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# Differential influence of landscape features and climate on nitrogen and phosphorus transport throughout the watershed

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**Abstract** Anthropogenic activities have led to increased transfers of nitrogen (N) and phosphorus (P) to surface waters where changes in the absolute amounts of N and P delivery, and in N:P ratios, threaten water quality. While models of riverine fluxes are increasingly good at predicting total annual nutrient loads, our understanding of which features of a watershed differentially affect N and P transport downstream is still limited. In this study, we used linear mixed models to quantify the relative transport of N and P through different landscape and limnoscape compartments (e.g. hill slopes, lakes, reservoirs,) under a variety of climate regimes over 26 years in 18 watersheds of the St. Lawrence Basin. Water retention capacity and precipitation patterns were the features that most strongly influenced nutrient export from land to water, where P was preferentially retained in the landscape over N when water retention capacity was highest. Lakes and reservoirs also emerged as features that influenced nutrient fluxes, where lakes preferentially retain more P over N and reservoirs tended to export N. Factors that favor erosion, such as flashiness of precipitation and land-use change also alter N:P ratios in receiving waters, largely by mobilizing legacy sources of P.

**Keywords** Watershed · Nitrogen · Phosphorus · Dams · Lakes · Nutrient fluxes · Stoichiometry

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## Introduction

Anthropogenic activities such as urban development and the widespread use of fertilizers for industrial agriculture have led to increased transfers of nutrients to surface waters, often resulting in aquatic eutrophication at great economic cost (Carpenter et al. 1998; Dodds et al. 2009). While changes in the absolute amounts of nutrient influx influence productivity of aquatic ecosystems, alterations in N: P export ratios influence community structure (Sterner and Elser 2002) potentially favoring toxic species of cyanobacteria (Scott et al. 2013; Van de Waal et al. 2014).

Models of nutrient fluxes to riverine ecosystems are becoming increasingly good at predicting total annual nutrient loads (Kroeze et al. 2012; Chen et al. 2018). However, our understanding of how various watershed features differentially affect the relative export of N versus P remains limited (Collins et al. 2017), despite our knowledge of the key differences in their biogeochemistries and elemental cycles (Maranger et al. 2018). Although previous studies have explored how climate, geomorphology, or land use affect the delivery of N or P downstream (Harrison et al. 2009; Seitzinger 2010; Howarth et al. 2012), few have specifically identified the importance of these features on the relative rates of N and P transport. Characterizing how different landscape and climatic features act as control points (Bernhardt et al. 2017), defined here as a feature that disproportionally transports or retains one nutrient over the other within watersheds, could provide guidance to maintain water quality by helping us understand how different features influence N: P export ratios.

N and P may be differentially retained within watersheds at varying time scales depending on landscape characteristics of the catchment basin and/or the hydrological configuration of lakes and streams (i.e., limnoscape) (Soranno et al. 1999; Jarvie et al. 2013; Sebilo et al. 2013). In the catchment, for example, nitrate moves more freely through soil matrix given its higher solubility (Hill et al. 1999; Frank et al. 2000), whereas phosphate tends to be adsorbed to soil particles and is potentially often exported from watersheds in particulate form (Holtan et al. 1988; Ockenden et al. 2016). Furthermore P can accumulate for decades in agricultural soils resulting in legacy P that can continue to enter waterways decades after application (Sharpley et al. 2013). P also has no meaningful gaseous loss term, whereas a large fraction of the N can be lost to the atmosphere rapidly through denitrification (considered here as N retention), particularly in flatter watershed areas (Galloway et al. 2004; Schlesinger and Bernhardt 2013). Thus, land use together with catchment slope, land use histories, and precipitation patterns may modify relative nutrient movement (Seitzinger et al. 2006), as well as influence the delivery of different nutrient forms.

N and P continue to be retained or transported in receiving waters (Newbold et al. 1981; Wollheim 2006; Maranger et al. 2018), but as within the landscape, various limnoscape features may act as differential control points between both nutrients, and the nature of how these control points function may change over time. Gaseous N loss, for example, is heavily influenced by high water–sediment contact due to the redox conditions that favour denitrification which is why streams tend to have very high N loss rates (Mulholland et al. 2008; Wollheim 2008). Increased water residence time of rivers and lakes favours denitrification loss as well (Saunders and Kalff 2001; Seitzinger et al. 2006; Harrison et al. 2009), but lakes also promote water column P loss through sediment storage via particle settling (Kirchner and Dillon 1975; Larsen and Mercier 1976; Soranno et al. 2015). Human-made reservoirs, however, are increasingly recognized as distinctive from lakes in terms of ecological functioning (Thornton et al. 1990; Hayes et al. 2017). In terms of net removal, reservoirs retain a disproportionate amounts of P (Maavara et al. 2015) and N compared to lakes (Harrison et al. 2009), but it is not known whether they differentially influence nutrient export ratios. That said, both lakes and reservoirs can become net sources of nutrients when stores are remobilized and exported (Nowlin et al. 2005; Teodoru and Wehrli 2005; Wurtsbaugh et al. 2005; Powers et al. 2015). Thus, certain conditions, be they intrinsic (ecosystem shape) or extrinsic (land use history), may result in lentic water bodies changing how they act as control points at different moments in time.

The transport and retention of nutrients throughout the watershed are largely influenced by water residence time within a basin and soil/sediment contact rates (Vought 1994; Nixon et al. 1996; Harrison et al. 2009; Maranger et al. 2018). One metric that might capture the integrative influence of climate, geomorphology and landscape features on hydrology, and thereby influence the overall nutrient transport at the watershed scale, is the annual Runoff to Precipitation ratio (Roderick and Farquhar 2011; Zhou et al. 2015). Indeed, given equations of catchment water balance (Budyko 1974), the proportion of precipitation that reaches the river's outlet as runoff (Runoff: Precipitation, mm $mm^{-1}$) varies as function of precipitation, evapotranspiration, and watershed characteristics such as soil type, land use, and geomorphology. Hence, annual runoff and precipitation, considered together, either as separate complementary terms or through their ratio, are a proxy for catchment water retention capacity, which ultimately influences nutrient delivery at the annual timescale. Wetter years and extreme precipitation events, for example, may increase downstream nutrient transfers (Howarth et al. 2006; Zhou et al. 2014), whereas years with a high frequency of extreme events may favor the delivery of more particulate forms, as evidenced by co-occurrence of high sediments/colloids together with TP loads (Heathwaite et al. 2005; Ockenden et al. 2016). But, if annual runoff is kept unchanged through greater retention of precipitation within the basin as a function of its geomorphology and different landscape and limnoscape features, then overall downstream nutrient transfers may be partially buffered, but again differentially, potentially altering N:P export ratios.

Here, we aim to assess how catchment slope, water retention capacity and climate patterns (categorized as "land to water" variables), as well as the type of lentic water body (lakes or reservoirs; categorized as "within aquatic networks" or limnoscape variables) act as differential control points to alter the relative transport of N versus P including the delivery of different chemical forms to rivers. To evaluate this, we reconstructed annual anthropogenic N and P surpluses for 18 moderately sized watersheds of the St-Lawrence Basin (1688–10,666 km$^2$) across a gradient of land use and geomorphic characteristics and calculated annual loads of N and P at their outlet from 1986 to 2011. This study focuses on the annual fractional export of anthropogenic nutrient surpluses at watershed outlets rather than the absolute riverine nutrient loads. This allowed us to specifically evaluate how different features influence the transport of nutrients throughout the watersheds of an entire region.

## Methods

### Study area

The 18 watersheds used in this study drain part of the St. Lawrence River Basin and are entirely located in the province of Quebec, Canada. These watersheds range in size from 1688 to 10,666 km$^2$, have different land use and landscape features, and are subject to different climate conditions and geological properties (Fig. 1; Natural Resources Canada 2003). Watersheds on the right bank of the St-Lawrence, situated on the Interior Plain (Fig. 1), are largely agricultural with a number of small dams; whereas basins to the north, on the left bank are located mostly on the Canadian Shield, covered largely by boreal forest, with many lakes and some with large reservoirs for hydropower. The St. Lawrence Basin, located north of 40°N, is subject to a strong seasonality that promotes snow pack accumulation in winter and an important spring freshet.

### N and P budget construction (NANI and NAPI)

We constructed N and P budgets for each of the 18 watersheds (Fig. 1) at a 5 year time interval from 1986 to 2011, corresponding to agricultural census years. These budgets were linearly interpolated to estimate net anthropogenic nutrient inputs throughout the 26 year period. We quantified all known anthropogenic N and P inputs (N and P fertilizer use, biological N fixation from cultivated crops, atmospheric N deposition, P in detergents and imports of N and P in food and feed), and outputs (exports of N and P in food and feed) and used these to calculate Net Anthropogenic N and P Inputs (NANI and NAPI). Details can be found in Goyette et al. (2016) for estimates to these specific watersheds. Briefly, the NANI/NAPI model uses a mass balance approach to account for "new" anthropogenic N or P inputs into a watershed (Howarth et al. 1996; Russell et al. 2008). Fluxes of nutrients to watersheds as a function of human activities are derived largely from publically available sources of information, primarily agricultural censuses and demographic data that allow for an empirical evaluation of net estimate of input.

### Riverine N and P exports

Annual riverine exports of total nitrogen (TN) and total phosphorus (TP) were estimated from 1985 to 2011 for all 18 rivers. Different chemical forms were considered: total N (TN), dissolved inorganic N (DIN; by summing $NO_x + NH_3$), Organic N (ON; by subtracting DIN from TN), total P (TP), total suspended P (TSP) and total dissolved P (TDP). Annual riverine N and P loads of all chemical forms (with the exception of ON) were calculated from daily discharge (Centre d'Expertise Hydrique du Québec 2018) and monthly or bi-monthly nutrient concentrations (Banque de données sur la Qualité du Milieu

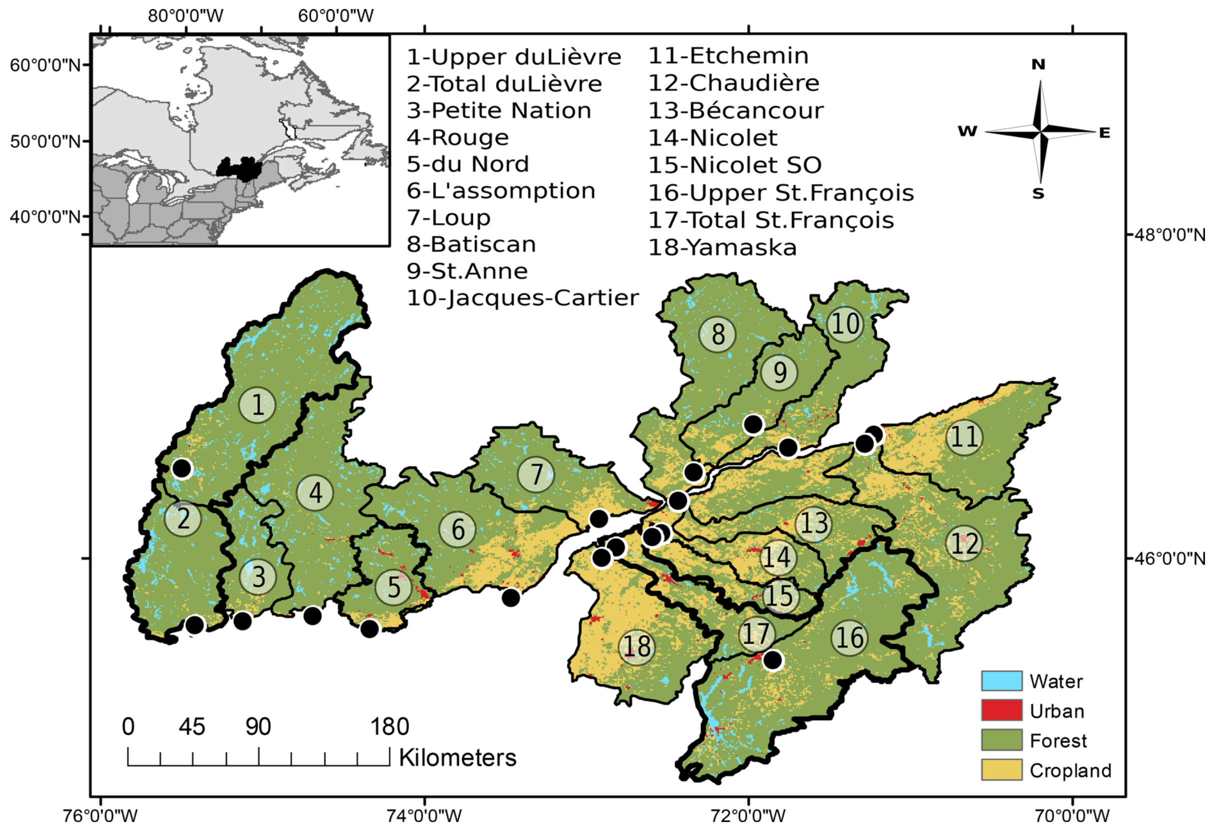


**Fig. 1** The 18 watersheds considered in this study. General land use categories and water quality monitoring stations (black dots) are shown

Aquatique 2018), using the LOADEST procedure (Runkel 2004) in R with package loadflex (Appling et al. 2015). LOADEST is an approach that allows for flow-weighted interpolations of the discrete concentration measurements, thus reducing bias by accounting for exceptionally high or low daily discharge events. From nine potential models tested, the best model was selected based on the corrected Akaike information criterion (AICc). For each river and each focal year, models were calibrated over a 5-year time interval (i.e., from 1994 to 1998 for the focal year 1996) before being used in combination with daily discharge to predict annual loads. When gauging stations were not located where water chemistry was sampled, discharge was estimated from sampled discharge ($m^3$ $km^{-2}$) that was corrected for the drainage area ($km^2$) of the monitoring site. Mass yield (kg N or P $km^{-2}$ $year^{-1}$) was calculated by dividing annual load by drainage area.

## Dominant chemical forms

We explored how the different chemical forms contributed to total N and P annual loads and how they varied over space and time. First, linear regressions were used to relate loads of all N and P chemical forms (TN, DIN, ON, TP, TSP and TDP) to NANI and NAPI, respectively. Secondly, we calculated the contribution of DIN to total N load (%DIN) and of TSP to total P load (%TSP) and explored how that changed with level of watershed enrichment (NANI and NAPI). Finally, we assessed how the fractional export of the different chemical forms was influenced by key spatial and temporal drivers in multiple regressions (details below in "Statistical analyses" section).

## Geospatial data

Mean watershed slope was calculated from digital elevation models at 30 $m^2$ resolution. Surface area of lentic water bodies (reservoirs and lakes) was retrieved from Natural Resources Canada (2003). To estimate total lake area per watershed, reservoir surface area (at full pool) was subtracted from the lentic total. Specific information on reservoirs (location, volume, area, dam height) was retrieved from Centre d'Expertise Hydrique du Québec (2018). Two morphometric variables were computed; mean reservoir depth (ResZ) and Volume Development (Dv), which characterizes water basin shapes (Kalff 2002). *ResZ* was calculated by dividing volume with area while *Dv* was calculated as three times the depth ratio (mean depth over maximum depth; Table 1). *Dv* values around 1.3 are representative of systems with shallow margins and a deep hole while $Dv > \sim 2$ reveal systems with flat floors and steep sides. Dam height was used as a proxy for maximum depth. *ResZ* and *Dv* were then calculated as an integrative mean per watershed. The number of dams within a basin was normalized per unit area ($km^{-2}$) for cross comparison among watersheds.

Annual runoff was calculated as the sum of daily discharge at the outlet. The coefficient of variation (CV) of daily runoff within a year (*CVflow*) was used as an indicator of flow regime. Similarly, we used the CV of daily precipitation within each year (*CVprec*) as a proxy of flashiness of rainfall events, arguing that high CV values represent years with flashier precipitation patterns. Annual and daily precipitation were obtained for the period of the present study (1986–2011) at a spatial resolution of 10 km using thin plate smoothing splines (McKenney et al. 2011). The annual water balance of catchments (or catchment water retention capacity) was estimated as a single variable through the annual *Runoff* to *Precipitation* ratio (*R*:*P*; Table 1). Calculations of all geospatial variables were conducted using ArcGIS 10.0.

## Statistical analyses

To assess the different retention patterns and pathways of N and P through the landscape, we evaluated which set of predictors best explained fractional N and P export. Fractional export is defined as the annual load of N or P exported at the watershed outlet relative to total "new" anthropogenic N or P inputs to that watershed within the same year (NANI or NAPI). In order to identify the factors that most strongly influenced fractional export, we used linear mixed models (LMMs; Zuur et al. 2009), where intercepts and/or slopes were set to vary between "Watersheds" or "Years" (as random factors). The random factor in LMM controls for the hierarchical structure of the dataset. This allowed us not only to correct for pseudoreplication, but to explore the spatial and temporal structure of the data independently by centering all explanatory variables within groups (watersheds or years) as suggested by Enders and Tofighi (2007). Details are described and exemplified in the Supplementary Information section (see Fig S1). Briefly these models estimate the mean effect of each selected predictor (1) across all years (years set as random), thus revealing the main drivers of spatial variability and (2) across all watersheds (watershed set as random), thus revealing main drivers of temporal variability. All variables were considered as potential predictors of spatial variability with the exception of *CVflow* and *CVprec*. Instead, the latter variables were used to capture the influence of storm events on nutrient transport within a given watershed, and so were used to explain temporal variability only. *Dam*-related variables and *Lakes* were not tested in temporal models as these variables were fixed throughout the study period (Table 1). However, we tested how the density of lentic waters (lakes and reservoirs proportional area within watersheds) could buffer the impact of inter-annual changes in climate (annual runoff and flashiness) on fractional export by comparing the potential different responses across watersheds using LMM (details in SI).

One disadvantage of LMM is that it does not specifically account for alternative model structures, which may affect model coefficients. To assess the sensitivity of our models, we compared our final LMMs to a partial least square (PLS) approach (Carrascal et al. 2009) that explicitly accounted for alternative model structures. Results of this comparison showed that the two approaches led to very similar results, supporting our choice to use LMM. Prior to conducting our analyses, we used variance inflation factor (VIF) analysis to identify which independent variables were collinear (Graham 2003; Blanchet et al. 2008). VIF values greater than 5 or 10 suggests autocorrelation (Mason et al. 2003), and a threshold of 5 was used in this study to remove collinear variables (Tables S1). The random structures of LMMs were identified and selected first, resulting in models with varying intercepts only. This was

**Table 1** Variables tested in multiple regression models (lower table), symbols, units and data sources

| Symbols | Description | Units | Source |
|---|---|---|---|
| | *Information used to calculate some variables considered in mixed models* | | |
| *WA* | Watershed area | $km^2$ | Calculated from geospatial data[1] |
| *LenticA* | Lentic water area | $km^2$ | |
| *#Dams* | Number of Dams | # | CEHQ[3] |
| *ResA* | Reservoir max area | $m^2$ | |
| *ResVol* | Reservoir volume | $m^3$ | |
| *maxZ* | Maximum depth estimated from dam height | m | |
| *LakeA* | Lake area | $km^2$ | *LakeA = LenticA - ResA*10 $^6$* |
| *NANI* | Net anthropogenic N inputs | kg $km^{-2}$ $yr^{-1}$ | Goyette et al. (2016) |
| *NAPI* | Net anthropogenic P inputs | kg $km^{-2}$ $yr^{-1}$ | |
| *TN* | riverine TN export | kg $km^{-2}$ $yr^{-1}$ | Calculated herein from BQMA[2] and CEHQ[3] |
| *TP* | riverine TP export | kg $km^{-2}$ $yr^{-1}$ | |
| | *Variables considered as fixed effects in mixed models* | | |
| *FrN* | Fractional N export | % | *FrN = river TN load/NANI* |
| *FrP* | Fractional P export | % | *FrP = river TP load/NAPI* |
| *spDams* | Dam density | # $km^{-2}$ | spDams = #Dams/ WA |
| *ResZ* | Mean of reservoirs mean depth within watersheds | m | *ResZ = mean(ResVol/ResA)* |
| *Dv* | Mean of reservoirs developpment volume within a watershed | $m^3$ | *Dv = mean(ResZ/maxZ*3)* |
| *Lakes* | Percentage watershed area as lakes | % | *Lakes = LakeA/WA* |
| *Slope* | Watershed mean slope | ° | Calculated from geospatial data[1] |
| *Runoff* | Annual runoff | mm | Calculated from CEHQ[3] |
| *Prec* | Annual precipitation | mm | McKenney et al. (2011) |
| *R: P* | Annual runoff to precipitation ratio | % | *R: P = Runoff/Prec* |
| *Temp* | Mean annual temperature | °C | McKenney et al. (2011) |
| *CVflow* | CV of daily discharge per watershed per year | unitless | Calculated from CEHQ[3] |
| *CVPrec* | CV of daily precipitation per watershed per year | unitless | McKenney et al. (2011) |

[a]Natural Resources Canada (2003)

[b]Banque de données de la Qualité du Milieu Aquatique (2018)

[c]Centre d'Expertise Hydrique du Québec (2018)

followed by a backward selection of predictor variables (fixed effects), using the corrected Akaike information criterion (AICc) to assess model performance (Zuur et al. 2009). All variables were log-transformed to meet normality assumptions of linear regression and fully standardized to allow comparison of model coefficients as indicators of the relative strengths of predictors. Since LMM is fitted with maximum likelihood and does not provide a traditional $R^2$, *Pseudo*-$R^2$s were calculated following Nakagawa and Schielzeth (2013).

We compared N and P models by evaluating the difference in the effect size of each driver. This was done by comparing standardized regression coefficients of specific model terms. To assess significant differences, the comparison was done using the standard errors of each coefficient to calculate z scores and p values (Cohen et al. 2013). Additionally, variables not selected in the backward selection approach were tested in alternative models to explore their potential influence on N and P export. All analyses were conducted in R and LMM were fitted following (Zuur et al. 2009) using restricted maximum likelihood in the lme4 package (Team 2013; Bates 2014).

As a preliminary evaluation of watershed sensitivity to inter-annual changes, the variability in fractional N and P export was calculated through standard deviation of fractional export within each watershed. To remove long term trends and focus the analysis on inter-annual variability only, we conducted linear regressions between log-transformed fractional export and time (years) for each watershed and kept the residuals. We then calculated the standard deviation of those residuals (detrended data) within each watershed.

## Results

### Relation between NANI/NAPI and river nutrient loads

Riverine loads of TN and TP were well predicted by NANI ($R^2 = 0.62$) and NAPI ($R^2 = 0.68$), respectively (Fig. 2a, b). Fractional N and P export, however, varied both across watersheds and among years within a watershed (Fig. 2c, d). Mean fractional export over the 26 year period ranged from 16 to 69% across all watersheds for N (overall mean of 30%) and from 5 to 49% for P (overall mean of 16%; Table 2; Fig. 2c, d), thus highlighting differences in nutrient retention among basins. We also observed inter-annual variability in fractional export within watersheds. On average across all watersheds, standard deviation of fractional export over time (detrended data) was 0.25 for N (range 0.15–0.52) and 0.37 for P (range 0.19–0.51), indicating that inter-annual variability in riverine export was greater in some watersheds than others, and more so for P. Disproportionately large transfers were observed in some years where export exceeded net annual inputs (163% and 187% for N and P, respectively), whereas in other years, fractional export was as low as 2% and 8% for N and P, respectively.

### Range of independent variables

The 18 watersheds used in this study varied considerably in terms of climate, geomorphology, land-use, impoundment density as well as the differential morphometry of reservoirs (Table 2). This wide range allowed us to explore which features more strongly influence the relative retention or export of both nutrients. In terms of human made changes in hydrologic flow, dam density ranged from one dam every 4 $km^2$ of drainage area to approximately one dam per 100 $km^2$. Overall reservoir mean depth (*ResZ*) varied from 1.82 to 5 m across watersheds, and *Dv* of reservoirs, from 1.43 to 2.89 suggesting not only a diversity in depth, but also in water basin shape. While the long term mean of annual Precipitation did not vary much among watersheds (overall mean of $\sim$ 1142 mm; CV of 7%), annual Runoff varied considerably, from 607 to 1115 mm (Table 2) highlighting large differences in annual water retention capacity across basins (*R: P* ratios ranging from 0.53 to 0.83). Mean *Slope* also varied across watersheds ranging from 1.7 to 8° (Table 2). The VIF analysis revealed strong autocorrelation of *R: P* with both annual *Runoff* and *Precipitation* (Tables S1 and S2). *R: P* was therefore excluded in the first round of backward selection to identify the best models of fractional export, yet was tested in alternative models. In terms of response variables, fractional N and P exports varied much more over all years and watersheds (CV of 63% for N and 89% for P) than the molar N: P ratio (CV of 47%). This low variability of N: P

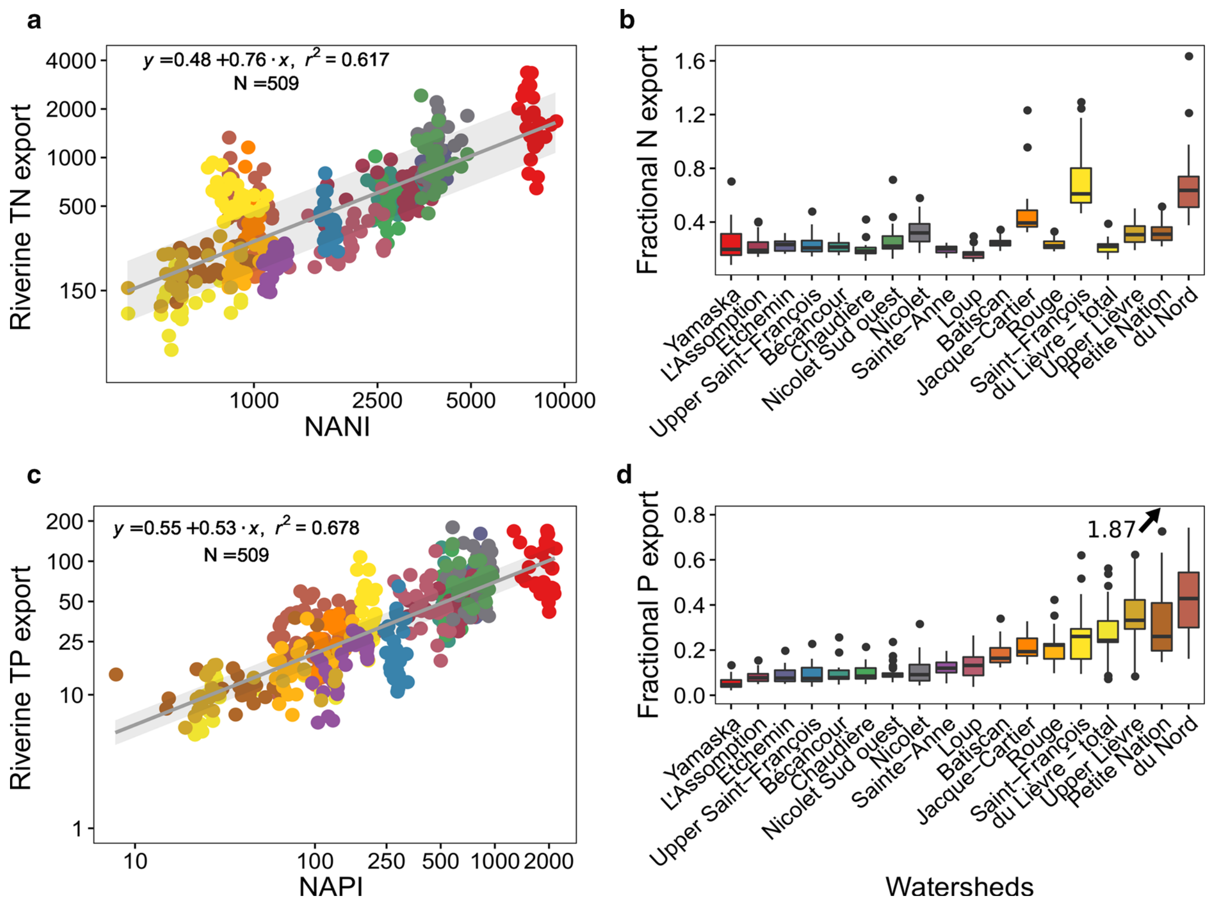


**Fig. 2** Log–Log Relationships between riverine N or P loads (Kg N or P $km^{-2}$ $year^{-1}$) and net anthropogenic N or P inputs to watersheds (NANI/NAPI; Kg N or P $km^{-2}$ $year^{-1}$), **a** and **c** respectively. Regressions were fitted using linear mixed models (LMM) with "Years" as random factors varying between intercepts only. Variability in fractional N or P export across years and in different watersheds is explicitly shown on right panels; **b** and **d** respectively. Colors in **a** and **c** are related to their associated watersheds identified in **b** and **d**. The box delimits the interquartile range (IQR; 25th to 75th percentiles) of the distribution, while whiskers span 1.5 times the IQR and dots represent outliers

ratios is likely due to the high collinearity of N and P loads (Fig S2) where for high riverine loads of N, P was also highest.

## Factors influencing fractional nutrient export (downstream transport) across space

We characterized which variables (Table 2) best described the different fractional N or P export across space. Although, we were not able to explain any of the changes in N: P ratios likely due to a lack of statistical power resulting from low variability among sites (Table 2), our models of N and P fractional export included the same set of six independent variables (Table 3). Although dam density was not statistically significant in the P model, we opted to compare these same six variables, since the PLS analysis, which accounts for alternative model structures, led to similar results with regards to relative slope coefficients, thus supporting our comparison of coefficients between N and P models frN6 and frP6 in Table 3, respectively. Comparing the slope coefficients of each driver between N and P models allowed us to consider their relative influence on downstream transport of both nutrients. In terms of climate related variables, the annual runoff entered both models with similar slope coefficients (0.31 and 0.32 for N and P, respectively), highlighting increased nutrient transfers to surface waters in wetter regions (Table 3; Fig. 3). Annual precipitation entered both models in addition

**Table 2** Average of different watershed characteristics over the study period (1985–2011)

| Watershed name | Area ($km^2$) | *Spatial* | | | | | *Spatial &Temporal* | | | | *Temporal* | | NANI | NAPI | TN export | TP export | Fractional export (%) | | Mean concentration ($mg\ L^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **#dams** | **Reservoir Mean depth (m)** | **Dv** | **Lake area ($km^2$)** | **Slope (°)** | **Runoff (mm)** | **Prec (mm)** | **R:P** | **Temp (°C)** | **CVprec** | **CVflow** | | | | | | | | |
| | | | | | | | | | | | **(CV)** | | ($Kg\ km^{-2}\ yr^{-1}$) | | | | N | P | N | P |
| Batiscan | 5023 | 131 | 2.00 | 1.83 | 553 | 5.5 | 816 | 1178 | 0.69 | 6.57 | 162 | 95 | 1009 | 115 | 250 | 22 | 24.7 | 19.1 | 0.278 | 0.024 |
| Bécancour | 2567 | 54 | 3.70 | 2.89 | 26 | 3.2 | 769 | 1175 | 0.65 | 7.84 | 156 | 132 | 2911 | 573 | 626 | 54 | 21.5 | 9.4 | 0.892 | 0.074 |
| Chaudière | 6600 | 220 | 2.15 | 2.09 | 462 | 3.5 | 713 | 1160 | 0.61 | 7.9 | 179 | 153 | 2682 | 561 | 517 | 55 | 19.3 | 9.9 | 0.736 | 0.078 |
| du Lièvre - total | 7099 | 218 | 5.00 | 2.18 | 426 | 5.1 | 866 | 1023 | 0.85 | 7.67 | 189 | 69 | 609 | 44 | 125 | 9 | 20.5 | 20.4 | 0.146 | 0.01 |
| du Nord | 2224 | 543 | 2.49 | 2.37 | 133 | 6.4 | 763 | 1110 | 0.68 | 8.36 | 184 | 118 | 930 | 92 | 611 | 38 | 65.8 | 41.0 | 0.799 | 0.051 |
| Etchemin | 3936 | 183 | 2.12 | 1.85 | 394 | 3.4 | 837 | 1196 | 0.70 | 7.83 | 196 | 132 | 3847 | 795 | 883 | 70 | 22.9 | 8.8 | 1.054 | 0.084 |
| Jacque-Cartier | 3191 | 124 | 2.66 | 2.28 | 447 | 7.6 | 1115 | 1347 | 0.83 | 6.65 | 198 | 101 | 973 | 118 | 460 | 25 | 47.2 | 21.4 | 0.325 | 0.018 |
| L'Assomption | 5204 | 746 | 2.64 | 2.31 | 1197 | 4.9 | 654 | 1082 | 0.60 | 8 | 183 | 127 | 2948 | 622 | 627 | 49 | 21.3 | 7.9 | 0.971 | 0.076 |
| Loup | 3289 | 248 | 2.42 | 2.19 | 789 | 5.3 | 596 | 1077 | 0.55 | 6.9 | 186 | 124 | 2050 | 409 | 327 | 52 | 15.9 | 12.7 | 0.241 | 0.038 |
| Nicolet | 1692 | 36 | 1.95 | 1.43 | 344 | 2.3 | 778 | 1137 | 0.68 | 7.98 | 176 | 151 | 3837 | 790 | 1260 | 81 | 32.8 | 10.2 | 0.753 | 0.048 |
| Nicolet Sud ouest | 1688 | 32 | 1.82 | 1.66 | 332 | 2.1 | 750 | 1123 | 0.66 | 7.85 | 179 | 148 | 3688 | 723 | 989 | 76 | 25.8 | 9.6 | 0.618 | 0.047 |
| Petite Nation | 2189 | 47 | 1.85 | 1.57 | 153 | 5.6 | 607 | 1079 | 0.56 | 7.57 | 181 | 89 | 728 | 54 | 233 | 15 | 32.0 | 27.3 | 0.387 | 0.024 |
| Rouge | 5549 | 219 | 2.14 | 2.11 | 333 | 6.4 | 705 | 1108 | 0.63 | 8.21 | 183 | 91 | 926 | 91 | 217 | 19 | 23.5 | 21.1 | 0.307 | 0.027 |
| Saint-François | 10666 | 460 | 2.61 | 1.84 | 320 | 2.1 | 877 | 1131 | 0.77 | 8.15 | 184 | 88 | 863 | 195 | 592 | 49 | 68.5 | 25.1 | 0.682 | 0.055 |
| Sainte-Anne | 2758 | 113 | 2.17 | 2.18 | 55 | 8.0 | 911 | 1301 | 0.70 | 6.88 | 170 | 115 | 1169 | 151 | 226 | 19 | 19.4 | 12.4 | 0.182 | 0.015 |
| Upper Lièvre | 7099 | 111 | 4.55 | 1.80 | 462 | 5.1 | 659 | 1023 | 0.65 | 7.67 | 189 | 69 | 609 | 44 | 194 | 11 | 31.8 | 24.8 | 0.294 | 0.017 |
| Upper Saint-François | 8255 | 369 | 2.68 | 1.82 | 248 | 3.9 | 877 | 1194 | 0.73 | 7.97 | 176 | 88 | 1735 | 283 | 409 | 26 | 23.6 | 9.0 | 0.458 | 0.028 |
| Yamaska | 4626 | 287 | 2.70 | 2.09 | 1203 | 1.7 | 599 | 1116 | 0.53 | 8.09 | 176 | 151 | 7885 | 1838 | 1890 | 97 | 24.0 | 5.3 | 3.164 | 0.163 |

Bolded variables were tested as predictors of either spatial or temporal variability (or both) in fractional N and P export to annual runoff and was negatively correlated with fractional export. Accounting for the amount of runoff, the precipitation term was significantly stronger for P (− 0.32) than for N (− 0.16) ($p < 0.001$; Fig. 3). Mean watershed slope had a strong positive effect on the fractional export of P (coefficient of 0.27), highlighting increased transfers in steeper watersheds. Conversely, a negative correlation was observed in the case of N (coefficient of − 0.08), highlighting accentuated downstream transfers of N in flatter watersheds.

In terms of processing within aquatic networks, our results showed that deeper reservoirs increased the retention of both nutrients with no significant difference in the strength of that effect (slope coefficient of ResZ = − 0.19 and − 0.24 for N and P, respectively; Table 3; Fig. 3). In opposition, the specific number of dams (per $km^{-2}$) showed positive correlations with fractional N export yet no significant relationship was observed in the case of P. Finally, lakes on the landscape retained significantly more P ($p = 0.024$) given that the slope coefficient for P (− 0.24) was twice that of N (− 0.12).

In alternative models (Table S2), *R: P* was tested as a substitute to both *Runoff* and *Precipitation* and showed a positive correlation ($p < 0.001$) with fractional nutrient export, highlighting increased downstream nutrient transfers in watersheds with lower annual water retention capacities (high *R*:*P*). However, the N and P models that included *Runoff* and *Precipitation* as separate terms (Table S2) were stronger (lower AIC), although for N that difference was minimal (ΔAIC = 2; Tables 3, S3). Also, as a substitute to *ResZ*, *Dv* entered both N and P models as a significant predictor (at $\alpha = 0.05$) of fractional export, showing that bowl-shaped reservoirs with limiting areas of riparian shallow waters promoted nutrient retention (Table S2). This effect was slightly stronger ($p = 0.08$) for P (coefficient of − 0.18) than for N (− 0.13).

### Factors influencing inter-annual variability in downstream transfers of nutrients

We characterized which variables (Table 2) best described the different fractional N or P export over time. The best models of N and P fractional export included *Runoff* and *CVflow* only, but for N, the latter variable was only significant at $p = 0.09$ level (Table 4; Fig. 4). The slope coefficient for annual Runoff was significantly higher ($p = 0.002$) for P (0.20) than for N (0.13) highlighting a greater influence of water yield on P transport (Fig. 4). The positive slope coefficients of flow regime (*CVflow*; 0.02 and 0.07 for N and P, respectively; Table 4 and Fig. 4) suggested that, for a same amount of annual runoff, flashier discharge patterns promoted the export of both nutrients, but this effect was more pronounced for P ($p = 0.050$; Fig. 4). With regards to the potential effect of lakes and reservoirs at buffering the impact of inter-annual changes in climate (annual runoff and flashiness) on fractional N and P export, we observed no statistically significant influence through our additional analysis, but a slight influence on P retention was observed (SI; Table S3 and Fig S3).

### Riverine export of the different N and P forms

Loads of the different N and P forms were also well predicted by NANI and NAPI (Fig S4). TSP and TDP showed a good fit with NAPI ($R^2$= 0.55 and 0.48, respectively) yet TP had the strongest relationship ($R^2$= 0.68). In the case of N, NANI was much better at predicting DIN ($R^2$ = 0.64) and TN ($R^2$= 0.62) rather than Org. N ($R^2$ = 0.20; Fig S4). The relative proportion of the different chemical forms to total loads appeared to vary both over space and time (Fig S5). As an overall mean, 65% of total P was exported as TSP with low variability across watersheds (CV = 12%) while DIN dominated N exports with an overall mean of 60% and higher variability (CV = 27%; Fig S6).

#### *Spatial variability in the dominant chemical forms*

The contribution of DIN to total N riverine load increased with the level of anthropogenic N surpluses however no such pattern emerged for P (Fig. 5). We then tested how annual *Runoff* and *Precipitation* (previously identified as dominant drivers of spatial variability in both fractional TN and TP export; see section "Factors influencing fractional nutrient export (downstream transport) across space"), influenced the delivery of the different chemical forms. Both variables entered the models as significant predictors in all cases (Table 5). Comparison of coefficients showed that water retention capacity (greater Precipitation given a same amount of Runoff in different watersheds) may have more strongly influenced the

**Table 3** Linear mixed models of spatial variability of fractional N (A) and P (B) export using a backwards-stepwise selection based on AIC

| Models | Intercept | τ | Runoff | Prec | ResZ | Dams | Watershed Slope | Lakes | Dv | σ | AIC | BIC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (A) Nitrogen | | | | | | | | | | | | |
| FrN0 | − 1.33 (0.03) | 0.12 (0.06–0.18) | x | x | x | x | x | x | x | 0.47 (0.44–0.5) | 705 | 718 |
| FrN1 | − 1.33 (0.03) | 0.12 (0.07–0.18) | 0.165 (0.019) | x | x | x | x | x | x | 0.44 (0.41–0.47) | 649 | 666 |
| FrN2 | − 1.33 (0.03) | 0.13 (0.07–0.18) | 0.255 (0.025) | − 0.139 (0.025) | x | x | x | x | x | 0.43 (0.4–0.46) | 630 | 651 |
| FrN3 | − 1.33 (0.03) | 0.13 (0.08–0.18) | 0.320 (0.025) | − 0.199 (0.025) | − 0.131 (0.019) | x | x | x | x | 0.41 (0.39–0.44) | 598 | 623 |
| FrN4 | − 1.33 (0.03) | 0.13 (0.08–0.19) | 0.334 (0.024) | − 0.203 (0.024) | − 0.126 (0.019) | 0.083 (0.018) | x | x | x | 0.40 (0.38–0.43) | 586 | 616 |
| FrN5 | − 1.33 (0.03) | 0.13 (0.08–0.19) | 0.339 (0.024) | − 0.197 (0.024) | − 0.125 (0.018) | 0.096 (0.018) | − 0.051 (0.018) | x | x | 0.40 (0.38–0.43) | 587 | 621 |
| **FrN6** | − **1.33** (0.03) | **0.13** (0.08– 0.19) | **0.313** (0.025) | − **0.164** (0.025) | − **0.192** (0.024) | **0.150** (0.021) | − **0.081** (0.019) | − **0.123** (0.028) | **x** | **0.40** (0.37–0.42) | **579** | **617** |
| FrN7 | − 1.33 (0.03) | 0.13 (0.08–0.19) | 0.309 (0.025) | − 0.152 (0.026) | − 0.148 (0.039) | 0.155 (0.021) | − 0.073 (0.02) | − 0.095 (0.035) | − 0.04 (0.03) | 0.39 (0.37–0.42) | 584 | 626 |

| Models | Intercept | τ | Watershed Slope | Runoff | Prec | ResZ | Lakes | Dams | Dv | σ | AIC | BIC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (B) Phosphorus | | | | | | | | | | | | |
| FrP0 | − 2.01 (0.04) | 0.16 (0.07–0.26) | x | x | x | x | x | x | x | 0.70 (0.65–0.74) | 1104 | 1117 |
| FrP1 | − 2.02 (0.04) | 0.17 (0.1–0.27) | 0.293 (0.028) | x | x | x | x | x | x | 0.63 (0.59–0.67) | 1014 | 1031 |
| FrP2 | − 2.02 (0.04) | 0.18 (0.11–0.27) | 0.277 (0.025) | 0.123 (0.028) | x | x | x | x | x | 0.62 (0.58–0.66) | 1003 | 1024 |
| FrP3 | − 2.01 (0.04) | 0.18 (0.11–0.27) | 0.299 (0.026) | 0.339 (0.034) | − 0.338 (0.035) | x | x | x | x | 0.57 (0.53–0.60) | 925 | 950 |
| FrP4 | − 2.01 (0.04) | 0.19 (0.11–0.27) | 0.300 (0.025) | 0.389 (0.037) | − 0.385 (0.037) | − 0.1 (0.027) | x | x | x | 0.56 (0.52-0.59) | 919 | 948 |
| **FrP5** | − **2.01** (0.04) | **0.19** (0.12–0.27) | **0.267** (0.024) | **0.32** (0.036) | − **0.319** (0.036) | − **0.24** (0.033) | − **0.233** (0.033) | **x** | **x** | **0.53** (0.50–0.57) | **880** | **914** |
| **FrP6** | − **2.01** (0.04) | **0.19** (0.12–0.27) | **0.265** (0.027) | **0.32** (0.036) | − **0.319** (0.037) | − **0.24** (0.035) | − **0.236** (0.041) | **0.004** (0.03) | **x** | **0.53** (0.50–0.57) | **887** | **925** |
| FrP7 | − 2.01 (0.04) | 0.19 (0.12–0.27) | 0.270 (0.028) | 0.318 (0.057) | − 0.312 (0.038) | − 0.21 (0.036) | − 0.220 (0.05) | 0.007 (0.03) | − 0.03 (0.04) | 0.53 (0.50–0.57) | 893 | 936 |

All variables were log-transformed and clustered by year (see methods for details). Model coefficients and associated standard errors (SE) are presented, along with the random term (τ) * and model residuals (σ)** with their associated 95% CI, as well as AIC and BIC. Sample size was 527 for all models. Models shown in bold represent potential best models given lower AIC. Variables not included in a model are represented with an x

*Standard deviation of the varying year-specific intercepts around the average

**Standard deviation of residuals

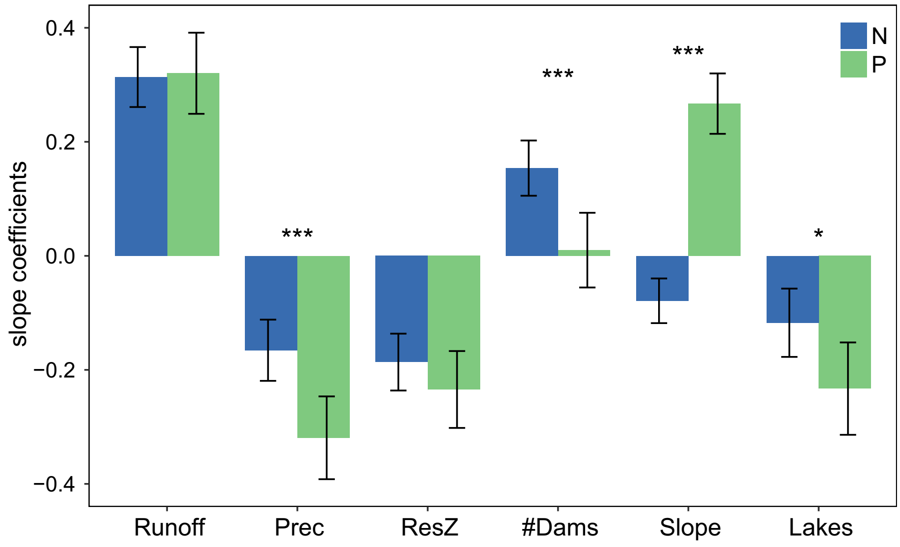


**Fig. 3** Differential effects of regional variables on N versus P fractional export. Slope coefficients of predictor variables in spatial N and P models (frN6 and frP6 in Table 3, respectively) are presented with their 95% confidence intervals as error bars, following the stepwise selection order of the N model. Asterisks (*) indicate a significant difference between N and P slope coefficients ($p < 0.001$***, $p < 0.01$**, $p < 0.05$*)

retention of particulate forms, particularly for P (coefficient of − 0.28 for TSP relative to − 0.23 for TDP).

### *Inter-annual variability in the dominant forms*

In terms of temporal variability, wet years appeared to favor the export of the dominant N and P forms, DIN and TSP. This inter-annual variability in the relative contribution of the chemical forms was also apparent in Fig. 5, with data from a single watershed, represented by a single colour, being spread along the y axis. We therefore tested how annual *Runoff* and *CVflow* (previously identified as the main drivers of temporal variability in fractional TN and TP exports; see section "Factors influencing inter-annual variability in downstream transfers of nutrients"), influenced the export of the distinct chemical forms. Both variables entered the models as significant predictors of all forms (Table 6). Comparing coefficients, flashy discharges (high *CVflow*) favored downstream transfers of particulate (TSP and Organic N) over dissolved forms (DIN and TDP; Table 6), and this pattern was particularly pronounced for P (coefficient of 0.14 for TSP vs. 0.06 for TDP).

## Discussion

We used an integrative empirical approach to quantify the relative transport of N and P through different landscape and limnoscape compartments as well as under different climate regimes in order to evaluate the differential impact of these drivers on riverine fluxes. Identifying where and how these various control points differentially retain N and P within a watershed and the aquatic network can improve nutrient management in linked terrestrial-aquatic systems. This study focuses on the annual fractional export of nutrient surpluses at watershed outlets rather than the absolute riverine nutrient loads. Given this focus, we evaluate more specifically how different control points influence the relative transport of anthropogenic N and P throughout watershed. We found that precipitation patterns and water retention capacity within the landscape (which would include evaporation and transient water storage > 1 year) were the features that most strongly influenced nutrient export from land to water at the annual timescale, whereas lakes and reservoirs emerged as features within the aquatic network that influenced retention. More importantly, landscape and climate features as well as the presence of lakes altered the relative fluxes of N and P downstream. By empirically identifying the magnitude of how each driver or control point influences the relative transport of each nutrient, we provide valuable information of their integrative impact on the potential N: P ratios in receiving waters.

**Table 4** Linear mixed models of temporal variability in downstream export of anthropogenic N and P identified using a backwards-stepwise selection based on AIC

| Models | Intercept | τ | Runoff | CVflow | temp | σ | AIC | BIC |
|---|---|---|---|---|---|---|---|---|
| Nitrogen | | | | | | | | |
| FrN0 | − 1.30 (0.09) | 0.39 (0.28–0.53) | x | x | x | 0.29 (0.27–0.31) | 270 | 283 |
| **FrN1** | − **1.30** (0.09) | **0.39** (0.28–0.53) | **0.121** (0.012) | **x** | **x** | **0.26** (0.25–0.28) | **181** | **198** |
| FrN2 | − 1.30 (0.09) | 0.39 (0.28–0.53) | 0.129 (0.012) | 0.023 (0.012) | x | 0.26 (0.25–0.28) | 186 | 208 |
| FrN3 | − 1.30 (0.09) | 0.39 (0.28–0.53) | 0.129 (0.012) | 0.024 (0.012) | 0.007 (0.012) | 0.26 (0.25–0.28) | 195 | 221 |
| Phosphorus | | | | | | | | |
| FrP0 | − 1.93 (0.14) | 0.62 (0.45–0.86) | x | x | x | 0.42 (0.4–0.45) | 667 | 680 |
| FrP1 | − 1.93 (0.14) | 0.62 (0.45–0.86) | 0.175 (0.017) | x | x | 0.38 (0.36–0.41) | 578 | 595 |
| **FrP2** | − **1.93** (0.14) | **0.62** (0.42–0.86) | **0.198** (0.018) | **0.066** (0.018) | **x** | **0.38** (0.35–0.4) | **573** | **594** |
| FrP3 | − 1.93 (0.14) | 0.62 (0.45–0.86) | 0.198 (0.018) | 0.065 (0.018) | − 0.009 (0.017) | 0.38 (0.35–0.4) | 581 | 606 |

All variables were log-transformed and clustered by watershed (see methods for details). Model coefficients and associated standard errors (se) are presented, along with the random term (τ)* and model residuals (σ)** with associated 95% CI, AIC and BIC. Sample size was 527 for all models. Models shown in bold represent potential best models given lower AIC. Variables not included in a model are represented with an x

*Standard deviation of the varying watershed-specific intercepts around the average

**Standard deviation of residuals

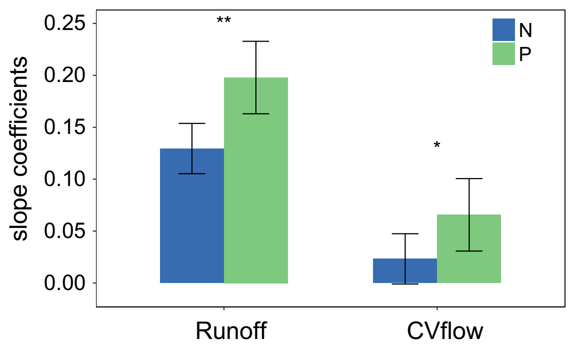


**Fig. 4** Differential effects of inter-annual variables on downstream export of N and P. Slope coefficients of predictors in the best temporal N and P models (identified in Table 4) are presented with their 95% confidence intervals as error bars. Stars (*) indicate if the slope coefficient of a given predictor was significantly different for N and P ($p < 0.01$**, $p < 0.05$*)

## Nutrient transport and the role of precipitation patterns/flow regimes

Overall, fractional export of N was greater than that of P (Fig. 2), highlighting the more labile and lithophilic properties of N and P, respectively (Green and Finlay 2010). Indeed, nitrate ($NO_3^-$) is highly soluble and moves much more freely in soils and aquatic networks than phosphate ($PO_4^+$) which tends to sorb to soil particles (Holtan et al. 1988). Greater fractional export of N as compared to P has been previously shown at the watershed scale of multiple basins in the Baltic Sea in Europe (Hong et al. 2012) and St. Lawrence River in North America (Goyette et al. 2016). It has also been demonstrated that a higher proportion of agricultural activity as well as the agricultural type within the watershed tends to increase N concentrations relative to P in lakes (Arbuckle and Downing 2001; Collins et al. 2017). Annual runoff was the main driver of fractional export for both N and P at the basin scale (Figs. 3, 4). Given that fractional export was partially determined through daily discharge, this result is not surprising. Nevertheless, interesting patterns emerge given the intimate relationship between nutrient and water movement. Wet years resulted in higher loads of both nutrients, however the forms that entered differed: N entered predominantly as dissolved inorganic N (DIN), given its higher solubility, whereas P entered as total suspended P (TSP), which is typically bound to particles, likely as a function of erosion. Although this has not been demonstrated conclusively, studies from the U.K. (Ockenden et al. 2016) and Northern U.S. (Green et al. 2007) strongly support this latter possibility. Some studies have also reported increased dissolved P loads as a function of climate, even in places where buffers

**Table 5** Linear mixed models of spatial variability in downstream export of different N and P chemical forms

| Models | Intercept | τ | Runoff | Prec | σ | dAIC | dBIC | n |
|---|---|---|---|---|---|---|---|---|
| Nitrogen | | | | | | | | |
| TN | − 1.32 (0.03) | 0.12 (0.07–0.18) | 0.25 (0.03) | − 0.14 (0.03) | 0.42 (0.4–0.45) | 92 | 83 | 527 |
| DIN | − 1.74 (0.09) | 0.12 (0.06–0.19) | 0.21 (0.03) | − 0.10 (0.03) | 0.48 (0.45–0.51) | 50 | 41 | 500 |
| ON | − 2.06 (0.06) | 0.24 (0.16–0.35) | 0.30 (0.04) | − 0.12 (0.04) | 0.65 (0.61–0.7) | 56 | 47 | 470 |
| Phosphorus | | | | | | | | |
| TP | − 2.01 (0.11) | 0.16 (0.09–0.26) | 0.32 (0.04) | − 0.28 (0.04) | 0.65 (0.61–0.69) | 165 | 157 | 527 |
| TDP | − 3.42 (0.09) | 0.41 (0.3–0.57) | 0.31 (0.05) | − 0.23 (0.05) | 0.76 (0.71–0.81) | 41 | 33 | 501 |
| TSP | − 2.62 (0.11) | 0.56 (0.43–0.77) | 0.32 (0.05) | − 0.28 (0.05) | 0.74 (0.7–0.79) | 47 | 39 | 500 |

All variables were log-transformed and clustered by year (see methods for details). Model coefficients and associated standard errors (SE) are presented, along with the random term (τ)* and model residuals (σ)** with associated 95% CI. Delta AIC and BIC relative to null models (that included varying intercepts only) are presented, as well as models sample sizes (n)

*Standard deviation of the varying year-specific intercepts around the average

**Standard deviation of residuals

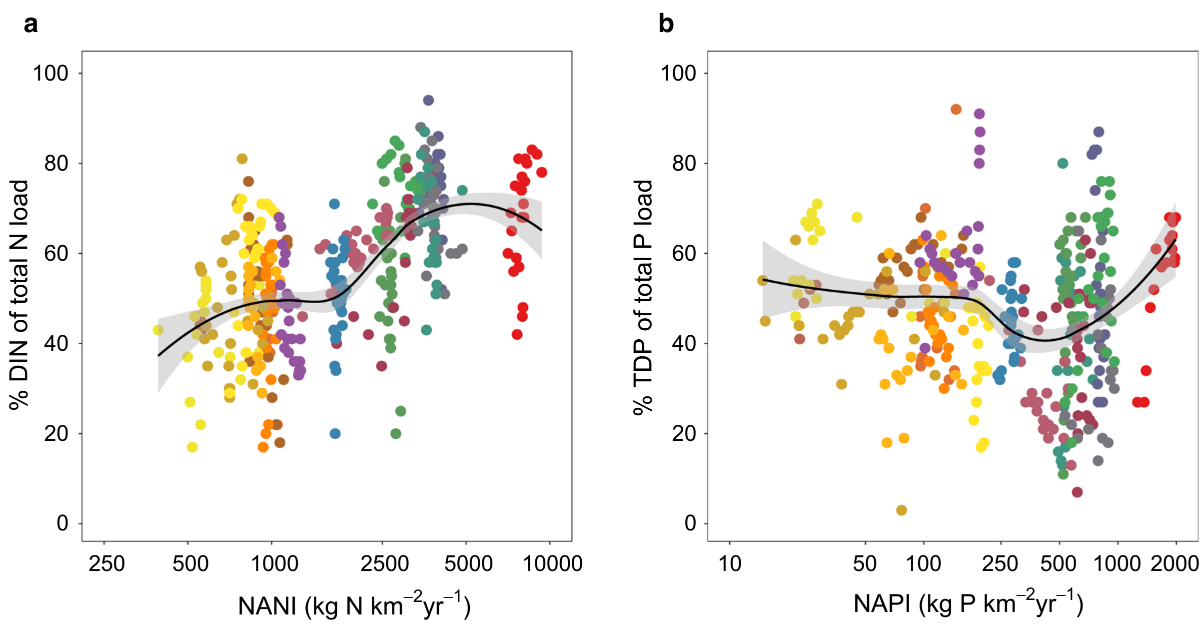


**Fig. 5** **a** Contribution of DIN to total annual N riverine loads relative to NANI (Kg N km$^{-2}$ year$^{-1}$), and **b** contribution of TDP to total annual P riverine loads relative to NAPI (Kg P km$^{-2}$ year$^{-1}$). Colors indicate the different watersheds (see Fig. 2)

have been restored (Joosse and Baker 2011); however we saw no significant increases in dissolved P export.

In terms of inter-annual variability, wet years favored disproportionate P delivery compared to N (Fig. 4), again likely because of erosion of P accumulated in different landscape compartments. More flashy daily discharge (*CVflow*) within a year also favored P export relative to N through the transport of particulate forms, however this pattern was not as strong as anticipated. One possible explanation is that LOADEST models are regression-based and this may underestimate strong nutrient pulses under extreme precipitation events. This could explain why our indices of flow regime or flashiness of precipitation patterns (*CVflow* and *CVPrec*) did not emerge more strongly in our analyses. Despite this potential shortcoming, our findings support previous work showing that P transport from watersheds are generally more

**Table 6** Linear mixed models of temporal variability in downstream export of different N and P chemical forms

| Models | Intercept | τ | Runoff | CVflow | σ | dAIC | dBIC | n |
|---|---|---|---|---|---|---|---|---|
| Nitrogen | | | | | | | | |
| TN | − 1.30 (0.09) | 0.38 (0.28–0.53) | 0.13 (0.01) | 0.02 (0.01) | 0.26 (0.25–0.28) | 544 | 536 | 527 |
| DIN | − 1.75 (0.1) | 0.44 (0.33–0.63) | 0.15 (0.01) | 0.03 (0.01) | 0.25 (0.24–0.27) | 633 | 624 | 500 |
| ON | − 2.04 (0.11) | 0.49 (0.36–0.71) | 0.10 (0.03) | 0.07 (0.03) | 0.52 (0.49–0.56) | 13 | 4 | 470 |
| Phosphorus | | | | | | | | |
| TP | − 1.92 (0.14) | 0.60 (0.45–0.86) | 0.20 (0.02) | 0.07 (0.02) | 0.38 (0.35–0.40) | 583 | 575 | 527 |
| TDP | − 3.31 (0.16) | 0.70 (0.52–1.01) | 0.05 (0.05) | 0.06 (0.05) | 0.57 (0.54–0.61) | 305 | 297 | 501 |
| TSP | − 2.54 (0.11) | 0.65 (0.48–0.95) | 0.14 (0.03) | 0.14 (0.03) | 0.71 (0.67–0.76) | 100 | 82 | 500 |

All variables were log-transformed and clustered by watershed (see methods for details). Model coefficients and associated standard errors (SE) are presented, along with the random term (τ)* and model residuals (σ)** with associated 95% CI. Delta AIC and BIC relative to null models (that included varying intercepts only) are presented, as well as model sample size (n)

*Standard deviation of the varying watershed-specific intercepts around the average

**Standard deviation of residuals

episodic than that of N (Green and Finlay 2010), particularly with increasing storm events (Ockenden et al. 2016; Carpenter et al. 2017) and during spring freshets (Cooke and Prepas 1998). Our work also provides empirical evidence that erosion influences N delivery, albeit to a lesser extent than P, through mobilization of particulate organic N.

## Nutrient retention within watershed compartments

Our study highlights three main features that can promote a greater retention of P relative to N in these watersheds: (1) the annual water retention capacity of the landscape, (2) the presence of lakes and dams, and (3) the morphometry of reservoirs. While precipitation promotes downstream transport of nutrients, the water retention capacity of the landscape plays a critical role at buffering this export. The annual catchment water retention capacity (conceptualized and quantified here as the amount of runoff relative to precipitation), serves as an integrative metric of different watershed characteristics that influence water residence time and emerged as a strong predictor of nutrient export. As it depends on climate and landscape characteristics that influence water movement (such as precipitation, evapotranspiration, geomorphology and soil types), both annual runoff and precipitation entered as complementary predictors of nutrient export in our models. The negative coefficients observed for precipitation however showed that, for the same amount of annual runoff (keeping the runoff coefficient constant), relatively more precipitation remains in those basins configured in such a way that favors nutrient retention, especially with regards to P (Table 3; Fig. 3). Given that the interplay between hydrology, geomorphology and nutrient movement is so critical (Seitzinger et al. 2006; Kusmer et al. 2018), landscape compartments that retain water favour particle settling (of both N and P), the sorption of different nutrient forms, and microbial processes that can eliminate N from the systems. For example, wetlands act as important control points of N retention at the watershed scale (Hansen et al. 2018). Interestingly, there has been a marked change in land use in the St. Lawrence region, particularly with a dramatic loss in wetland cover in exchange for agricultural and urban development (Pellerin and Poulin 2013). In that sense, we observed a reduction in the annual water retention capacity within nearly half of our 18 watersheds throughout the study period (mean increase in *R: P* of 0.14), suggesting that 14% more water from precipitation made its way to the outlet in 2011 relative to 1986. These observations support a previous study that suggested catchment water balances in the St. Lawrence region are influenced predominantly by changes in land use (> 60%) rather than climate (Zhou et al. 2015). In terms of relative effect on N and P, we showed that this loss of water retention capacity through land use change would disproportionately favour P over N exports, thus lowering N: P ratios in downstream waters (Table 3).

In terms of altering the relative fluxes of N and P within aquatic networks, natural lakes and human made reservoirs tended to favour the retention of P over N. This pattern has also been observed in other systems (Alexander et al. 2008; Grantz et al. 2014). Watersheds with higher lake and dam density (on an areal basis) significantly retained P over N likely due to the effect of reduced hydraulic velocity on particle settling (Vollenweider 1976). In terms of reservoir morphometry, mean depth (*ResZ*) apparently did not alter N and P relative fluxes downstream in these watersheds, yet water basin shape did, as denoted by the Volume development metric (*Dv*). Bowl-shaped reservoirs favored P retention relative to N whereas broad systems with large areas of shallow waters had an increased capacity to retain N relative to P. Indeed, deeper systems are known to increase P settling and burial through increased water residence time (Saunders and Kalff 2001; Kõiv et al. 2011; Powers et al. 2015) while shallow systems tend to favor denitrification losses by increasing sediment–water contact (Stanley and Doyle 2002). Our study thus suggests that reservoir morphometry, and most likely that of lakes, influences the relative retention of N and P and ultimately the stoichiometric delivery to downstream waters and should be considered in future studies.

## Nutrient legacies

Several results from our study revealed the likely contribution of legacy nutrients to contemporary riverine loads. The strong pulses of water delivery, either at daily or annual scales (storm events, spring freshet or wet years), highlight this legacy effect where nutrients accumulated in the landscape overtime are remobilized and transferred downstream. Annual fractional exports in several of our watersheds exceeded the generally accepted means of 25% for N and 5–10% for P (Hong et al. 2012; Swaney et al. 2012; Goyette et al. 2016), and even occasionally were $> 100\%$, suggesting greater riverine exports relative to annual watershed inputs (Fig. 2). These fractions indicate the likely influence of legacy sources to contemporary loads (Goyette et al. 2018). Indeed, the relative increase in delivery of TSP and organic nitrogen forms under flashier climatic conditions also supports export of legacy stores via erosion.

Even though reservoirs can dampen nutrient enrichment of downstream waters in the short term, nutrient accumulation in the sediments of these human made systems over time may eventually result in the delivery of legacy sources (Nowlin et al. 2005; Teodoru and Wehrli 2005; Powers et al. 2015). Indeed, the presence of dams in our study basins appeared to favor N export. While this result might emerge from a statistical bias where dam density potentially co-varies with other drivers of nutrient transport not considered in this study, we think that the size of these dams and their ages may actually explain the legacy effect observed herein. Small dam reservoirs may act as sinks in their early years, but as nutrients accumulate over time, may potentially switch to net sources when nutrients are remobilized in the water column (Power et al. 2015), thus changing their role as control points. Most dams within our study watersheds are small and were constructed over 60 years ago with some prior to the 1900s (Centre d'Expertise Hydrique du Québec 2018), which support the possibility that nutrient retention capacity has been surpassed. Future work should consider at what moment under what circumstances do reservoirs of differing shapes tip from a nutrient sink to a nutrient source.

Results regarding the influence of watershed slope on nutrient export also suggest a contribution of legacy nutrients to riverine loads. When the amount of annual runoff and other land use characteristics were taken into account, accentuated downstream transport of P was observed in steeper watersheds likely as a function of the erosion of P-enriched soils and sediments with accumulated anthropogenic inputs, particularly under strong discharge pulses (Sharpley et al. 2013; Ockenden et al. 2016). In the case of N, legacies may operate in a more leaky and continuous manner through transient storage in groundwater (Hamilton 2012; Tesoriero et al. 2013; Van Meter and Basu 2015). The negative correlation between fractional export and watershed slope may reflect N legacies contributing to riverine loads in flat watersheds where water infiltration is favored (Soulsby et al. 2006; Price 2011) particularly through aquifers more prone to nitrate contamination due to intensive agriculture (Van Meter et al. 2017). Alternatively, this result may also reveal the effect of tile drainage that is a common practice in these flat agricultural watersheds (Kusmer et al. 2018), that may facilitate downstream transport of N (Billen and Garnier 1999), either coming from application in the same year or from legacy sources. Overall, the legacy effect appeared stronger for P than for N since *CVflow*, *Runoff* and *Slope* all influenced P delivery more strongly than N. This suggests the contribution of P legacies to be more sensitive to climate and potentially more pervasive through time relative to N legacies. Indeed, it has been suggested that N legacies may last a few decades (Sebilo et al. 2013; Tesoriero et al. 2013; Van Meter et al. 2018) whereas in the case of P, they may last for centuries (Carpenter 2005; Sharpley et al. 2013; Goyette et al. 2018). Thus, managing for legacy stores likely remains a challenge for long term sustainability of water quality in several of these basins.

### Uncertainties and limitations

One limitation in our study is that precise NANI and NAPI information was only available during 5-year intervals (agricultural census years) whereas riverine loads and climate variables were available annually. Thus, NANI and NAPI per basin were interpolated between census years potentially presenting some uncertainty in our fractional export terms, which depends on both the riverine exports and inputs to the watersheds. However, NANI and NAPI estimates either varied little in the last 30 years, or if it did, linear trends were rather obvious per basin, supporting our approach. More importantly, inter-annual variability in fractional export was disproportionately driven by variability in riverine loads rather than by variability in NANI or NAPI (Fig. S7). Indeed, the standard deviations of riverine loads over time was much higher than of NANI/NAPI (mean SD across all 18 watersheds was 0.25 and 0.32 for riverine N and P loads, respectively and only 0.05 and 0.15 for NANI and NAPI, respectively; Fig. S7). Similar results were found in previous studies where uncertainty analyses showed changes in riverine N flux over time to be more related to changes in flow regime or land use rather than to NANI (McIsaac et al. 2001; Huang et al. 2014; Chen et al. 2016). Hong et al. (2012) also showed that the variability in NANI/NAPI estimates (due to region-specific parameters applied for the Baltic Sea Basin) had little influence on final estimates of fractional export. Although we acknowledge that some model error may be due to the interpolation of NANI/NAPI, we think that the variability in our annual fractional export estimates are valid given that this is largely driven by changes in annual flow.

## Conclusion

Climate regimes and landscape features interact with human activities in complex ways that alter both the absolute magnitude of nutrient loads to rivers as well as their stoichiometric ratios. Understanding how both of these change along the aquatic continuum is essential to effectively tackle eutrophication at multiple spatial scales (Paerl 2009; Howarth et al. 2011). This requires a better understanding of what features alter the relative N and P fluxes throughout the watershed. Our study offers an integrative approach that identifies which key climate and landscape features act as differential control points of N and P fluxes at the annual timescale.

While lakes and reservoirs can play a significant role in retaining nutrients upstream, drivers that promote transport from land to water, such as anthropogenic nutrient surpluses, climate, and annual water retention capacity within the landscape, emerged as the dominant drivers of N and P transfers downstream. Water retention capacity of the watershed and lakes in the aquatic network are critical features that retain both elements, however P more so than N. Factors that favor erosion processes, such as flashiness, geomorphology and land-use will also alter the relative delivery of elements, largely mobilizing legacy sources of P as particulates. In light of these results, and given projections of increased precipitation and storm events due to climate change (IPCC 2014), combined with the expansion of urban development and agriculture that will reduce the landscape water retention capacity, P delivery downstream may be favoured over N.

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## References


Alexander RB, Smith RA, Schwarz GE, Boyer EW, Nolan JV, Brakebill JW (2008) Differences in phosphorus and nitrogen delivery to the gulf of Mexico from the Mississippi river basin. Environ Sci Technol 42:822–830

Appling AP, Leon MC, McDowell WH (2015) Reducing bias and quantifying uncertainty in watershed flux estimates: the R package loadflex. Ecosphere 6:1–25

Arbuckle KE, Downing JA (2001) The influence of watershed land use on lake N:P in a predominantly agricultural landscape. Limnol Oceanogr 46:970–975

Banque de Données Sur la Qualité du Milieu Aquatique (BQMA; Ministère du Développement Durable, de l'Environnement et de la Lutte Contre les Changements Climatiques) (2018) http://www.mddelcc.gouv.qc.ca/eau/Atlas_interactif/donnees_recentes/donnees_p_tot.asp#onglets

Bates D, Mächler M, Bolker B, Walker S (2014) Fitting linear mixed-effects models using lme4. arXiv:1406.5823

Bernhardt ES, Blaszczak JR, Ficken CD, Fork ML, Kaiser KE, Seybold EC (2017) Control points in ecosystems: moving beyond the hot spot hot moment concept. Ecosystems 20:665–682

Billen G, Garnier J (1999) Nitrogen transfers through the Seine drainage network: a budget based on the application of theRiverstrahler'model. Hydrobiologia 410:139–150

Blanchet FG, Legendre P, Borcard D (2008) Forward selection of explanatory variables. Ecology 89:2623–2632

Budyko MI (1974) Climate and Life. In: David H (ed) Miller. Academic Press, San Diego

Carpenter SR (2005) Eutrophication of aquatic ecosystems: bistability and soil phosphorus. Proc Natl Acad Sci USA 102:10002–10005

Carpenter SR, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol Appl 8:559–568

Carpenter SR, Booth EG, Kucharik CJ (2017) Extreme precipitation and phosphorus loads from two agricultural watersheds. Limnol Oceanogr 63:1221–1233

Carrascal LM, Galván I, Gordo O (2009) Partial least squares regression as an alternative to current regression methods used in ecology. Oikos 118:681–690

Centre d'Expertise Hydrique du Québec (2018) https://www.cehq.gouv.qc.ca/

Chen F, Hou L, Liu M, Zheng Y, Yin G, Lin X, Li X, Zong H, Deng F, Gao J (2016) Net anthropogenic nitrogen inputs (NANI) into the Yangtze River basin and the relationship with riverine nitrogen export. J Geophys Res 121:451–465

Chen D, Shen H, Hu M, Wang J, Zhang Y, Dahlgren RA (2018) Legacy nutrient dynamics at the watershed scale: principles, modeling, and implications. Adv Agron 149:237–313

Cohen J, Cohen P, West SG, Aiken LS (2013) Applied multiple regression/correlation analysis for the behavioral sciences. Routledge, London

Collins SM, Oliver SK, Lapierre JF, Stanley EH, Jones JR, Wagner T, Soranno PA (2017) Lake nutrient stoichiometry is less predictable than nutrient concentrations at regional and sub-continental scales. Ecol Appl 27:1529–1540

Cooke SE, Prepas EE (1998) Stream phosphorus and nitrogen export from agricultural and forested watersheds on the Boreal Plain. Can J Fish Aquat Sci 55:2292–2299

Dodds WK, Bouska WW, Eitzmann JL, Pilger TJ, Pitts KL, Riley AJ, Schloesser JT, Thornbrugh DJ (2009) Eutrophication of US freshwaters: analysis of potential economic damages. Environ Sci Technol 43:12–19

Enders CK, Tofighi D (2007) Centering predictor variables in cross-sectional multilevel models: a new look at an old issue. Psychol Methods 12:121

Frank H, Patrick S, Peter W, Hannes F (2000) Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments—the significance of water flow paths. Biogeochemistry 50:137–161

Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, Seitzinger SP, Asner GP, Cleveland CC, Green PA, Holland EA, Karl DM, Michaels AF, Porter JH, Townsend AR, Vorosmarty CJ (2004) Nitrogen cycles: past, present, and future. Biogeochemistry 70:153–226

Goyette JO, Bennett EM, Howarth RW, Maranger R (2016) Changes in anthropogenic nitrogen and phosphorus inputs to the St. Lawrence sub-basin over 110 years and impacts on riverine export. Global Biogeochem Cycles 30:1000–1014

Goyette J-O, Bennett E, Maranger R (2018) Low buffering capacity and slow recovery of anthropogenic phosphorus pollution in watersheds. Nat Geosci. https://doi.org/10.1038/s41561-018-0238-x

Graham MH (2003) Confronting multicollinearity in ecological multiple regression. Ecology 84:2809–2815

Grantz EM, Haggard BE, Scott JT (2014) Stoichiometric imbalance in rates of nitrogen and phosphorus retention, storage, and recycling can perpetuate nitrogen deficiency in highly-productive reservoirs. Limnol Oceanogr 59:2203–2216

Green MB, Finlay JC (2010) Patterns of hydrologic control over stream water total nitrogen to total phosphorus ratios. Biogeochemistry 99:15–30

Green MB, Nieber JL, Johnson G, Magner J, Schaefer B (2007) Flow path influence on an N:P ratio in two headwater streams: a paired watershed study. J Geophys Res. https://doi.org/10.1029/2007JG000403

Hamilton SK (2012) Biogeochemical time lags may delay responses of streams to ecological restoration. Freshw Biol 57:43–57

Hansen AT, Dolph CL, Foufoula-Georgiou E, Finlay JC (2018) Contribution of wetlands to nitrate removal at the watershed scale. Nat Geosci 11:127

Harrison JA, Maranger RJ, Alexander RB, Giblin AE, Jacinthe P-A, Mayorga E, Seitzinger SP, Sobota DJ, Wollheim WM (2009) The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochemistry 93:143–157

Hayes NM, Deemer BR, Corman JR, Razavi NR, Strock KE (2017) Key differences between lakes and reservoirs modify climate signals: a case for a new conceptual model. Limnol Oceanogr Lett 2:47–62

Heathwaite L, Haygarth P, Matthews R, Preedy N, Butler P (2005) Evaluating colloidal phosphorus delivery to surface waters from diffuse agricultural sources. J Environ Qual 34:287–298

Hill A, Kemp W, Buttle J, Goodyear D (1999) Nitrogen chemistry of subsurface storm runoff on forested Canadian Shield hillslopes. Water Resour Res 35:811–821
Holtan H, Kamp-Nielsen L, Stuanes A (1988) Phosphorus in soil, water and sediment: an overview. Hydrobiologia 170:19–34
Hong B, Swaney DP, Mörth C-M, Smedberg E, Eriksson Hägg H, Humborg C, Howarth RW, Bouraoui F (2012) Evaluating regional variation of net anthropogenic nitrogen and phosphorus inputs (NANI/NAPI), major drivers, nutrient retention pattern and management implications in the multinational areas of Baltic Sea basin. Ecol Model 227:117–135
Howarth RW, Billen G, Swaney D, Townsend A, Jaworski N, Lajtha K, Downing JA, Elmgren R, Caraco N, Jordan T, Berendse F, Freney J, Kudeyarov V, Murdoch P, Zhu ZL (1996) Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35:75–139
Howarth R, Swaney D, Boyer E, Marino R, Jaworski N, Goodale C (2006) The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Biogeochemistry 79:163–186
Howarth R, Chan F, Conley DJ, Garnier J, Doney SC, Marino R, Billen G (2011) Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. Front Ecol Environ 9:18–26
Howarth R, Swaney D, Billen G, Garnier J, Hong BG, Humborg C, Johnes P, Morth CM, Marino R (2012) Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. Front Ecol Environ 10:37–43
Huang H, Chen D, Zhang B, Zeng L, Dahlgren RA (2014) Modeling and forecasting riverine dissolved inorganic nitrogen export using anthropogenic nitrogen inputs, hydroclimate, and land-use change. J Hydrol 517:95–104
IPCC (2014) Climate change 2014–impacts, adaptation and vulnerability: regional aspects. Cambridge University Press, Cambridge
Jarvie HP, Sharpley AN, Spears B, Buda AR, May L, Kleinman PJ (2013) Water quality remediation faces unprecedented challenges from" legacy phosphorus". Environ Sci Technol 47:8997–8998
Joosse P, Baker D (2011) Context for re-evaluating agricultural source phosphorus loadings to the Great Lakes. Can J Soil Sci 91:317–327
Kalff J (2002) Limnology: inland water ecosystems. Prentice Hall, Upper Saddle River
Kirchner W, Dillon P (1975) An empirical method of estimating the retention of phosphorus in lakes. Water Resour Res 11:182–183
Kõiv T, Nõges T, Laas A (2011) Phosphorus retention as a function of external loading, hydraulic turnover time, area and relative depth in 54 lakes and reservoirs. Hydrobiologia 660:105–115
Kroeze C, Bouwman L, Seitzinger S (2012) Modeling global nutrient export from watersheds. Curr Opin Environ Sustain 4:195–202
Kusmer AS, Goyette J-O, MacDonald GK, Bennett EM, Maranger R, Withers PJA (2018) Watershed buffering of legacy phosphorus pressure at a regional scale: a comparison across space and time. Ecosystems. https://doi.org/10.1007/s10021-018-0255-z
Larsen DP, Mercier H (1976) Phosphorus retention capacity of lakes. J Fisheries Board Can 33:1742–1750
Maavara T, Parsons CT, Ridenour C, Stojanovic S, Dürr HH, Powley HR, Van Cappellen P (2015) Global phosphorus retention by river damming. Proc Natl Acad Sci USA 112:15603–15608
Maranger R, Jones SE, Cotner JB (2018) Stoichiometry of carbon, nitrogen, and phosphorus through the freshwater pipe. Limnol Oceanogr Lett 3:89–101
Mason RL, Gunst RF, Hess JL (2003) Statistical design and analysis of experiments: with applications to engineering and science. Wiley, London
McIsaac GF, David MB, Gertner GZ, Goolsby DA (2001) Eutrophication: nitrate flux in the Mississippi River. Nature 414:166
McKenney DW, Hutchinson MF, Papadopol P, Lawrence K, Pedlar J, Campbell K, Milewska E, Hopkinson RF, Price D, Owen T (2011) Customized spatial climate models for North America. Bull Am Meteor Soc 92:1611–1622
Mulholland PJ, Helton AM, Poole GC, Hall RO, Hamilton SK, Peterson BJ, Tank JL, Ashkenas LR, Cooper LW, Dahm CN (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202–205
Nakagawa S, Schielzeth H (2013) A general and simple method for obtaining R2 from generalized linear mixed-effects models. Methods Ecol Evol 4:133–142
Natural Resources Canada (2003), National scale frameworks hydrology—Drainage network, Canada (digital dataset). http://geogratis.cgdi.gc.ca/. Accessed June 2018
Newbold JD, Elwood JW, O'Neill RV, Winkle WV (1981) Measuring nutrient spiralling in streams. Can J Fish Aquat Sci 38:860–863
Nixon SW, Ammerman JW, Atkinson LP, Berounsky VM, Billen G, Boicourt WC, Boynton WR, Church TM, Ditoro DM, Elmgren R, Garber JH, Giblin AE, Jahnke RA, Owens NJP, Pilson MEQ, Seitzinger SP (1996) The fate of nitrogen and phosphorus at the land sea margin of the North Atlantic Ocean. Biogeochemistry 35:141–180
Nowlin WH, Evarts JL, Vanni MJ (2005) Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir. Freshw Biol 50:301–322
Ockenden M, Deasy CE, Benskin CMH, Beven KJ, Burke S, Collins AL, Evans R, Falloon PD, Forber KJ, Hiscock KM (2016) Changing climate and nutrient transfers: evidence from high temporal resolution concentration-flow dynamics in headwater catchments. Sci Total Environ 548:325–339
Paerl HW (2009) Controlling eutrophication along the freshwater–marine continuum: dual nutrient (N and P) Reductions are Essential. Estuar Coasts 32:593–601
Pellerin S, Poulin M (2013) Analyse de la situation des milieux humides au Québec et recommandations à des fins de conservation et de gestion durable. Rapport final présenté au Ministère du développement durable, de l'environnement, de la faune et des parcs
Powers S, Tank J, Robertson D (2015) Control of nitrogen and phosphorus transport by reservoirs in agricultural landscapes. Biogeochemistry 124:417–439

Price K (2011) Effects of watershed topography, soils, land use, and climate on baseflow hydrology in humid regions: a review. Prog Phys Geogr 35:465–492
Roderick ML, Farquhar GD (2011) A simple framework for relating variations in runoff to variations in climatic conditions and catchment properties. Water Resour Res 47:12
Runkel RL, Crawford CG, Cohn TA (2004) Load estimator (LOADEST): a FORTRAN program for estimating constituent loads in streams and rivers. CreateSpace Independent Publishing, Scotts Valley, pp 2328–7055
Russell MJ, Weller DE, Jordan TE, Sigwart KJ, Sullivan KJ (2008) Net anthropogenic phosphorus inputs: spatial and temporal variability in the Chesapeake Bay region. Biogeochemistry 88:285–304
Saunders DL, Kalff J (2001) Nitrogen retention in wetlands, lakes and rivers. Hydrobiologia 443:205–212
Schlesinger WH, Bernhardt ES (2013) Biogeochemistry: an analysis of global change. Academic Press, New York
Scott JT, McCarthy MJ, Otten TG, Steffen MM, Baker BC, Grantz EM, Wilhelm SW, Paerl HW, Smith R (2013) Comment: an alternative interpretation of the relationship between TN: TP and microcystins in Canadian lakes. Can J Fish Aquat Sci 70:1265–1268
Sebilo M, Mayer B, Nicolardot B, Pinay G, Mariotti A (2013) Long-term fate of nitrate fertilizer in agricultural soils. Proc Natl Acad Sci USA 110:18185–18189
Seitzinger S, Harrison JA, Böhlke J, Bouwman A, Lowrance R, Peterson B, Tobias C, Drecht GV (2006) Denitrification across landscapes and waterscapes: a synthesis. Ecol Appl 16:2064–2090
Seitzinger SP, Mayorga E, Bouwman AF, Kroeze C, Beusen AHW, Billen G, Van Drecht G, Dumont E, Fekete BM, Garnier J, Harrison JA (2010) Global river nutrient export: a scenario analysis of past and future trends. Glob Biogeochem Cycles 24:4
Sharpley A, Jarvie HP, Buda A, May L, Spears B, Kleinman P (2013) Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. J Environ Qual 42:1308–1326
Soranno PA, Webster KE, Riera JL, Kratz TK, Baron JS, Bukaveckas PA, Kling GW, White DS, Caine N, Lathrop RC (1999) Spatial variation among lakes within landscapes: ecological organization along lake chains. Ecosystems 2:395–410
Soranno PA, Cheruvelil KS, Wagner T, Webster KE, Bremigan MT (2015) Effects of land use on lake nutrients: the importance of scale, hydrologic connectivity, and region. PLoS ONE 10:e0135454
Soulsby C, Tetzlaff D, Rodgers P, Dunn S, Waldron S (2006) Runoff processes, stream water residence times and controlling landscape characteristics in a mesoscale catchment: an initial evaluation. J Hydrol 325:197–221
Stanley EH, Doyle MW (2002) A geomorphic perspective on nutrient retention following dam removal: geomorphic models provide a means of predicting ecosystem responses to dam removal. AIBS Bull 52:693–701
Sterner RW, Elser JJ (2002) Ecological stoichiometry: the biology of elements from molecules to the biosphere. Princeton University Press, Princeton
Swaney DP, Hong B, Ti C, Howarth RW, Humborg C (2012) Net anthropogenic nitrogen inputs to watersheds and riverine N export to coastal waters: a brief overview. Curr Opin Environ Sustain 4:203–211
Team, R. C. 2013. R: A language and environment for statistical computing
Teodoru C, Wehrli B (2005) Retention of sediments and nutrients in the Iron Gate I Reservoir on the Danube River. Biogeochemistry 76:539–565
Tesoriero AJ, Duff JH, Saad DA, Spahr NE, Wolock DM (2013) Vulnerability of streams to legacy nitrate sources. Environ Sci Technol 47:3623–3629
Thornton KW, Kimmel BL, Payne FE (1990) Reservoir limnology: ecological perspectives. Wiley, New Jersey
Van de Waal DB, Smith VH, Declerck SA, Stam E, Elser JJ (2014) Stoichiometric regulation of phytoplankton toxins. Ecol Lett 17:736–742
Van Meter KJ, Basu NB (2015) Catchment legacies and time lags: a parsimonious watershed model to predict the effects of legacy storage on nitrogen export. PLoS ONE 10:e0125971
Van Meter K, Basu N, Van Cappellen P (2017) Two centuries of nitrogen dynamics: legacy sources and sinks in the Mississippi and Susquehanna River Basins. Global Biogeochem Cycles 31:2–23
Van Meter K, Van Cappellen P, Basu N (2018) Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico. Science 360:427–430
Vollenweider RA (1976) Advances in defining critical loading levels for phosphorus in lake eutrophication. Memorie dell'Istituto Italiano di Idrobiologia, Dott. Marco de Marchi Verbania Pallanza
Vought LB-M, Dahl J, Pedersen CL, Lacoursiere JO (1994) Nutrient retention in riparian ecotones. AMBIO 23:342–348
Wollheim WM, Vörösmarty C, Peterson BJ, Seitzinger SP, Hopkinson CS (2006) Relationship between river size and nutrient removal. Geophys Res Lett 33:6
Wollheim WM, Vörösmarty CJ, Bouwman A, Green P, Harrison J, Linder E, Peterson BJ, Seitzinger SP, Syvitski JP (2008) Global N removal by freshwater aquatic systems using a spatially distributed, within basin approach. Glob Biogeochem Cycles. https://doi.org/10.1029/2007GB002963
Wurtsbaugh WA, Baker MA, Gross H, Brown P (2005) Lakes as nutrient "sources" for watersheds: a landscape analysis of the temporal flux of nitrogen through sub-alpine lakes and streams. Internationale Vereinigung für theoretische und angewandte Limnologie: Verhandlungen 29:645–649
Zhou M, Brandt P, Pelster D, Rufino MC, Robinson T, Butterbach-Bahl K (2014) Regional nitrogen budget of the Lake Victoria Basin, East Africa: syntheses, uncertainties and perspectives. Environ Res Lett 9:105009
Zhou G, Wei X, Chen X, Zhou P, Liu X, Xiao Y, Sun G, Scott DF, Zhou S, Han L (2015) Global pattern for the effect of climate and land cover on water yield. Nat Commun 6:5918
Zuur A, Ieno EN, Walker N, Saveliev AA, Smith GM (2009) Mixed effects models and extensions in ecology with R. Springer Science & Business Media, New York