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RESEARCH ARTICLE

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Key Points:

- Our long-term data set provides a robust perspective on patterns in watershed-scale stoichiometry and organic carbon and nutrient transport
- Flow regimes (floods and periods of low flow) are critical in shaping nutrient and organic carbon stoichiometry in aquatic ecosystems
- Lakes play an important role in nutrient and organic carbon removal within a stream network

Supporting Information:

Supporting Information may be found in the online version of this article.

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Role of Lakes, Flood, and Low Flow Events in Modifying Catchment-Scale DOC:TN:TP Stoichiometry and Export

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Abstract The balance of organic carbon (OC), nitrogen (N) and phosphorus (P) plays a crucial role in determining the processing, retention, and movement of these solutes across the aquatic continuum. Floods and droughts can significantly alter the quantity and ratios of OC:N:P export within inland waters, but how these ratios change, and are coupled within watersheds that integrate rivers and lakes, is not well known. We investigated the stoichiometry and export of dissolved organic carbon (DOC), total N (TN) and total P (TP) in two lake watersheds (10 inflows, 2 outflows) in the southern Boreal Shield over a 37-year period. Although DOC, TN, and TP concentration behaved similarly, DOC:TN:TP ratios varied seasonally, strongly modulated by stream discharge. DOC:TN, DOC:TP and TN:TP export initially increased rapidly with increasing discharge, peaking at 10%–20% exceedance of the annual discharge for DOC:TP and TN:TP ratios, indicating a rapid depletion of catchment OC sources. Both flood and low flow events resulted in lower DOC:TN and lower DOC:TP export—thereby increasing the relative contributions of stream TN and TP. Consequently, elevated annual discharge coupled with infrequent but high floods and periods of low flow events increased the contributions of TN and TP relative to DOC. Overall, the lakes retained DOC, while increasing TN relative to TP. Nonetheless, the flow regime played a role in modulating nutrient retention in the lakes, likely due to changes in residence time, and the interplay of physical, photochemical, and biological degradation processes.

Plain Language Summary How floods and droughts affect the relationship between organic carbon (OC) and nitrogen and phosphorus in terms of their alteration, removal from, or storage within, river and lake environments is not well known. We investigated two lake watersheds with their 10 inflowing and 2 outflowing streams over 37 years. The ratios of the OC to nutrients changed seasonally and were affected by intra-annual stream flow variability. Slightly higher than average flows (10%–20% higher) initially increased the amount of OC that was exported from the watershed compared to nitrogen and phosphorus, but this export was notably lower during low flows and floods. This highlights the effects of extremely high and low flows, resulting in increased nitrogen and phosphorus in the streams. Internal processing by lakes generally decreased OC, while adding nitrogen relative to phosphorus, however the lakes retained less OC and phosphorus when the number of annual floods increased. This is important as the frequency and intensity of floods and droughts are predicted to increase in the future which may change how nutrients are altered and removed along the inland-marine aquatic continuum. These potential changes could impact aquatic ecosystems and the ecosystem services they provide.

1. Introduction

Inland waters, which include streams and lakes are integral parts of the larger headwaters to oceans continuum, transform carbon and nutrients from terrestrial sources and carry these critical material and energy fluxes toward the ocean (Larson et al., 2007; Xenopoulos et al., 2017). Inland waters receive substantial amounts of carbon (C), nitrogen (N) and phosphorus (P), from their surrounding terrestrial landscape (Drake et al., 2017; Williamson et al., 2008). In particular, they receive vast amounts of organic carbon (OC), with an estimated global land-to-water flux of 5.1 Pg OC yr^{−1} (Drake et al., 2017). The stoichiometry of OC with other ecologically important elements, such as N and P, determine whether, and the extent to which, these elements are processed, retained and transported within inland waters (Stutter et al., 2018). Variations in the OC-to-nutrient ratios play a crucial role in regulating heterotrophic and autotrophic metabolism and thus nutrient cycling, influencing the release of nutrients their inorganic form, that is readily available to aquatic organisms (Stutter et al., 2018; P. G. Taylor &

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Townsend, 2010). For instance, higher organic matter C:nitrate ratios tend to lower nitrogen cycling rates, whereas lower ratios increase the release of reactive nitrogen (e.g., NO_3) downstream to receiving aquatic ecosystems (Gundersen et al., 2006; P. G. Taylor & Townsend, 2010). Additionally, the stoichiometry of C, N and P also regulates the transformation and flux of C by influencing microbial uptake and respiration (Stutter et al., 2018; Xu et al., 2015), in turn affecting ecosystem productivity and potentially eutrophication in receiving waters. Despite the ecological significance of these processes, few studies have examined the interplay between these elements. Moreover, understanding the coupling or decoupling of these elements in fluvial networks integrating terrestrial, lotic, and lentic subsystems remains limited.

The amount and ratios of C, N and P exported from terrestrial to aquatic environments are largely influenced by land use, catchment geology and climate (e.g., Frost et al., 2009; Prater et al., 2017). Intense rainfall and floods contribute significantly to the transport of terrestrial dissolved organic carbon (DOC) to aquatic systems (Fasching et al., 2016; Raymond & Saiers, 2010; Strohmeier et al., 2013; Xenopoulos et al., 2021), while simultaneously increasing nutrients (Sebestyen et al., 2008, 2014), although not necessarily at the same rate (e.g., Sebestyen et al., 2008; Strohmeier et al., 2020; Talbot et al., 2021). Due to varying affinities in the soil matrix, nitrogen and phosphorus accumulate and transport differently through catchments. Nitrate (NO_3^-) is relatively mobile in soils, and is easily exported via groundwater flow to streams (Hobbie et al., 2017; Vanni et al., 2001), whereas soluble reactive P, has a stronger affinity to soil particles, resulting in its accumulation in upper soil layers and subsequent transport to inland waters during high flows (Dupas et al., 2017; Holtan et al., 1988; Stutter et al., 2008). Indeed, stormflows can lead to the decoupling of elements transported to streams (Kaushal et al., 2018) by increasing the export of P relative to N, resulting in variable C:N:P ratios as elements move across ecosystems (Prater et al., 2017; Xenopoulos et al., 2017). This variable C:N:P stoichiometry becomes particularly important when quantifying carbon export, and regulation of N and P cycles with that of OC (Xenopoulos et al., 2021).

Floods can temporally deplete nutrients in soils (Butturini et al., 2006; Fasching et al., 2016) and modify the delivery of DOC and macronutrients via altered flow paths (Singh et al., 2014). This alters the source of macronutrients and their stoichiometry in riparian and hyporheic zones of lake tributaries and groundwater (Robinson, 2015). Furthermore, both direct and indirect flow paths may shift during storms, connecting less depleted or more distant soils, contributing C, N, and P to aquatic ecosystems during flow events and ultimately altering C:N:P ratios (Fasching et al., 2018; Inamdar et al., 2011). For example, flooding of forested areas can increase N and P release, while decreasing TN:TP ratios in reservoirs (Talbot et al., 2021). In forested landscapes, nutrient and DOC concentrations may decrease with stream discharge, due to a limited pool of readily mobilizable solutes (Basu et al., 2010; D'Amario et al., 2021; Fasching et al., 2018; Moatar et al., 2017), especially during snowmelt in northern landscapes influencing N export to streams (Sebestyen et al., 2009).

C to nutrient ratios determine the fate of C in ecosystems, determining whether a system is net autotrophic or heterotrophic. A relative nutrient-to-C limitation decreases C-use efficiency, influencing inorganic C fixation or organic C excretion by autotrophs, while heterotrophs respire more C (Hessen et al., 2004). The carbon:nitrate ratio, for instance, impacts nitrate accumulation in aquatic systems by regulating microbial processes that couple organic carbon and nitrate cycling (Taylor et al., 2020). Phosphorus is often limiting, and can be removed by biological uptake (Elser et al., 2009) or burial in lakes (Maranger et al., 2018), consequently reducing downstream P flux. Therefore, the stoichiometry of organic matter reflects the processing it has undergone, with lower OC-to-nutrient ratios indicating less processed organic matter, which may be more available to stimulate aquatic heterotrophic metabolism and mineralization (del Giorgio et al., 1998).

Lakes within fluvial networks play a significant role in buffering, moderating and attenuating DOC and nutrients received from their surrounding environments (Goodman et al., 2011; Larson et al., 2007). As a result, changes to the physical and biogeochemical processes within lakes can significantly affect ecosystems further downstream, and their ability to provide important ecosystem services. Despite this, few studies have incorporated lakes into processing of materials as they move downstream. The hydrodynamics and biological processes of lakes, profoundly influence the cycling of DOC and nutrients within these systems. Parameters such as mean residence time and seasonal variations in lake inflow and outflow are pivotal for regulating the production, transformation, and removal of DOC in lakes (Ejarque et al., 2018; Evans et al., 2017). Moreover, lake temperature is an important driver of in-lake biogeochemical cycling (Ejarque et al., 2018), and thus downstream nutrient and carbon export. However, the specific role of lakes within stream networks is not well studied. Recent shifts in flow regime, as a

result of changes in precipitation patterns and the frequency and extent of extreme events, affect lake hydrodynamics, and highlight the need for a better understanding of how lakes affect the movement and ratios of C:N:P exported downstream within fluvial networks. To address this gap, we conducted an analysis using a 37-year continuous monitoring data set.

We investigated the stoichiometry and export of DOC, total N (TN) and total P (TP) in two lake watersheds (10 inflows and 2 outflows and 2 lakes) within catchments located in the southern Boreal Shield, and how these ratios were regulated by season and flow events over a 37-year study period. Specifically, our hypothesis centered on the concept that fluctuations in high and low flow conditions might alter the concentration and processing of DOC, TN, and TP in streams, potentially reshaping the downstream export fluxes' stoichiometry and impacting retention and export dynamics from lakes. We expected that high flow conditions in streams would predominantly load higher amounts of TP and TN relative to DOC, potentially originating from upstream sources in the catchment. Conversely, during lower stream discharge, we predicted increased flows of shallow riparian groundwater into streams, leading to higher TP exports compared to other nutrients. Considering that the undisturbed study catchments largely consist of bedrock, we expect an overall negative relationship between nutrient concentration and discharge, and thus a dilution of macronutrients with increasing flow.

We also examined the movement of DOC, TN and TP through the lakes, and whether this was impacted by hydrological conditions. We hypothesized that variations in flow regimes would influence internal nitrogen cycling by altering nutrient inputs to the lakes and residence times within these systems (Maranger et al., 2018). Specifically, we hypothesized that high flow events would modify the DOC:TN:TP ratios exported from lakes, while lakes would retain the often-limiting macronutrient P through biological uptake or burial, as observed in efficient P burial in inland waters (Maranger et al., 2018). Additionally, we expected that lakes would likely retain C and nutrients during low flow periods, due to increased retention times, potentially influencing downstream nutrient and carbon ratios.

Our study investigating the effect of extreme flow events on DOC:TN:TP export and concentration in two watersheds, contributes to a limited body of research investigating the movement of solutes, and their ratios, through streams and lakes. Furthermore, the use of long-term data (37 years) allows for a robust and comprehensive analysis in watershed-scale stoichiometry and the transport of organic carbon and nutrients advancing our current understanding of how flow regime and climatic conditions affect the stoichiometry of C:N:P in aquatic ecosystems.

2. Methods

2.1. Study Site

We investigated the composition, flow, and nutrient export dynamics of dissolved organic carbon (DOC), total nitrogen (TN), and total phosphorus (TP) across 12 streams in the catchments of Harp Lake and Dickie Lake within the District Municipality of Muskoka, Ontario, Canada (Figure 1). Harp Lake spans 71 ha with a maximum depth of 37m and a mean depth of 13m, while Dickie Lake is slightly larger at 94 ha with a maximum depth of 12m and a mean depth of 5m. All inflows and outflows of both lakes were sampled, respectively. The lakes are oligotrophic, with a long-term mean residence time of 1.57 and 3.1 years respectively (Yao et al., 2008) and rarely experience oxygen deficit in the deeper water layers (Tan et al., 2018).

The study area, situated in the southern portion of the Boreal ecozone, experiences a humid continental climate, with an average annual mean temperature of 5.12°C, an average annual precipitation is 1,015 mm, and average summer and winter temperatures of 17.5 °C and −8.2°C respectively. Over the study period from 1979 to 2014, annual precipitation ranged from 696 mm (1998) to 1,278 mm (1980), with 30% of all precipitation occurring as snow (Buttle & Eimers, 2009; Yao, 2009). The average annual runoff for the region is 516 mm (range: 228–695 mm) (Yao, 2009). The majority of annual runoff (49%–77%) is delivered during spring snowmelt in mid-March to early May (McDonnell & Taylor, 1987). Site geology is predominantly characterized by a thin layer of humo-ferric podzolic soil, overlaying Precambrian Shield bedrock, ranging from exposed bedrock, areas with a thin layer of till, rock ridges, and plains with continuous till cover (ranging in depth from 1 to >10 m) (Devito et al., 1999). Land cover is mainly deciduous and mixed forests, consisting of maple, birch, and pine trees. The long-term N, P and OC biogeochemistry in Ontario, Canada, is generally punctuated by regional increases in NO₃ and DOC, but declines in TP (1977–2019) (D'Amario et al., 2021). However, it does appear that this region

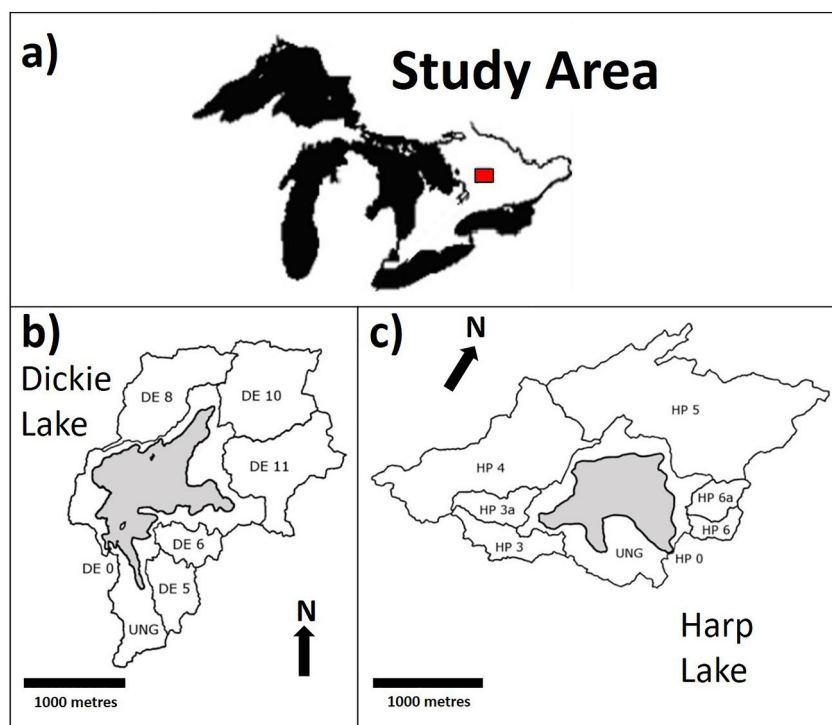


Figure 1. Study catchments located east of the Georgian Bay of Lake Huron (a), black shaded areas indicate the relative location of the Great Lakes to the sampling area. DE5-DE11 are five inflow streams and, DE0 is the outflow of Dickie Lake (b). HP3-HP6a are six inflow streams and HP0 the outflow of Harp Lake (c). For further information for Harp lake see Figure S1 in Supporting Information S1. UNG indicates the ungauged area around the lake's shoreline.

generally experiences declines in TP and N, and increases in DOC (Eimers et al., 2009; Imtiaz et al., 2020; Wu et al., 2022). Here we focused our analysis on DOC, TP, and TN. In our study streams TP is mostly organic, soil derived P in the streams and from phytoplankton in the lakes, with some dissolved organic P; inorganic P (soluble reactive phosphorus) is typically undetectable (Dillon & Molot, 1996; Hudson et al., 1999, 2000) and TN is predominantly organic nitrogen with Total Kjeldahl Nitrogen (~89%, Table 1). At stream HP4, for example, the average watershed-flux composition of TN, Total Kjeldahl Nitrogen, NO_3 and NH_4 is: 0.207, 0.16, 0.05, 0.015 $\text{g year}^{-1}\text{m}^{-2}$.

2.2. Sampling and Nutrient Analyses

The six inflow streams and the outflow stream around Harp Lake, in addition the five inflow streams and the outflow stream at Dickie Lake, are typical small headwater streams, gauged with V-notch or H-flume weirs for obtaining hourly (1979–2009) or 10-min interval (2010–2014) recordings of water stage. Water stage was converted to corresponding stream discharges using established rating curves (Yao, 2009; Yao et al., 2011). Stream water was sampled weekly or bi-weekly since 1979, at the above-mentioned gauging weir locations. All chemical concentrations or water quality indices were obtained by standard analytical chemistry methods at the laboratory of Dorset Environmental Science Center and follow historical provincial guidelines (James et al., 2022; Sutey et al., 2018; Yao et al., 2011). All samples were pre-sieved through a 80 μm nylon mesh to remove large debris and zooplankton (Dillon & Molot, 2005). Samples for DOC were collected into a Polyethylene Terephthalate container and TN samples were collected into a septum-capped (no airspace) acid washed glass vial. TP samples were filled into an acid washed borosilicate tube. All samples were kept in the dark at 4°C until analysis. DOC and TP concentrations were measured by colorimetry using Skalar Flow-Access and Techicon workstations. Total nitrogen (TN) was measured by chemiluminescence using a Shimadzu - TOC-Vcph according to the National Environment Methods Index (https://www.nemi.gov/methods/method_summary/5425/).

Table 1
Environmental Parameters (Daily Values), Annual Averages of Export Loads and Areal Fluxes of DOC, TN and TP of all Study Sites Averaged Across the Study Period (1979–2014) Across all Sites for the Study Period (1979–2014)

Site	Q (ls ⁻¹)	Conductivity (μS _{cm} ⁻¹)	DOC (mg l ⁻¹)	TP (μg l ⁻¹)	TN (μg l ⁻¹)	Total kjeldahl nitrogen (μg l ⁻¹)	DOC (t y ⁻¹)	TP (t y ⁻¹)	TN (t year ⁻¹)	DOC (g m ⁻² y ⁻¹)	TP (mg m ⁻² y ⁻¹)	TN (mg m ⁻² y ⁻¹)
DE0	81.95 ± 107.01	33.31 ± 5.06	5.92 ± 0.93	8.6 ± 3.02	364.33 ± 82.14	314.28 ± 72.35	14.92 ± 3.78	0.022 ± 0.006	0.966 ± 0.243			
DE10	12.87 ± 23.2	33.76 ± 15.3	19 ± 9.9	21.66 ± 22.45	591.02 ± 275.73	537.25 ± 269.63	5.12 ± 1.17	0.006 ± 0.001	0.173 ± 0.04	6.49 ± 1.48	7.29 ± 1.74	219.82 ± 50.75
DE11	12.71 ± 23.57	47.78 ± 20.65	24.13 ± 13.32	42.49 ± 59.1	651.68 ± 302.49	612.81 ± 307.82	6.2 ± 1.43	0.008 ± 0.002	0.181 ± 0.042	8.13 ± 1.87	10.94 ± 2.48	237.41 ± 55.12
DE5	5.25 ± 12.06	21.09 ± 5.84	16.79 ± 5.58	40.15 ± 58.54	448.7 ± 157.44	552.67 ± 245.34	1.94 ± 0.5	0.005 ± 0.001	0.054 ± 0.015	6.47 ± 1.66	15.1 ± 4.82	180.58 ± 50.29
DE6	3.86 ± 6.9	37.17 ± 22.03	22.24 ± 9.89	53.8 ± 76.98	611.2 ± 259.67	672.84 ± 343	1.79 ± 0.42	0.003 ± 0.001	0.051 ± 0.012	8.2 ± 1.91	15.75 ± 4.3	234.48 ± 56.37
DE8	11.47 ± 19.63	58.92 ± 29.09	18.74 ± 10.23	18.1 ± 20.23	735.18 ± 431.92	684.41 ± 412.49	4.53 ± 1.13	0.004 ± 0.001	0.179 ± 0.044	6.75 ± 1.69	6.1 ± 1.64	266.44 ± 66.23
HP0	90.61 ± 117.81	36.53 ± 3.42	4.3 ± 0.78	6.29 ± 2	330.03 ± 87.67	245.38 ± 67.06	11.78 ± 3.09	0.018 ± 0.005	1.002 ± 0.268			
HP3	4.78 ± 8.48	47.77 ± 21.36	10.57 ± 5.01	21.91 ± 21.18	481.57 ± 186.16	416.36 ± 185.85	1.22 ± 0.29	0.002 ± 0.001	0.062 ± 0.015	4.71 ± 1.13	9.17 ± 2.32	239.35 ± 58.49
HP3A	3.53 ± 7.15	33.74 ± 8.27	2.98 ± 0.85	6.47 ± 6.26	286.24 ± 138.52	187.44 ± 68.5	0.38 ± 0.1	0.001 ± 0	0.037 ± 0.01	1.92 ± 0.5	3.94 ± 1.21	188.72 ± 50.38
HP4	19.94 ± 31.89	35.84 ± 7.82	6.16 ± 1.66	12.91 ± 8.04	345.56 ± 103.97	292.16 ± 100.67	3.62 ± 0.92	0.009 ± 0.002	0.209 ± 0.053	3.04 ± 0.77	7.17 ± 2	175.83 ± 44.68
HP5	34.97 ± 65.49	34 ± 10.46	14.17 ± 7.07	27.39 ± 27.81	658.95 ± 687.07	588.19 ± 495.06	10.92 ± 2.85	0.017 ± 0.004	0.536 ± 0.143	5.73 ± 1.5	8.73 ± 2.16	281.19 ± 75.27
HP6	1.87 ± 3.32	70.06 ± 36.65	7.08 ± 3.61	17.18 ± 16.8	532.14 ± 266.67	381.32 ± 244.24	0.35 ± 0.09	0.001 ± 0	0.028 ± 0.007	3.55 ± 0.9	8.73 ± 2.65	285.01 ± 70.18
HP6A	2.35 ± 4.63	33.74 ± 21.61	10.08 ± 5.98	12.75 ± 12.94	433.45 ± 271.12	372.25 ± 222.07	0.51 ± 0.13	0.001 ± 0	0.023 ± 0.006	3.35 ± 0.87	4.11 ± 1.28	147.5 ± 39.46

All samples contain low amounts of debris particles $>80\ \mu\text{m}$ ($\sim 8\%$ of the total $80\mu\text{m}$ -screened concentration and in Harp Lake $<2\%$ (Brown & Yan, 2015). To keep a consistent approach in our monitoring system, the same methods have been employed over the entire sampling period which means our results track consistently through time.

2.3. Hydrology

We calculated standard flow-duration curves based on daily average discharge data for the study period (1979–2014) for each catchment. To account for varying precipitation, topography, and other catchment characteristics influencing hydrology, and to allow for comparison across all sites and years, we calculated catchment discharge exceedances - standardizing the discharge data. Discharge exceedances express discharge as the percentage of time during which discharge exceeds a specific value. For instance, a 10% discharge exceedance (Q10) indicates that a given discharge value was exceeded during 10% of the considered period. Exceedance probability was calculated as: $Q = 100 \times [m/(n + 1)]$, where ' Q ' is the percent probability that a given flow value will be equaled or exceeded in a given period of consideration, ' m ' is the rank of the flow value under consideration, ' n ' is the total number of events on record during the period of consideration. The period of consideration was the entire 37 years of hourly discharge data. We defined discharges greater than Q10 as high flow events and discharges greater than Q5 as flood events (Figure S2 in Supporting Information S1). These characteristic exceedance values can be easily obtained from the flow-duration curves. Finally, we calculated the number of days that floods (Q5), and periods of low flows (Q95), occurred per year, and the time (number of days) between the occurrence of these two events.

2.3.1. DOC and Nutrients Export Calculations

Stream discharge data provides a basis for estimating important water quality constituents, because their concentrations and loads vary naturally with stream flow. We used a Random Forest model to estimate the values of DOC and nutrients for unsampled days, based on stream discharge. Using Mean Absolute Percentage Error (MAPE), Mean Squared Error (MSE), Root Mean Squared Error (RMSE) and a pseudo R^2 (based on the squared correlation between predicted and original values) we validated the models given by linear regression, and equations given by the FORTRAN LOAD ESTimator (LOADEST), Support Vector Machine and Random Forest. All models were trained on 80% of the data and tested on the remaining 20%. Daily export of any chemical from a stream was calculated as the daily discharge multiplied by the chemical concentration for the specified day.

2.4. Data Analysis

We calculated DOC:TN:TP concentration ratios for each stream. We then further calculated the stoichiometric ratios of the annual export fluxes which are based on discharge (see previous chapter). Finally, we calculated weighted average annual DOC:TN:TP concentration ratios for the lake inflows and outflow (see Figure 1 for more information). Ratios were not molar corrected. Significant differences in the weighted average annual DOC:TN:TP concentration ratios between lake inflow and outflow were tested using a t -test, as implemented in base R (R Core Team, 2017). Redundancy analysis (RDA), based on the inflows, was carried out using the *vegan* package (Oksanen et al., 2013) to examine the impact of environmental variables on DOC:TN:TP stoichiometry. We tested environmental variables describing the catchments (thin till, minor till, peat, pond, bedrock) as well as climate (air temperature, precipitation), hydrological and chemical variables (discharge, flood duration, days after flood, conductivity). The environmental variables were selected using permutation tests employing the function *ordistep* in the *vegan* package. To assess the factors driving the ratios of DOC:TN:TP and their export fluxes (based on inflows), we used Generalized Additive Models (GAM). First, we modeled annual export fluxes of DOC, TN, and TP to examine the drivers of these fluxes across the year. In a second step, we modeled concentrations of DOC, TN, and TP of the lake inflow minus outflow (Delta DOC, Delta TN, Delta TP) to investigate under which conditions the lakes retained and released solutes. The explanatory variables included were: discharge (Q), flood frequency, the number of flood days (Q5), the number of days with low flow (Q95), the year, and site. GAMs were fitted using the *mgcv* package (Wood & Wood, 2015) for R . The function *gam* automatically assesses the extent of the smoothing, using penalized regression splines (Wood & Augustin, 2002), and allows both linear and non-linear relationships to be modeled.

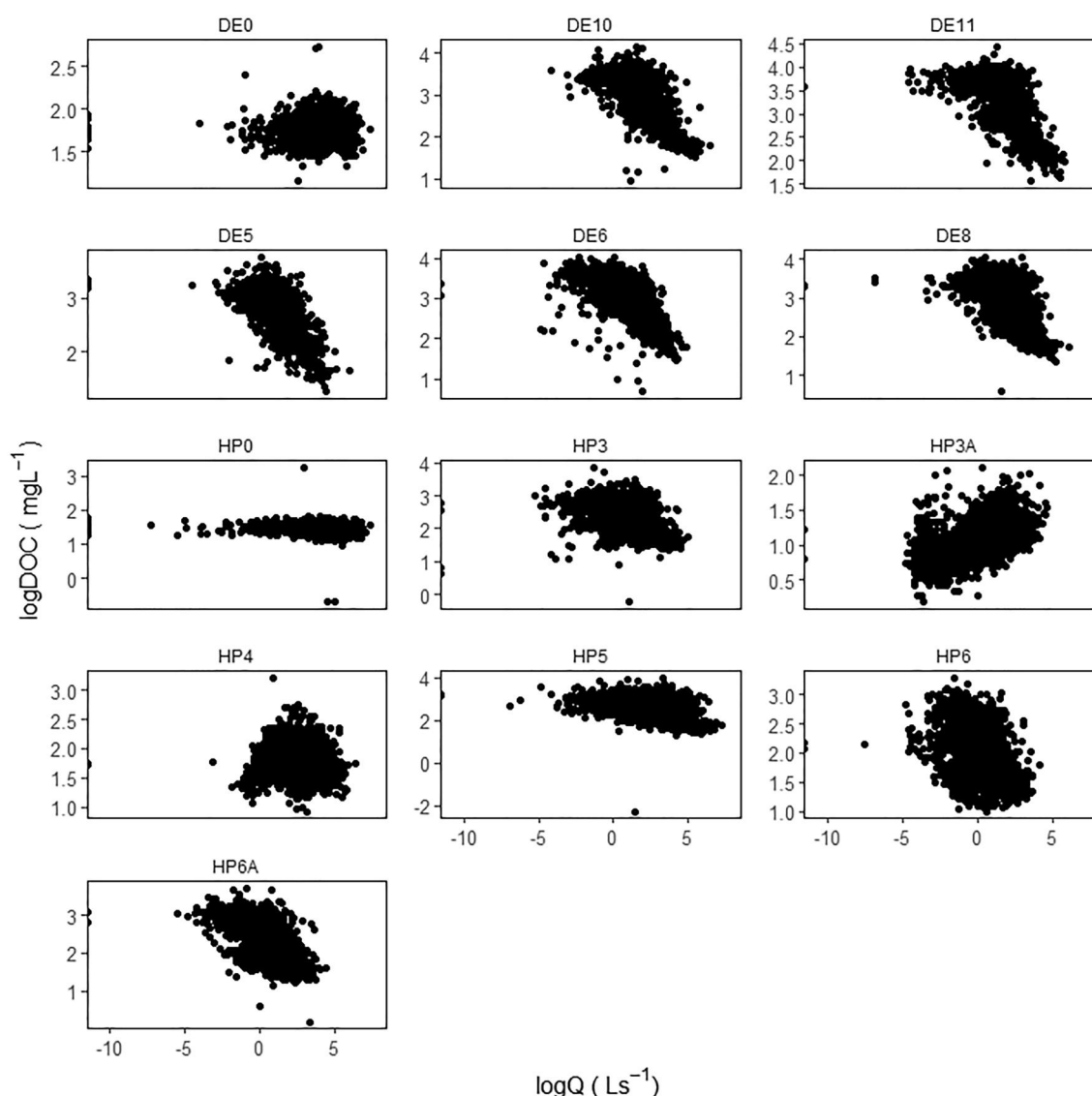


Figure 2. Concentration-discharge relationships for DOC for the complete study period (1979–2014) for the studied streams in the Dorset catchment, Ontario, Canada. HP0 and DE0 indicate streams draining the lakes, all others are inflows (see Figure 1 for more information).

3. Results

Long-term average discharge (1979–2014) of the 12 study streams ranged from 1.1 to 161 L s⁻¹, with the typical occurrence of distinct periods of low flow in summer, and floods in spring (Table 1). Annual export fluxes of DOC, TP and TN ranged from 1.92 ± 0.5 to 8.2 ± 1.91 g m⁻² yr⁻¹ for DOC, 3.94 ± 1.21 to 15.75 ± 4.3 mg m⁻² yr⁻¹ for TP, and 147.5 ± 39.46 to 285.01 ± 70.18 mg m⁻² yr⁻¹ for TN, respectively (Table 1). During the 37-year study period, 3.1 ± 1.5 high flow events (Q10, annual range: 0 to 8) and 1.9 ± 0.9 floods (Q5, annual range: 0 to 5) occurred annually per catchment, which were responsible for elevated exports of DOC and nutrients. In fact, Q5 and Q10 flows accounted for $26 \pm 10\%$ and $40 \pm 11\%$ of annual DOC exports, respectively. TN and TP concentrations ranged from 286 to 735 $\mu\text{g L}^{-1}$ and 6.29–53.8 $\mu\text{g L}^{-1}$, respectively (Table 1). DOC concentration ranged from 0.1 to 65 mg L⁻¹, and often decreased with discharge. Increases in discharge typically diluted DOC concentration (Figure 2), but given the underlying bedrock geology, most DOC (area corrected flux) was exported from the surrounding riparian zone to the stream during high flow events, especially during Q10 and Q5 flow events, with an average 2.05 ± 0.98 g yr⁻¹ m⁻² and 1.29 ± 0.65 g yr⁻¹ m⁻² DOC exported (Figure S4 in Supporting Information S1), respectively. Similarly, most TN and TP was exported

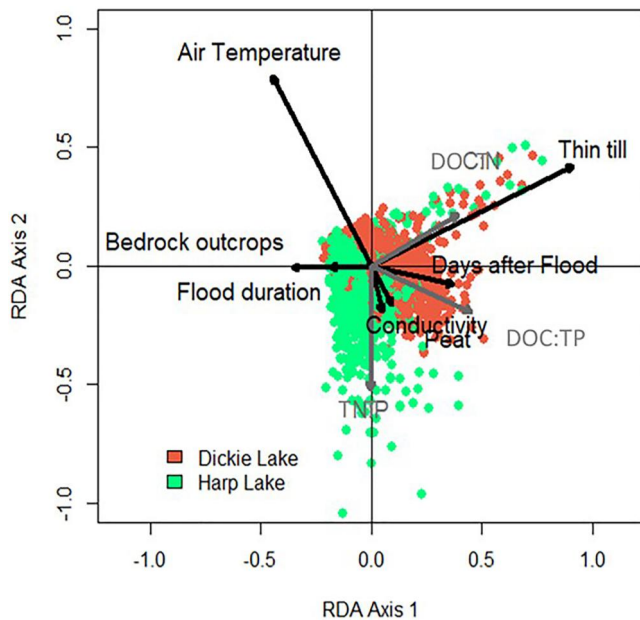


Figure 3. Redundancy Analysis (RDA) of DOC:TN, DOC:TP and TN:TP ratios (grams) of daily data (1979–2014) for the 10 inflows in both catchments. Orange is used to denote the Dickie Lake catchment and green is used for the Harp lake catchment ($r^2 = 0.23$, $p < 0.005$, $n = 6,833$). Only significant variables are shown (see Table 2).

temperature, a proxy for seasonality and the flow regime of streams (Redundancy analysis; Figure 3, Table 2). During warmer temperatures in summer, all nutrients increased (Figure S6 in Supporting Information S1), causing a decline DOC:TP in the streams. Further, flow regime factors, such as the time since the last flood event, and duration of the last flood, also impacted DOC:TN:TP ratios. Moreover, the presence of thin till increased DOC:TN, while higher occurrence of peatland increased TN:TP and DOC:TP, particularly during shorter flood duration.

3.2. DOC: TN: TP Annual Export Fluxes

Inter-annual variability in flow regime, influencing annual discharge and flooding frequency, interacted to modulate DOC:TN:TP export fluxes. We found higher export of TN and TP relative to DOC with increasing annual discharge, while increased flooding frequency led to higher DOC export (Figure 4, Table 3). More specifically, smaller, but more frequent floods throughout the year increased DOC:TN and DOC:TP export fluxes, while infrequent larger floods and low flow periods caused the export of more TN and TP relative to DOC (thus lower DOC:TN and DOC:TP export ratios) (Figures 4a and 4b). TN:TP export decreased with increasing annual discharge, but increased with flooding frequency, indicating that large, less frequent floods and low flow periods increased the fraction of TP relative to TN (Figure 4, Table 3).

3.3. Annual Flux and Retention of DOC, TN and TP Through Lakes

The lakes generally exhibited the removal of DOC and TP, while increasing TN fluxes (Figure 5b). However, both lakes significantly modulated the ratios of DOC:TN:TP of their outflowing waters when compared to inflows (Figure 5a). By averaging concentrations of all inflows and outflows to examine the role of lakes on the annual export of solutes, we found in both lakes, DOC:TN concentration decreased rapidly, while TN:TP increased from the inflows to the outflow (t -test, $p < 0.001$, $n = 37$, for DOC:TN and TN:TP of both Dickie and Harp lakes). In Dickie Lake, DOC:TP

Table 2
Redundancy Analysis (RDA) of C:N, C:P and N:P Ratios of Daily Data (1979–2014) of all 12 Streams ($r^2 = 0.23$, $p < 0.005$, $n = 6,833$)

Constraint	RDA1	RDA2	RDA3	F	Pr (>F)
Air temperature	−0.41	0.84	−0.20	788.51	0.005
Q	0.00	−0.02	0.40	13.24	0.005
Flood duration	−0.17	0.00	0.01	42.48	0.005
Days after flood	0.34	−0.08	−0.57	65.25	0.005
Conductivity	0.04	−0.20	0.18	68.16	0.005
Thin till	0.84	0.44	0.18	806.41	0.005
Peat	0.09	−0.17	−0.77	79.71	0.005
Bedrock	−0.33	−0.01	0.28	21.21	0.005

Note. Only significant variables are shown.

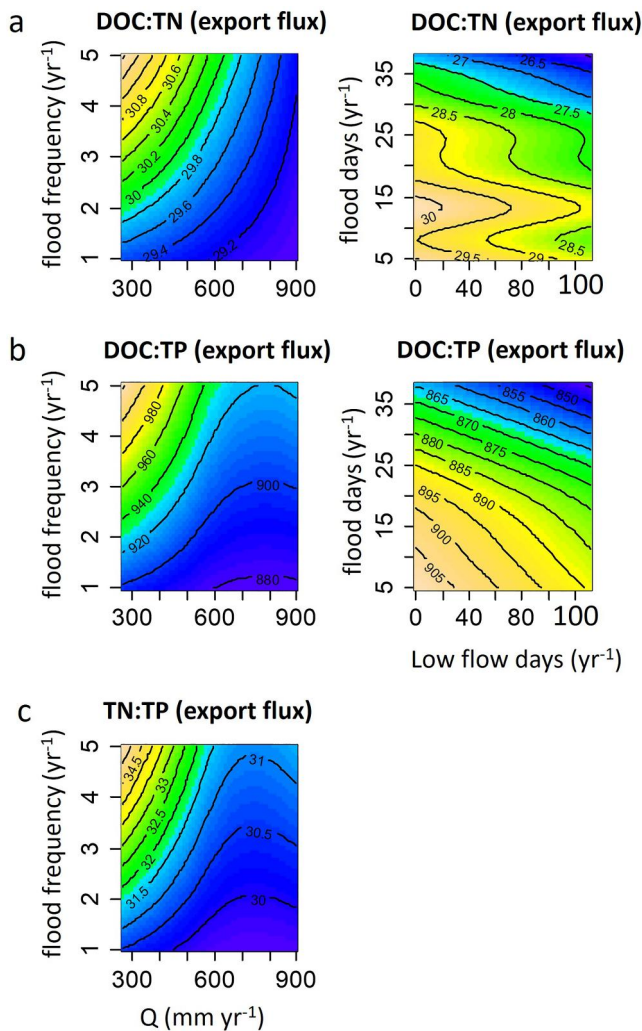


Figure 4. General Additive Models (GAMs) of the stoichiometry (a) DOC:TN, (b) DOC:TP and (c) TN:TP, in grams of yearly (1979–2014) export fluxes for the 10 inflows (see Table 3 for model results). Smoothing functions were applied to predictors and gamma was set to 1.4 to avoid overfitting. The color scale indicates the range of the stoichiometric ratios with yellow indicating increased values and are specific to individual subplots (see contour line values for exact numbers).

concentration was higher at the inflows compared to its outflow, while the DOC:TP was higher at the outflow of Harp Lake (t -test, $p < 0.001$, $n = 37$, for both lake inflow vs. outflow comparisons).

Stream flow regime influenced lake nutrient fluxes and retention, with annual discharge, flooding frequency and the number of days where low or high flows occurred, determining whether each lake acted as a source or sink for DOC and nutrients (Figure 6, Table 4). More specifically, low annual discharge but increased days of flooding (i.e., few, but high floods) lowered the retention of DOC and TP. However, on an annual basis the lakes remained DOC and TP sinks (Figure 5b). High annual discharges increased the export of TN.

4. Discussion

Inland waters receive large amounts of C and nutrients from their surrounding terrestrial environment. Extreme events have the potential to disrupt flow patterns, resulting in significant alterations to flow paths, carbon and nutrient inputs, and residence times within aquatic systems (Boodoo et al., 2020; Palmer & Ruhi, 2019; Xenopoulos et al., 2021). Such changes can significantly affect the solubility, reactivity and mobility of solutes, potentially decoupling element fluxes and impacting the ratios of transported solutes in downstream ecosystems (Kaushal et al., 2018; Moatar et al., 2017). Here we showed the importance of flow regime and climate in influencing the stoichiometry, transport, and retention of DOC, TN and TP using a 37-year continuous data set for two lakes and their respective inflows and outflows. Our results link catchment hydrology, particularly floods (Q5) and high flow events (Q10), to the variability and uncoupling of DOC, TP, and TN export. This variability in DOC:TN:TP export ultimately influence nutrient and carbon retention, processing, and transport in aquatic ecosystems. Our findings suggest that although DOC, TN and TP show similar patterns, the frequency and extent of floods and high flow events impact downstream DOC:TN:TP ratios, and the cycling and retention behavior of solutes in lakes within watersheds. Specifically, infrequent, yet intense floods and prolonged periods of low flows increase the relative contributions of TN and TP in the streams via the delivery of nutrients along altered flowpaths and catchment processes. Our results underscore that using a stoichiometric approach significantly enhances our ability to monitor water quality and their biogeochemical impacts beyond single extreme events, thereby enabling predictions regarding potential alterations in the biogeochemistry of lake ecosystems caused by current and future events.

4.1. Discharge and Seasonal Effects DOC:TN:TP Concentration Ratios

The concentrations and export ratios of DOC:TN:TP were primarily influenced by the seasonal variability of discharge, characteristic of boreal landscapes flow regimes. Consistent with observations in other biomes, the concentrations and ratios of stream water DOC, TN, and TP, exhibit seasonal fluctuations (Bernal et al., 2005; Sebestyen et al., 2009; Shousha et al., 2021). Spring floods were associated with marked decreases in DOC:TN (Figure S8 in Supporting Information S1), as would be expected from infiltration of meltwater flushing N from the soils (Boyer et al., 2000; Crossman et al., 2016). While in northern regions the presence of snowmelt typically contributes to increased DOC in streams (Laudon et al., 2011), our catchment primarily comprised of bedrock, likely resulted in lower in-stream concentrations of DOC during snowmelt. This increases the relevance of mechanisms such as atmospheric deposition as a N-source (Elser et al., 2009; Mosello et al., 2001). Thus, the decline in DOC:TN during snowmelt may also be attributed to direct N deposition from the snowpack (Kothawala et al., 2011). Similarly, a study found that the most N-enriched events occurred during spring in headwater streams of the northeastern United States (Kincaid et al., 2020). In winter, the cyclical freezing and thawing

Table 3
Summary of General Additive Model (GAM) of the Stoichiometry of Yearly Fluxes From all Study Streams (DOC:TN, DOC:TP and TN:TP)

Predictors		Response variable		
		DOC:TN	DOC:TP	TN:TP
f(Q: Flood frequency)	EDF	2	2.89	3.08
	β	5.5	5.16	2.38
	p - value	**	**	*
f(Flood days)	EDF	5.22	1	1
	β	8.87	8.78	0.03
	p - value	***	**	n.s.
f(year)	EDF	7.54	7.33	2.13
	β	16.39	10.61	4.71
	p - value	***	***	**
f(Low flow days)	EDF	1	1	1
	β	25.1	3.73	0.22
	p - value	***	n.s.	n.s.
Site	DF	10	10	10
	β	2164	607.3	501.6
	p - value	***	***	***
Intercept		0.03	0.87	29.45
r²		98.8	94.7	94.2

Note. Shown are standardized regression coefficients (β), *t*-values, estimated degrees of freedom (EDF) and the deviance explained (%). Smoothing functions were applied to predictors indicated by “f” and gamma was set to 1.4 to avoid overfitting. Star notation indicates significance levels (****p* < 0.001, ***p* < 0.01, **p* < 0.05, and n.s. not significant).

process can lead to the decomposition of fine roots within, increasing solubility of nitrogen soil. This process results in the export of NO_3^- from soils during spring through meltwater runoff (Campbell et al., 2014; Kincaid et al., 2020; Mitchell et al., 1996). Consequently, snowmelt often accounts for the majority of the annual nutrient export flux and marked seasonal differences in TN and TP export fluxes (Corriveau et al., 2013). Finally, warmer air temperatures and prolonged low flow periods were related to lower TN:TP and DOC:TP concentration ratios in our study streams, leading to decreased TN:TP export flux ratios. During the summer months, the increase in DOC is likely due to periods of low flow and warmer temperatures that enhance biological activity in biofilms and algae, consequently increasing DOC (Kaplan & Bott, 1989) and nutrient turnover in the streams. Warmer temperatures can lead to increased loss of C during summer through photo-bleaching (e.g., Maavara et al., 2021), potentially explaining the lower DOC:TP ratios. Additionally, increases in TP levels in summer may also reflect changes in the position of lateral groundwater flowpaths as the water table drops, resulting in contributions from the riparian zone characterized by higher concentrations of soluble reactive P due to shallow groundwater interactions with the organic soil horizons, a phenomenon observed in headwater catchments in Germany (Dupas et al., 2017). Similarly, maxima of NO_3^- and soluble reactive phosphorus have been recorded in summer in forested headwater streams, reflecting greater inputs of deep groundwater in summer (Mulholland & Hill, 1997). Although DOC, TN and TP all increased in concentration during the summer in our study streams, TN, TP, and DOC originate from distinct sources. While TN and TP may increase rapidly due to deposition rates in our study streams (Eimers et al., 2018), the increase in DOC may be slower due to production processes like phytoplankton growth and exudation, potentially causing lower DOC:TN and DOC:TP in summer. Furthermore, summer droughts may lead to the decoupling of microbial C, N, and P cycling in soils, possibly resulting in faster rates of N and C processing

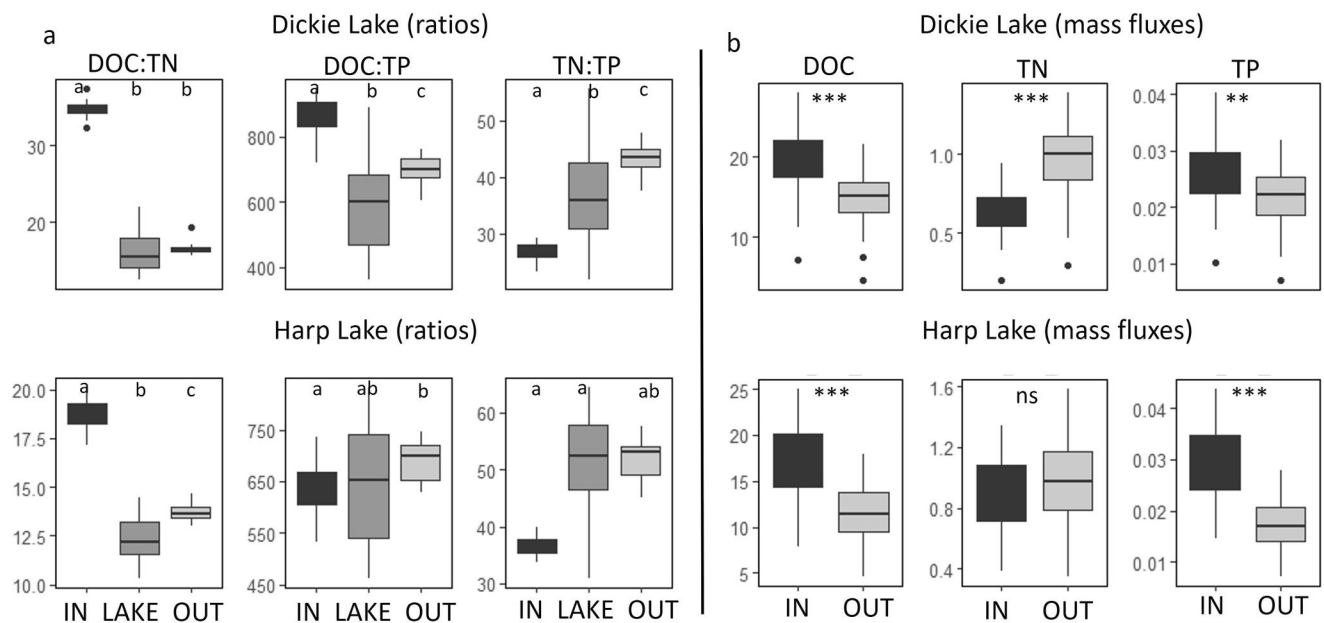


Figure 5. Comparison of lake inflows and outflow for (a) DOC:TN, TN:TP, DOC:TP ratios (annual averages across all 37 years in grams) and (b) mass fluxes. Letter (or star) notation denotes significant differences between sites, with significance levels set at 95% confidence. Significance levels were corrected for multiple comparisons (Dunn-Sidak correction (Sokal, 1995)), for panel (a).

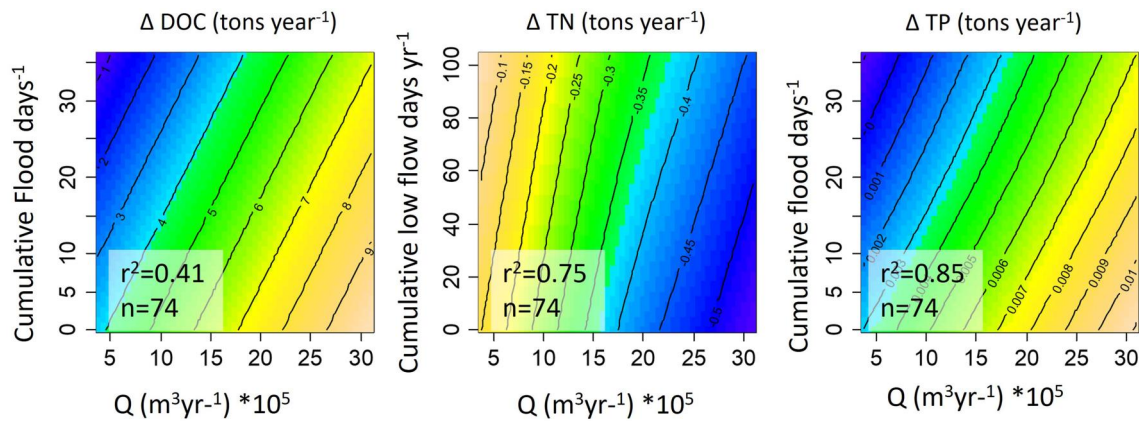


Figure 6. General Additive Models (GAMs) of lake inflow minus outflow (Delta DOC, Delta TN, Delta TP) for different solute (1979–2014) export fluxes for both lakes (see Table 4 for model results). Blue colors indicate uptake by the lakes and yellow colors indicate less uptake, or even export (see contour line values for exact numbers). Smoothing functions were applied to predictors and gamma was set to 1.4 to avoid overfitting.

Table 4
Summary of General Additive Model (GAM) Results of the Lake Outflow Minus Inflow (ΔDOC , ΔTN , ΔTP)

Predictors		Response variable		
		Delta DOC	Delta TN	Delta TP
f(Q)	EDF	1	2.44	1
	β	10.28	5.66	7.98
	p - value	**	**	**
f (Flood frequency)	EDF	1	1	1.19
	β	6.83	3.6	3.24
	p - value	*	n.s.	n.s.
f (Flood days: catchment DE)	EDF	1	1	1
	β	5.62	2.6	4.35
	p - value	*	n.s.	*
f (Flood days: catchment HP)	EDF	1	1	1
	β	0.84	2.6	2.78
	p - value	n.s.	n.s.	n.s.
f (year)	EDF	1.54	1	1
	β	0.31	0.4	1.24
	p - value	n.s.	n.s.	n.s.
f (# of drought days)	EDF	1	1	1
	β	1.3	5.35	0.32
	p - value	n.s.	*	n.s.
Catchment ID	β	−1.13	0.3	0.005
	p - value	*	***	***
Intercept		5.51	−0.37	0.005
Deviance explained (%)		46.8	76.2	86.6

Note. Shown are standardized regression coefficients (β), t-values, estimated degrees of freedom (EDF) and the deviance explained (%). Smoothing functions were applied to predictors indicated by “f” and gamma was set to 1.4 to avoid overfitting. Star notation indicates significance levels (*** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, and n.s. not significant).

compared to P (Mooshammer et al., 2017). This scenario could potentially increase the TP flushed into streams during increasing discharge.

As discharge increased, there was a noticeable increase in the ratios of DOC:TN, DOC:TP, and TN:TP concentration (contrary to snowmelt), peaking around 10%–20% of the annual discharge for DOC:TP and TN:TP. This pattern suggests an initial rapid depletion of TN and TP sources in the catchment, outpacing DOC depletion. However, during high flows and floods, these ratios decreased. Our results align with previous research; for example, in an intermittent stream draining an unpolluted Mediterranean forested catchment, DOC:DON decreased following drought while nitrate and DON increased during storms (Bernal et al., 2005). Altogether these results suggest that N, P and DOC have different source areas in the catchment (Kincaid et al., 2020).

TN:TP concentration in our study streams initially increased before decreasing with discharge. This trend might suggest that phosphate (PO_4^{3-}) adsorbed to soil particles in upper soil horizons (Holtan et al., 1988; Ockenden et al., 2016) and were mobilized by floods. This would suggest a transport limitation of N and P (Figure S3 and Figure S8 in Supporting Information S1) which had accumulated in the upper catchment soils. There appears to be a link between discharge frequency and intensity, and TN:TP export, likely due to more rapid use of nutrients compared to carbon respiratory losses in soils (Mooshammer et al., 2017). This dynamic directly impacts on the inputs from the surrounding catchment into streams and lakes. In support of this notion, we found an increase in DOC:TN and DOC:TP (concentrations) with time since the last flood. Similarly, in aquatic systems nutrients are utilized more rapidly relative to carbon losses, and longer water residence times result in higher C:N and C:P (Frost et al., 2009; Maranger et al., 2018).

The composition of the catchment bed material significantly influenced the DOC:TN:TP concentration ratios in the streams. Thin till and peat led to a higher proportion of DOC relative to TN and TP, especially during shorter floods, while catchments dominated by higher contributions of bedrock showed lower relative contributions of TN and TP, decreasing notably during prolonged floods, indicating a limitation in sources. Similarly, in a boreal catchment in Finland, peat cover was found to increase the export of TOC and

TN (Kortelainen et al., 2006). We found that for our study streams, the catchment bed material plays a major role in influencing stoichiometric ratios, often constraining the amount of DOC exported during floods relative to TN and TP. Within this constraint, biogeochemical processes determine stoichiometric ratios in the streams.

4.2. DOC, TN and TP Annual Export Fluxes and Their Ratios

DOC fluxes in our study streams generally were within the range of fluxes from small, forested watersheds in the northeastern USA ($0.5\text{--}5.7\text{ g m}^{-2}\text{ yr}^{-1}$; Raymond & Saiers, 2010). Our DOC, TN, and TP was exported during high flow events, similar to that of other headwater streams (e.g., Ockenden et al., 2016). So far no clear changes in long-term DOC exports in our catchments have been detected (Wu et al., 2023). The highest fluxes of DOC, TN and TP from our study catchments occurred in spring, during snowmelt, which is similar to other studies reporting the highest share of annual export of TN and DOC during snowmelt, in response to infiltrating meltwater (Boyer et al., 2000; Sebestyen et al., 2009). Similarly, previous studies have shown that export fluxes of DOC, TP and TN change across seasons (Clair et al., 2008; Corriveau et al., 2013; Rattan et al., 2017). Although the export of DOC, and TN and TP changed with discharge (Boyer et al., 2000; Butturini et al., 2006; Fasching et al., 2016), our study is the first to show that the ratios of DOC:TN:TP also varied, likely due to the biological and chemical factors described above, with potential consequences for biogeochemical processing and downstream transport of solutes.

Floods may lead to DOC and nutrient depletions (Butturini et al., 2006; Fasching et al., 2018) while extended low flow periods, and less frequent floods per year, may promote N and P build up and export to the stream. Consequently, years that were characterized by a few larger floods (and high annual discharge) resulted in decreased annual DOC:TN and DOC:TP in export fluxes, increasing the relative contributions of TN and TP in the streams. All our study streams were generally N and P limited, but not OC limited (according to Stutter et al., 2018), possibly impacting heterotrophic pathways. Therefore, future large floods and droughts can increase contributions of TN and TP, while increasing the TN:TP ratio, which may have implications for downstream resource stoichiometry, as well as the structure and nutrient fluxes within downstream communities. For example, altered stoichiometry may potentially reduce food chain length and invertebrate community diversity (Singer & Battin, 2007), stimulate bacterial growth efficiency which is often limited by N and P (del Giorgio et al., 1998) and have implications for lake ecosystem metabolism (Corman et al., 2023).

4.3. Annual Flux and Retention of DOC, TN and TP Through Lakes

Overall, within the studied watersheds, TN:TP increased from the inflow toward the outflow, indicating either biological uptake of the often-limiting P (Elser et al., 2009) or efficient burial (Maranger et al., 2018) as water moved through the lake. Similarly, the ratio of particulate nitrogen to particulate phosphorus has been shown to increase along the flow path from the tributaries of Lake Erie, to the lake itself, and its outflow (Prater et al., 2017). An N-mass balance for our two study lakes showed that there was no significant decline of N in the lakes, although the N and P loads from catchments declined strongly over time (Yao et al., 2017). This discrepancy could be caused, in part, by the decreased biological N uptake due to decreased nutrient P loads (Yao et al., 2017). Considering annual averages however, DOC:TN was lower in both lakes compared to their respective inflows, caused by a decrease in DOC and increase in TN concentration. This may point to N sources from the ungauged shoreline, and C uptake and/or photochemical and biological degradation of DOC within the lakes (Fasching & Battin, 2012; Maavara et al., 2021). In fact, photochemical degradation of organic matter has been shown previously in Canadian boreal lakes (Lapierre et al., 2013). The retention and uptake behavior of DOC, TN and TP concentrations in our study lakes was further modulated by the flow regime, which in turn influenced lake residence times. Within our watersheds, the lakes removed DOC and TP, while increasing TN depending on the flow regime. Increasing durations of low flow periods within a year stimulated TN removal from lakes, possibly driven by denitrification, while lower annual discharge but increased days of flooding (i.e., few, but high floods) lowered the lakes ability to retain DOC and TP. Floods may decrease residence times in the lakes, therefore also decreasing the opportunity for biological transformation and processing of nutrients and organic matter, and possibly resulting in decreased DOC and nutrient retention. In fact, residence time has been shown to determine lake DOC export across several European and North American lakes, as well as in marine waters (Fransner et al., 2016), with longer residence times allowing for photochemical removal and increased opportunity for the biological consumption and production of DOC (Evans et al., 2017). However, the observed trends are likely complicated by varying nutrient deposition rates (Elser et al., 2009; Mosello et al., 2001) and

biological nutrient demand. In any case, with large floods and droughts that are predicted under future climate scenarios (Burn & Whitfield, 2016; Kunkel, 2003; Vincent & Mekis, 2016) consequences for lake cycling and retention of DOC and nutrients are expected. Our results indicate that lakes may change and even decrease their ability to retain DOC and TP, impacting annual lake nutrient export fluxes.

4.4. Conclusions

Our analysis spanning 37 years of continuous data provides a comprehensive and robust perspective on trends and patterns in watershed-scale stoichiometry and the transport of organic carbon and nutrients. Our study illustrates the dynamic shift in the movement of N, P, and OC, along with their respective ratios, within two integrated watersheds including streams and lakes. We underscore the pivotal role of the flow regime, particularly floods, high flow events, and periods of lowflow, in influencing macronutrient stoichiometry in streams and the retention of nutrients in lakes. We emphasize the importance of not only examining individual nutrients but also investigating their interrelations and stoichiometry over extended periods. While initial observations might suggest similar concentration and export trends of DOC, TN and TP concerning discharge and seasonal variations, our findings reveal that extreme events like floods and droughts—projections for which indicate an increase in the future can significantly alter DOC:TN:TP stoichiometry (Burn & Whitfield, 2016; Kunkel, 2003; Tan et al., 2017; Vincent & Mekis, 2016). These events tend to enhance the relative contributions of TN and TP in streams and can impact the retention of DOC and nutrients in lakes. Such changes are crucial as they can potentially reshape the processing pathways of DOC and nutrients from catchments to oceans.

Expected alterations in flow regime—changes in the frequency, magnitude and timing of flow events—can markedly influence the residence times of lakes and the fluxes of aquatic carbon, nutrients, and energy to downstream ecosystems across the continuum from inland to marine environments. These changes may significantly alter the structure and function of aquatic ecosystems, including their ability to provide essential ecosystem services. Changes in the balance of C:N:P can impact aquatic metabolism, and potentially facilitate algal blooms, yet managers and policymakers typically only focus on one solute and element at a time. Thus, a better understanding of DOC:nutrient ratios, across the inland - marine continuum facilitates better prediction and management of nutrient loading in these ecosystems. This understanding is essential for guiding policy and management strategies aimed at mitigating potential negative social, economic, and environmental impacts of changes in inland hydrology on these important ecosystems.

One essential next step would be to characterize TN and TP fractions, which differ in reactivity and likely vary considerably due to differences in geology, land-use corresponding loading sources and the calculation of nutrient balances. While our study was set in a pristine environment, there is a need to carry out long-term studies in anthropogenically impacted regions across stream-lake continua to allow for robust analyses and prediction of how these systems may react to changing climate.

Data Availability Statement

The data on which this article is based are available in Fasching et al. (2024).

Acknowledgments

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