogeochemical reactions are strongly mediated by redox or moisture limitations, concentrations will be variable in response to changes in connectivity patterns. A study at the Krycklan catchment in Sweden demonstrated that heterogeneity in catchment water flow and soil moisture controlled delivery of total organic C to the riparian zone, which regulated stream chemistry (Grabs *et al.*, 2012). Flowpaths connecting source areas to the stream will vary with changing runoff and air temperature patterns, thereby contributing to variability in stream chemistry (Köhler *et al.*, 2009). Both models (Stieglitz *et al.*, 2003) and conceptual frameworks (Buttle, 2006) suggest that the topographic influences on solute mobility between hillslopes and streams become less important as catchments dry out seasonally.

In south-central Ontario, proximal catchments with similar atmospheric deposition, forest cover, climate and bedrock vary widely in concentrations of biogeochemically active nutrients, including DOC, $NO_3$-N and TP (Dillon and Molot, 1997; Schiff *et al.*, 2002; Creed and Beall, 2009; O'Brien *et al.*, 2013). These differences in solute concentration are often ascribed to differences in catchment wetland proportion, which is widely used as a predictor of stream DOC and TP, both within south-central Ontario and across northern boreal and

temperate forests (Dillon and Molot, 1997; Creed *et al.*, 2008; Laudon *et al.*, 2012) Similarly, catchment topography and wetland proportion have been suggested to be equally important drivers of stream $NO_3$-N, as steeper slopes in the near-stream zone allow $NO_3$-N to bypass organic rich soils in wetlands and riparian areas where $NO_3$-N may be otherwise consumed (Casson *et al.*, 2014; Enanga *et al.*, 2017), thereby enriching groundwater $NO_3$-N export (Schiff *et al.*, 2002). Observations such as these suggest that wetlands that are hydrologically connected to the stream may exert an outsized influence on biogeochemically active elements such as DOC, $NO_3$-N and TP, which are strongly influenced by redox or moisture limitations. In contrast, base cations such as Ca and Mg are either produced via weathering or enter the catchment via deposition (Watmough and, Dillon 2003), and thus the proportion and distribution of wetlands may be less important in determining stream concentration dynamics.

Riparian zones are hydrological source areas that remain connected to the stream even under dry conditions and during dry seasons (Johnson *et al.*, 1997; Hooper *et al.*, 1998; Stieglitz *et al.*, 2003). Seasonal dryness therefore offers the potential to test the hypothesis of hydrologic connectivity, as relationships between near-stream topographic features including riparian wetlands and stream water chemistry should be clearest during the summer and in dry years, when low flow conditions limit hydrologic connectivity to the near-stream zone. In contrast, wet years, and higher flow seasons (e.g. spring) should show weaker correlations between near-stream wetland proportion and solute export at the catchment outlet, as a result of a larger contributing area. Furthermore, unlike DOC, $NO_3$-N and TP, weathering products like Ca and Mg are expected to show weak or negligible relationships with wetland proportion in geologically similar catchments, and relationships with wetland proportion should not improve in dry years.

The objective of this study was to test these hypotheses and investigate the predictive power of wetland proportion in the near-stream zone vs wetland proportion in the whole catchment for estimating solute concentrations. To address this question, we quantified relationships between annual and seasonal stream water quality (TP, DOC, $NO_3$-N, Ca and Mg concentrations) and wetland coverage at 10 forested catchments in central Ontario, and then investigated how these relationships change when considering a) biogeochemically active (DOC, $NO_3$-N, TP) vs. weathering products (Ca, Mg), b) seasonal concentrations; c) dry years; and d) wetland proportion only in the near-stream zone (i.e. within 20m of the stream channel).

## 2. Methods

### *2.1 Study area*

Relationships between wetland proportion extent and stream chemistry were investigated at 10 forested headwater catchments (Harp (HP)3, HP3A, HP4, HP5, HP6, HP6A, Dickie (DE)6, DE8, DE10 and Plastic (PC)1) located in the Muskoka-Haliburton district of south-central Ontario, within a 50 km radius of Dorset, Ontario (45°13'N, 78°56'W) (Figure 1). These catchments have been monitored for streamflow and water chemistry by the Ontario Ministry of the Environment and Climate Change (OMOECC), Dorset Environmental Science Centre (DESC), since the mid-1970s. The study catchments range in size from 10.0 (HP6) to 191 ha (HP5) (Table 1). The catchments are situated on the Precambrian Shield, where bedrock consists of biotite granite and hornblende gneiss, with some amphibolite and schist (Watmough and Dillon, 2003). Surficial geology ranges from exposed bedrock, thin till (< 1m thick) interrupted by rock ridges, to plains with continuous till cover 1 - 10 m thick (Devito *et al.*, 1999).

The catchments are part of the Great Lakes St. Lawrence forest region, and upland areas are covered by mixed hardwood forests dominated by sugar maple (*Acer saccharum*), although white pine (*Pinus strobus*) is dominant in some catchments (e.g. PC1). Soils are mainly acidic brunisols (cambisols) and podzols (Jeffries and Snyder, 1983; Soil Classification Working Group, 1998) and are generally thin and sandy. Wetlands in this area are located in low-lying topographic depressions, and are generally treed *Sphagnum* swamps dominated by a mixture of deciduous (e.g. *Acer rubrum, Betula alleghaniensis, Fraxinus nigra*) and coniferous species (e.g. *Pinus strobus, Tsuga canadensis, Abies balsamea, Thuja occidentalis*, *Picea mariana* and *Larix laricina*) (Watmough *et al.*, 2004). Wetland soils are gleysols and histosols (Jeffries and Snyder, 1983; Soil Classification Working Group, 1998).

*2.2 Spatial data analysis*

All spatial analyses were performed using pre-processed Light Detection and Ranging (LiDAR)-derived digital elevation models (DEMs) ($1m^2$ grid size) of each catchment in the open source GIS SAGA (System for Automated Geoscientfic Analyses). Wetland areas were taken from (Richardson *et al.*, 2009), where a hydrogeomorphic edge detection algorithm was used to delineate wetlands at these sites based on the same LiDAR data used in the present study.

The stream channels were estimated in SAGA using a constant proportion of catchment area as the initiation threshold needed to begin a channel. The proportion was set to match both personal observations combined with inspections of other published maps of the catchments. Observations of stream channel length were made during the snow-free season, when the ground was visible, meaning that stream channels were mostly observed during the drier part of the year (i.e. summer and early fall). Once stream channels were delineated, a buffer zone extending perpendicular from the centre of each stream at a distance of 20m was mapped

(Figure 2). This is an approach that has been used extensively in other studies of stream and lake chemistry to estimate the influence of adjacent features (Baker *et al.*, 2006; Soranno *et al.*, 2015). The distance of 20m was chosen based on a review of forest management guidelines which suggested that mean riparian buffer widths varied from 15.1 to 29.0 m in jurisdictions across North America (Lee *et al.*, 2004). Percent wetland proportion was computed both across the entire catchment and within 20 m of the stream.

*2.3 Chemical and runoff parameters*

The 10 streams have been historically sampled at a weir located at each catchment outlet on a weekly to bi-weekly basis. For this study, data from 1 June 1981 to 31 May 1997 were considered as this time period was the longest, continuous period when all catchments had a complete and reliable hydrological record, and relatively high frequency of chemical sampling (average sample frequency = 1 sample per 4.5 days). Flow-weighted concentrations of DOC, $NO_3$-N, TP, Ca and Mg were determined using methods described in (Ontario Ministry of the Environment, 1983). Discharge was monitored continuously at all catchment outflows, and used to calculate long-term average seasonal runoff. Long-term average volume-weighted annual (based on water year beginning on June 1) and seasonal concentrations of all analytes were calculated for each catchment following (Eimers *et al.*, 2008) with the seasons defined as: winter (December 1 – February 28), spring (March 1 – May 31), summer (June 1 – August 31) and fall (September 1 – November 30). These averages were calculated both for the full 16-year record and for dry years, defined as years where summer and fall runoff were less than the 33$^{rd}$ percentile (i.e. the 5 driest years on record) (Figure 3; Supplementary Table 1). This definition was based on other studies in the region examining the importance of no- or low-flow conditions during summer and fall in determining annual stream solute behavior (e.g. Eimers and Dillon., 2002; Senar *et al.*, 2018).

*2.4 Statistical analysis*

Relationships between flow-weighted stream solute concentrations (annual and seasonal, both using the full record and only the dry years) and wetland proportions (both across the whole catchment and with 20m of the stream channel) were assessed using simple linear regression models where $\alpha$=0.05. The $NO_3$-N and TP concentration data were log-transformed to meet the conditions of normality; all other solute and catchment data were assessed to be normally distributed based on a Shapiro-Wilks test ($\alpha$=0.05). Models were evaluated based on an information-theoretic approach (Burnham and Anderson 1998) using Akaike's Information Criterion (AIC). The difference between the catchment model and the 20m model, the model using only dry years and the 20m model using only dry years were calculated as $\Delta$AIC. Models were considered to have substantially more support than those using all years of stream solute chemistry and the catchment wetland proportion if $\Delta AIC < -2$ (Wagenmakers and Farrell, 2004). All statistical tests were implemented in R (R Core Team, 2017).

## 3. Results

*3.1 Predicting annual and seasonal stream chemistry*

The proportion of wetland in the catchment was an excellent predictor of annual flow-weighted DOC concentrations ($r^2$=0.96; $p<0.001$) (Table 2). For $NO_3$-N and TP, the amount of variance explained was less in all cases than for DOC ($r^2$ = 0.71 and 0.55, respectively). The relationship between TP and wetland proportion was leveraged by one site with high TP and high wetland proportion (DE6). If this site was removed, the relationship was no longer significant (p=0.32). There were no significant relationships between annual flow-weighted Mg or Ca concentrations and wetland proportion (p = 0.58 and p=0.16, respectively).

Wetland proportion was a strong predictor of flow-weighted DOC concentration in each season, and although the AIC values suggest that the winter and spring models are stronger than the annual model, and the summer and fall models are not as strong (Table 3), there was consistently a high proportion of variance explained ($r^2$ values ranging from 0.89 to 0.97; Table 2). Similarly, the models predicting winter and spring TP from catchment wetland proportion had more support than the annual model, although without the DE6 catchment, none of these relationships were significant. Seasonal flow-weighted $NO_3$-N concentrations were significantly related to catchment wetland proportions, although both the $r^2$ values (ranging from 0.59 to 0.65) and the ΔAIC values suggested that these models were not as strong as the annual model. Similar to the annual data, there were no significant relationships between seasonal flow-weighted Ca or Mg concentrations and wetland proportion (Table 2).

### *3.2 Predicting stream chemistry in dry years*

There was considerable inter-annual variability in all solutes, with Ca and Mg displaying the highest degree of coherence among catchments, particularly during dry years (Figure 3). The response of the other three solutes to dry years was not consistent among catchments, and did not depend on catchment wetland proportion. For $NO_3$-N the catchments which showed the least coherence during dry years were generally the ones where the proportion of wetlands in the near-stream zone deviated the furthest from the proportion of wetlands across the whole catchment (i.e. HP3, HP5, HP6A and DE8) (Table 1; Figure 3). This pattern was not evident for DOC or TP; for both of these solutes, the patterns among catchments were not related to whether or not it was a dry year.

The relationships between wetland proportion and stream chemistry remained largely unchanged in dry years (Table 3). Wetland proportion was a strong predictor of seasonal flow-weighted DOC concentrations, and similar to the results with all years included, the

winter and spring models had more support than the annual model (Table 3). The results were again similar for TP, with stronger models in the winter and spring, although the $r^2$ values were again much lower than for DOC (ranging from 0.41 to 0.48), and again the relationships were only significant if the DE6 catchment was included. Prediction of $NO_3$-N was substantially weaker in all seasons in dry years, and particularly poor during the fall and summer (Table 3). There were no significant relationships between flow-weighted Ca or Mg concentrations and wetland proportion during dry years (Table 2).

*3.3Predicting stream chemistry using near-stream wetland proportion*

In general, wetland proportion within 20m of the stream was a better predictor of flow-weighted $NO_3$-N concentrations, particularly in dry seasons or years, but a weaker predictor of DOC and TP. Although the relationships remained significant with DOC, the amount of variance explained by wetland proportion within 20m of the streams decreased, both when considering the full record ($r^2$ values ranging from 0.81 to 0.84; Table 2) and considering dry years only ($r^2$ values ranging from 0.73 to 0.86). Using the 20m buffer also substantially increased the model AIC values in all cases (Table 3). The opposite held true for $NO_3$, where AIC values decreased in all cases except the fall, and $r^2$ values increased in winter and summer when considering the full record (to 0.78 and 0.77, respectively; Table 3 2). During dry years, the $r^2$ values increased in winter and summer (to 0.76 and 0.75, respectively), and the AIC values decreased during winter and spring. The results for TP followed a similar pattern to DOC, where using the 20m buffer did not result in substantial improvements. Using a 20m buffer did not result in significant relationships between wetland proportion and flow-weighted Ca or Mg concentrations (Table 2).

## 4. Discussion

The results of this study demonstrate that while wetland proportion is a good predictor of biogeochemically active solutes (DOC, $NO_3$-N and TP), the strength of these relationships declines under dry conditions, including drier seasons (e.g. summer or fall) and during dry years. This is particularly the case for $NO_3$-N; relationships between wetland proportion and DOC remain robust regardless of season and the relationships with TP had marginal explanatory power. To test the hypothesis that near-stream wetland proportion exerts a strong control over stream chemistry, we compared relationships between wetland proportion within 20m of the stream and flow-weighted DOC, $NO_3$-N and TP concentrations with ones where catchment wetland proportion was the predictor. In general, near-stream wetland proportion was a worse predictor of DOC and TP, and a better predictor of $NO_3$-N. For Ca and Mg, there were no significant relationships observed under any of the conditions tested in this study. Stream nutrient dynamics depend on both catchment biogeochemical processes and hydrological transport. The different behaviors of solutes in this study can give insight into both of these sets of processes under varying wetness conditions.

A strong relationship between average wetland cover in catchments and DOC has been reported in other studies (Clair *et al.*, 1994; Dillon and Molot, 1996; Creed *et al.*, 2008) and is particularly robust when wetlands are mapped using digital terrain analysis of high resolution data (Creed *et al.*, 2003; Richardson *et al.*, 2009). Forested wetlands are major stores of carbon, as high soil moisture and low oxygen availability result in slow decomposition rates. In contrast, DOC produced in upland areas is generally adsorbed onto subsurface mineral soils and/or mineralized to carbon dioxide, and so uplands are generally a minor source of stream DOC compared with wetlands (Schiff *et al.*, 1998; Webster *et al.*, 2008). Work from other regions has suggested that organic matter accumulation within riparian zones may be

the major source of DOC to streams (Ledesma *et al.*, 2015), particularly during dry periods when the stream may become hydrologically disconnected from more distal wetlands (McGlynn and McDonnell, 2003). The weaker models using just wetland proportion in the near-stream zone is a somewhat surprising result from this work; this perhaps suggests that the fixed 20m buffer width is not adequately capturing the riparian zone, which can be substantially more dynamic under changing patterns of hydrological connectivity (Liu *et al.*, 2014).

Previous work in the study region has found that TP loading to streams is correlated with wetland extent (Dillon and Molot, 1997). This study similarly found that annual TP concentrations were correlated with wetland proportion. However, the strength of this relationship was likely driven by one site with very high TP concentrations and a large proportion of wetland (DE6). Without this site, TP was not significantly correlated with any topographic measure. This suggests that factors other than wetland cover influence TP concentrations at these sites. O'Brien *et al.*, (2013) found that although TP concentrations were high directly below a small, discrete wetland, they were not detected at the catchment outlet, suggesting that P released from wetlands may be biologically processed within the stream channel or that it may be adsorbed to mineral soils via deeper flow paths. Weak correlations between average TP and DOC across sites (when the DE sites are removed) also suggest that wetlands are not solely responsible for TP stream export (Eimers *et al.*, 2009). Deposition and weathering of P-containing minerals are two non-wetland sources of inorganic P; deposition is relatively constant across the region, but localized pockets of apatite may result in differences in P-weathering amongst catchments (Eimers *et al.*, 2009; Casson *et al.*, 2012; O'Brien *et al.*, 2013). Furthermore, P export from these catchments is

very sensitive to forest and wetland disturbance, which may complicate the observed relationships with wetland proportion (Pinder *et al.*, 2014; Crossman *et al.*, 2016)

There was an overall negative relationship between wetland area and $NO_3$-N concentrations, likely driven by net production in upland soils and net consumption in wetlands as is documented in the literature (Devito *et al.*, 1999; Schiff *et al.*, 2002; Creed and Beall, 2009). These processes persist under the snowpack, leading to strong negative relationships between wetlands and $NO_3$-N even during the winter and spring (Casson *et al.*, 2014; Enanga *et al.*, 2016). However, this relationship did not hold during the fall or either annually or seasonally during dry years. This pattern may be due to the fact that many N transformations including nitrification and denitrification are redox dependent, and therefore during dry periods, the wetlands may not consume as much $NO_3$-N and/or produce more $NO_3$-N. These shifts in N behavior in riparian zones and wetland soils have been well documented in the literature, and understanding what controls these complex dynamics remains one of the challenges in N catchment biogeochemistry (e.g. McClain *et al.*, 2003; Burt *et al.*, 2010).

In all cases, these relationships were improved by considering near-stream wetland proportion, suggesting that N transformations occurring in the riparian zone exert a strong influence over stream $NO_3$-N dynamics. Furthermore, while there was a correlation between catchment wetland proportion and near-stream zone wetland proportion, the catchments that deviated from this relationship also showed the biggest deviations in $NO_3$-N dynamics, further suggesting that differences in the near-stream zone are important for predicting patterns of stream $NO_3$-N concentrations. These observations are consistent with the field-based observations by Ross *et al.*, (2012), where stream concentrations were more related to measurements taken near the stream than across the whole catchment. It is also important to note that the relationship between wetland proportion and $NO_3$-N concentrations is much

stronger in upland dominated catchments, because wetland dominated catchments generally have low and less variable $NO_3$-N concentrations. Catchments with large wetlands near the stream channel, like the DE catchments may have high rates of $NO_3$-N production in mineral soils that are comparable with upland-dominated catchments (Casson *et al.*, 2014; Enanga *et al.*, 2017), but stream outlet concentrations are much lower because of attenuation by wetlands located near the stream.

Stream export of Ca and Mg is subject to a different set of controls compared with DOC, $NO_3$-N and TP. Concentrations of these solutes are largely invariant through time, especially compared with water fluxes (Godsey *et al.*, 2009). Much of the work on base cation dynamics in these catchments has been motivated by the legacy of acid deposition in the study region. Not only are the trends in export coherent through time, the long-term annual averages of these solutes are remarkably similar amongst catchments (Watmough and Dillon, 2003). Given that upland, mineral soils are the primary sites for weathering fluxes of Ca and Mg, it is perhaps surprising that sites with a higher proportion of wetland (and therefore a lower proportion of mineral soils) do not have lower export of these solutes. Indeed, this has been observed at the Krycklan catchment in Sweden, where differences in landscape element type were related to spatial variability in base cation concentrations (Ledesma *et al.*, 2013). However, in the study region, base cation weathering rates are low and tree growth is often limited by Ca availability (Reid and Watmough, 2016). Mineralogy and till depth exert a greater control on base cation weathering and hence stream export (Watmough and Dillon, 2003). Although surficial geology is regionally consistent (Jeffries and Snyder, 1983), small-scale variation in these two factors can be substantial among catchments (Buttle and Eimers 2009). . Furthermore, cycling and transport of Ca and Mg are less sensitive to redox

conditions compared with the other solutes considered in this study, and thus do not vary as substantially with landscape position and climate.

The statistical approach to evaluating the importance of the near-stream zone on stream solute chemistry used in this study has limitations, but nonetheless sets up a conceptual model that can be tested with future, process-based studies. Using a fixed buffer width does not account for the dynamic nature of the riparian zone, which in particular can expand and contract with varying hydrological conditions (Ledesma *et al.*, 2013; Liu *et al.*, 2014). While this fixed buffer width approach was chosen based on forest management guidelines, future studies could incorporate a dynamic definition with widths defined by field-based measurements. The approach taken in this paper does not account for changes to in-stream processing that may be associated with changing hydrological conditions (Doyle 2005). This is particularly important for TP dynamics in catchments with substantial stream segments (O'Brien *et al*., 2013). Finally, this study does not take into account the relatively position of landscape units within the catchment (Gannon *et al.*, 2015). Future studies could investigate the ways in which different patterns of hydrological connectivity among landscape units result in climate-sensitive variability in stream solute concentrations.

## 5. Conclusions

In headwater catchments of southern Ontario, wetland proportion is a good predictor of biogeochemically-active solutes, including DOC, TP and $NO_3$-N. Concentrations of solutes derived from weathering processes (e.g. Ca, Mg) are less variable and do not depend on catchment wetland proportion. The relationships with DOC, TP and $NO_3$-N are mediated by hydrological and climatic variability. During dry seasons, especially the summer, or dry years, wetland proportion in the near-stream zone is a better predictor of $NO_3$-N concentrations than the wetland proportion across the whole catchment. These results

emphasize that using long-term annual average values for solutes can mask seasonal and inter-annual variability, particularly in solutes that are driven by climatic processes. Furthermore, these results suggest that care should be taken when relating point-based measurements of catchment biogeochemical processes to stream chemistry. This simple, linear regression-based approach is descriptive, but can set up future, process-based studies investigating the mechanisms between the observed patterns. Biogeochemical processes are notoriously heterogeneous in space and time, but using this type of framework can help predict where and when hot spots of nutrient cycling activity might occur and will allow researchers to tailor sampling protocols to address the appropriate questions.

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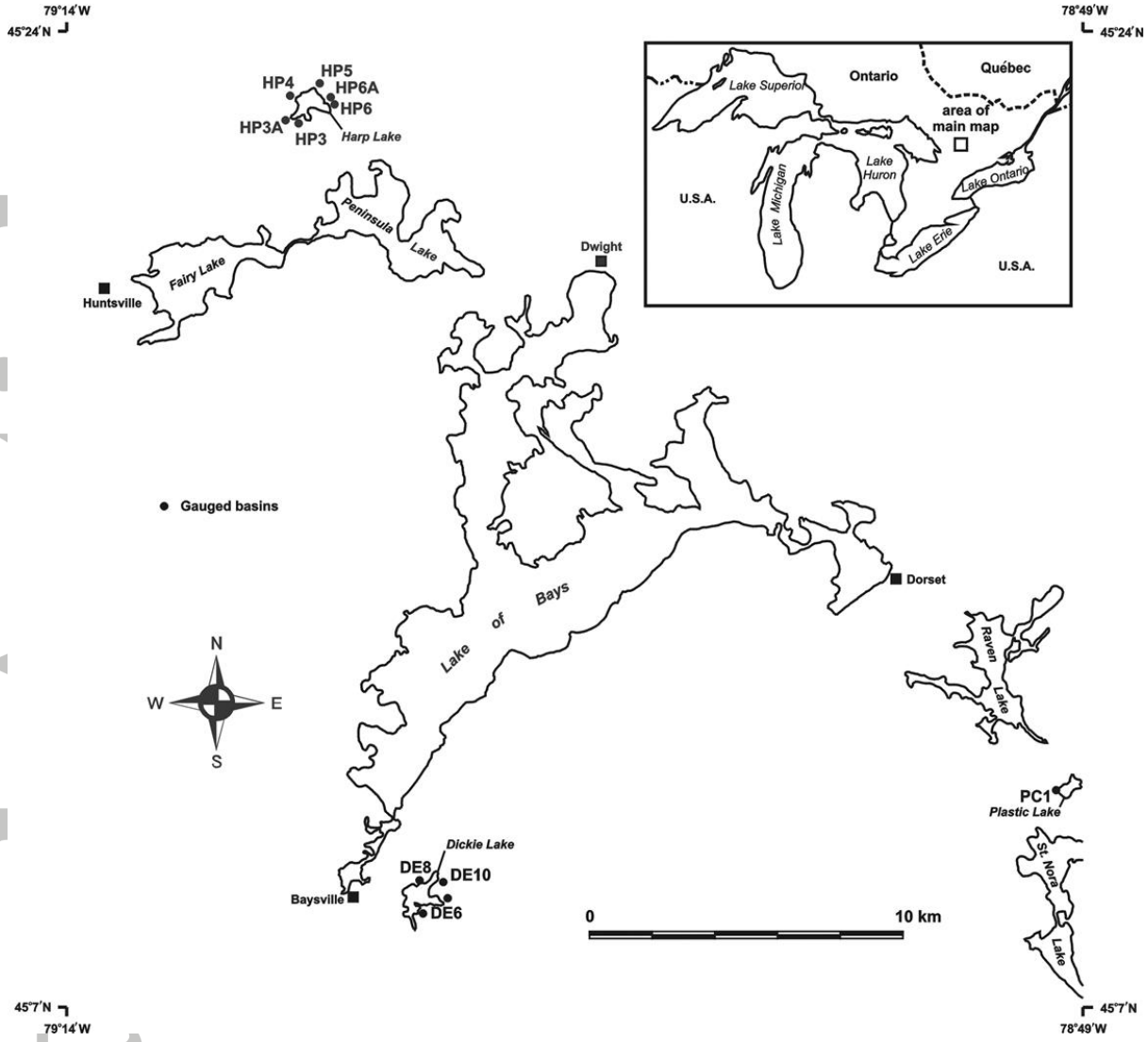


**Figure 1:** Study area

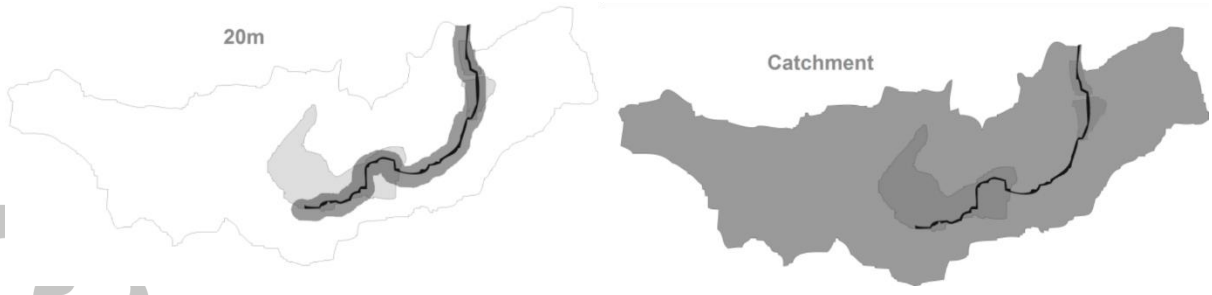


**Figure 2:** Example of buffer zone delineation (Harp 3). The buffer zone extends out from the stream channel by 20m on both sides. Wetlands are shown in light grey, the buffer zone is shown in dark grey and the stream channel is shown in black. Total wetland percentage was calculated both across the whole catchment and within the 20m buffer zone.

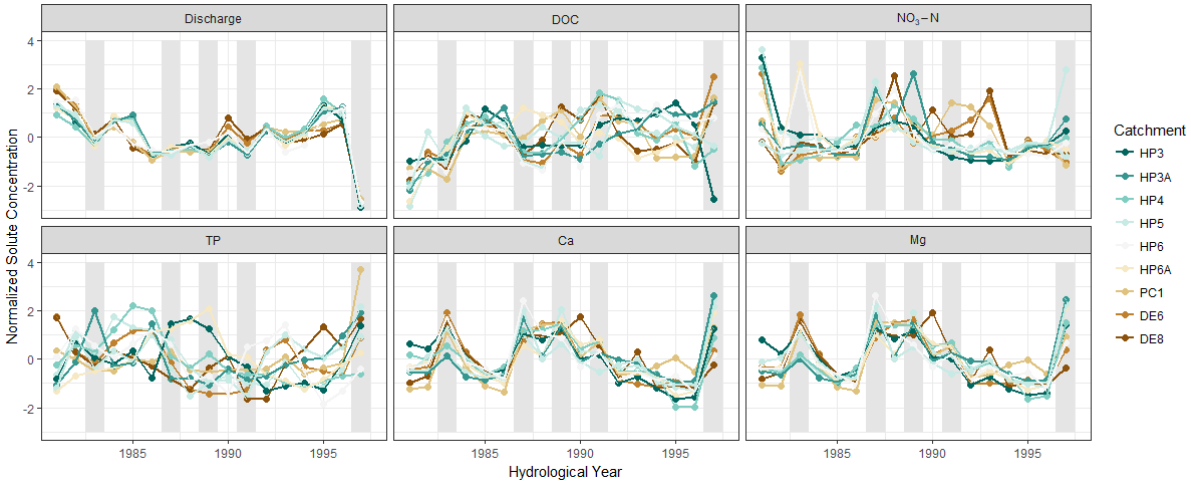


**Figure 3:** Normalized (z-score) solute concentrations for DOC, $NO_3$-N, TP, Ca and Mg from 1981 to 1997. Dry years (identified as years where the fall and summer runoff was less than the 33$^{rd}$ percentile) are indicated with light grey bars.

**Table 1:** Catchment area, wetland proportion, across the whole catchment, wetland proportion within the near-stream zone and residuals of the linear relationship between the two wetland proportion for the 10 study catchments.

| Catchment | Area (ha) | Catchment wetland proportion (%) | Near-stream zone wetland proportion (%) | Residuals of catchment wetland ~ near-stream zone wetland relationship |
|---|---|---|---|---|
| HP3 | 26.0 | 8.6 | 56.0 | 25.3 |
| HP3A | 19.7 | 0.7 | 2.0 | -8.9 |
| HP4 | 119.0 | 9.7 | 23.0 | -10.4 |
| HP5 | 191.0 | 13.7 | 4.0 | -39.4 |
| HP6 | 10.0 | 4.5 | 17.0 | -3.4 |
| HP6A | 15.3 | 9.2 | 56.0 | 23.8 |
| PC1 | 23.4 | 13.2 | 43.0 | 0.8 |
| DE6 | 21.8 | 32.9 | 91.0 | -0.5 |
| DE8 | 66.7 | 18.5 | 69.0 | 13.5 |
| DE10 | 78.9 | 19.5 | 57.0 | -1.0 |

**Table 2:** Coefficients of variation from the simple linear regression models relating stream solute chemistry to wetland proportion, using both all years and dry years only and using wetland proportion across the whole catchment and within 20m of the stream. All models were assessed at $\alpha$=0.05. Negative relationships are indicated by an asterisk.

| | All Years | | | | | | | | | | Dry Years | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Entire Catchment | | | | | Near-stream zone | | | | | Entire Catchment | | | | | Near-stream zone | | | | |
| | Annual | Winter | Spring | Summer | Fall | Annual | Winter | Spring | Summer | Fall | Annual | Winter | Spring | Summer | Fall | Annual | Winter | Spring | Summer | Fall |
| DOC | 0.96 | 0.97 | 0.95 | 0.89 | 0.97 | 0.84 | 0.99 | 0.96 | 0.89 | 0.95 | 0.96 | 0.83 | 0.84 | 0.81 | 0.82 | 0.8 | 0.87 | 0.85 | 0.73 | 0.76 |
| $NO_3$-N | 0.71* | 0.64* | 0.59* | 0.65* | 0.65* | 0.81* | 0.64* | 0.53* | 0.76* | 0.66* | 0.74* | 0.78* | 0.68* | 0.77* | 0.66* | 0.76* | 0.76* | 0.63* | 0.75* | 0.57* |
| TP | 0.55 | 0.62 | 0.52 | 0.53 | 0.51 | 0.41 | 0.48 | 0.45 | ns | 0.46 | 0.46 | 0.44 | ns | 0.44 | ns | ns | 0.31 | ns | 0.3 | ns |
| Ca | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |
| Mg | ns | ns | 0.41* | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns | ns |

**Table 3:** Akaike's Information Criterion (AIC) for models relating stream solute chemistry to wetland proportion. ΔAIC was calculated for models using only dry years, models using wetland proportion within 20m of the stream and models using dry years and wetland proportion within 20m of the stream. Bold values indicate models with substantially more support (ΔAIC< -2), relative to the model using all years and catchment wetland proportion, in their respective seasons. Given the lack of interpretable models, Ca and Mg data are not presented.

| | AIC Catchment | ΔAIC (dry years) | ΔAIC (20m buffer) | ΔAIC (20m buffer in dry years) |
|---|---|---|---|---|
| | DOC | | | |
| Annual | 5.80 | *3.14* | *14.38* | *18.67* |
| Winter | -2.66 | **-5.12** | *17.35* | *17.00* |
| Spring | -5.96 | 1.28 | *12.53* | *15.14* |
| Summer | 23.72 | **-1.52** | *5.31* | *7.35* |
| Fall | 9.20 | *7.96* | *18.65* | *23.64* |
| | $NO_3$-N | | | |
| Annual | -27.93 | 1.19 | **-4.25** | 0.45 |
| Winter | -23.99 | 0.37 | **-4.84** | **-3.72** |
| Spring | -23.72 | -0.95 | **-2.37** | **-3.39** |
| Summer | -26.25 | *2.37* | **-4.31** | *2.92* |
| Fall | -24.51 | *4.70* | -0.19 | *7.02* |
| | TP | | | |
| Annual | -32.96 | 1.38 | *2.65* | *3.96* |
| Winter | -36.15 | 1.49 | *3.88* | *4.24* |
| Spring | -36.45 | 0.12 | *3.17* | *2.53* |
| Summer | -29.41 | *2.17* | 1.77 | *3.88* |
| Fall | -33.13 | *2.72* | *2.76* | *5.92* |