Decadal Changes in Anthropogenic Inputs and Precipitation Influence Riverine Exports of Carbon, Nitrogen, and Phosphorus, and Alter Ecosystem Level Stoichiometry

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Abstract

Changes in precipitation and land use influence carbon (C), nitrogen (N) and phosphorus (P) exports from land to receiving waters. However, how these drivers differentially alter elemental inputs and impact subsequent ecosystem stoichiometry over time remains poorly understood. Here we quantified long-term (1979-2020) trends in C, N, and P exports at three sites along the mainstem of a north temperate river, that successively drains forested, urban, and more agriculturally impacted land-use areas. Riverine N and to a lesser degree C exports tended to increase over time, with major inter-annual variation largely resolved by changes in precipitation. Historical increases in net anthropogenic N inputs on land (NANI) also explained increases in riverine N exports, with about 35% of NANI reaching the river annually. Despite higher Net anthropogenic P inputs, NAPI, over time, P exports tended to decrease at all riverine sites. This decrease in P at the forested site was more gradual, whereas a precipitous drop was observed at the downstream urban site, following legislated P removal in municipal wastewater. Changes in historical ecosystem stoichiometry reflected the differential elemental exports due to natural and anthropogenic drivers and ranged from 174: 23: 1 to 547: 76: 1 over the years. Our work shows how C, N, and P have responded to different drivers in the same catchment over the last four decades, and how their differential riverine exports have influenced ecosystem stoichiometry.

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Key Points:

- 40 years of riverine export data show a differential response for carbon, nitrogen, and phosphorus to climatic and anthropogenic drivers.
- Higher anthropogenic nutrient inputs to land explained nitrogen increases over time, but phosphorus decreased because of human interventions.
- Precipitation drove carbon export variability, which combined with nutrients resulted in variable ratios along the river and over decades.

Abstract

Changes in precipitation and land use influence carbon (C), nitrogen (N) and phosphorus (P) exports from land to receiving waters. However, how these drivers differentially alter elemental inputs and impact subsequent ecosystem stoichiometry over time remains poorly understood. Here we quantified long-term (1979-2020) trends in C, N, and P exports at three sites along the mainstem of a north temperate river, that successively drains forested, urban, and more agriculturally impacted land-use areas. Riverine N and to a lesser degree C exports tended to increase over time, with major inter-annual variation largely resolved by changes in precipitation. Historical increases in net anthropogenic N inputs on land (NANI) also explained increases in riverine N exports, with about 35% of NANI reaching the river annually. Despite higher Net anthropogenic P inputs, NAPI, over time, P exports tended to decrease at all riverine sites. This decrease in P at the forested site was more gradual, whereas a precipitous drop was observed at the downstream urban site, following legislated P removal in municipal wastewater. Changes in historical ecosystem stoichiometry reflected the differential elemental exports due to natural and anthropogenic drivers and ranged from 174: 23: 1 to 547: 76: 1 over the years. Our work shows how C, N, and P have responded to different drivers in the same catchment over the last four decades, and how their differential riverine exports have influenced ecosystem stoichiometry.

Keywords: river, stoichiometry, carbon, nitrogen, phosphorus, decadal trends

Introduction

Carbon (C), nitrogen (N), and phosphorus (P) are at the base of aquatic ecosystem metabolism (von Schiller et al., 2017), but excess loadings of these elements from land to water can adversely impact ecosystem functioning (Stutter et al., 2018). There have been widespread increases in the export of C, N, and P from land to water in response to changing climate and human modifications to the landscape (Ballard et al., 2019; Howarth et al., 1996; Kritzberg et al., 2020), resulting in eutrophication and loss of aquatic ecosystem services (Carpenter et al., 1998; Graeber et al., 2021). However, terrestrial transfers of nutrients and carbon to a river may differ across or within a watershed as a function of different land use practices or physical watershed features affecting the elemental stoichiometries of the receiving systems (Goyette et al., 2019). As such, aquatic ecosystem stoichiometry, defined as the combined elemental gain and loss patterns at the watershed scale is a useful integrative framework to understand global change impacts on receiving waters (Maranger et al., 2018). The approach has been successfully applied along the mainstem of a river, where stark differences were measured as a function of seasonal climate and upstream-downstream land use gradients (Shousha et al., 2021). However, how long-term changes in land use and climate variation may influence C, N, and P on land and in the water, and influence aquatic ecosystem stoichiometry, remains poorly understood.

It is well known that C, N, and P exports have been influenced by land use changes and/or climate variation (Carpenter et al., 1998; Zarnetske et al., 2018). Increasing C loading to freshwaters has been indirectly related to changes in precipitation (Vidon et al., 2008; Zarnetske et al., 2018), recovery from acid rain (Clark et al., 2010; Kritzberg et al., 2020), and reforestation practices (Kritzberg, 2017). Land use change has been shown to influence dissolved riverine C concentrations and composition, but these vary in direction and magnitude (Xenopoulos et al., 2021), and composition often tracks nutrients (Shousha et al., 2022). Anthropogenic N and P inputs to land have increased over time (Carpenter et al., 1998; Steffen et al., 2015) mostly because of urban population growth and intensive agriculture where N has outpaced P inputs (Glibert et al., 2014; Monchamp et al., 2014), influencing ecosystem stoichiometry. Atmospheric N deposition can also be a significant human-derived input on the landscape particularly in remote regions where land use change is limited (McCrackin & Elser, 2010). Historical legislative acts, however, such as the Clean air and Clean water acts in North America for example, have resulted in reductions in N and P respectively to water (Goyette et al., 2016; Keiser & Shapiro, 2019). As such, elemental exports as well as their stoichiometries may be highly variable through time and across space, even within a single system.

In terms of nutrient transfers from land to water, N, as nitrate, is more mobile in the soil matrix (Caraco & Cole, 1999), and precipitation or runoff has been shown to increase the anthropogenic N fraction exported to rivers (Han et al., 2009; Howarth et al., 2012; Howarth et al., 2006). P on the other hand is highly reactive and tends to bind to the soil matrix (Sharpley et al., 2013). P often enters rivers in a particulate form (Holtan et al., 1988; Paytan & McLaughlin, 2011) where increased exports tend to be influenced by flashier discharge patterns rather than annual precipitation (Goyette et al., 2019). In managed watersheds, delivery pathways are also a function of landscape modifications that promote runoff. For example, tile drainage has been shown to accelerate N transport accounting for > 80% of inputs loaded to waters (McIsaac & Hu, 2004), whereas stormwater runoff from even moderately urbanised regions have higher P loads than less managed regions (Yang & Toor, 2018). However, understanding how these three elements respond to different drivers of change that influence riverine exports remains limited.

Quantifying Net Anthropogenic N and P Inputs (NANI/NAPI) to land using a simple mass balance approach (Howarth et al., 1996) has successfully tracked historic and stoichiometric changes on the catchment and in riverine exports (Goyette et al., 2016, 2019). The NANI and NAPI mass balances have been done extensively in the United States (Hong et al., 2011), the Baltic Sea watershed (Hong et al., 2017), the United Kingdom (Howarth et al., 2012), Europe (using a similar approach, GRAFS; Billen et al., 2021), China (Gao et al., 2014; Han et al., 2013), India (Swaney et al., 2015), and certain parts of Canada (Goyette et al., 2016; Van Staden et al., 2021), but at relatively broad spatial scales. Anthropogenic inputs are estimated using census data compiled at different administrative scales (for example: country vs municipality), and applying this approach at the finest scale possible could enable scientists and managers to target precise areas for intervention. However, applying changes in input type at finer scales over time remains to be explored. Here we combined historical changes in NANI and NAPI at the finest scale available (the municipality) together with precipitation to disentangle riverine C, N, and P export and consequences on aquatic ecosystem stoichiometry along the mainstem through time. We quantify these changes at three sites along a river's mainstem with an increasing gradient of human pressure in the sub-watersheds over a 40-year period to understand the differential sources and fates of these essential elements.

Methods

The *Rivière du Nord* watershed is situated north-west of Montreal, in the Laurentians region of Québec, Canada. The mainstem, a 140 km-long river of Strahler order 5, initially drains a largely forested landscape, then an urban, and finally an agricultural one (Figure 1a). Agricultural land use is constrained to fertile plains of the St. Lawrence Lowlands located in the southern-most third of the watershed. North of the St. Lawrence Lowlands is the Canadian Shield, a geological province covered with very little topsoil, a mix of conifer and deciduous trees, lakes and rivers. Most urban development occurred along the river banks.

Three sites along the *Rivière du Nord* mainstem have been sampled periodically by the *Ministère de l'Environnement et de la Lutte contre les changements climatiques, Forêt faune et parc* (MELCCFP, 2022b) since ~1980, with measurements available for dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP) in the *Banque de données sur la qualité du milieu aquatique* (BQMA). Data were available for three sites, named based on their location along the mainstem, using the outlet as river kilometer 0 (RKm 0, Figure 1a). These sites coincided with major changes in land cover and land use (Natural Resources Canada, 2009; Shousha et al., 2021).

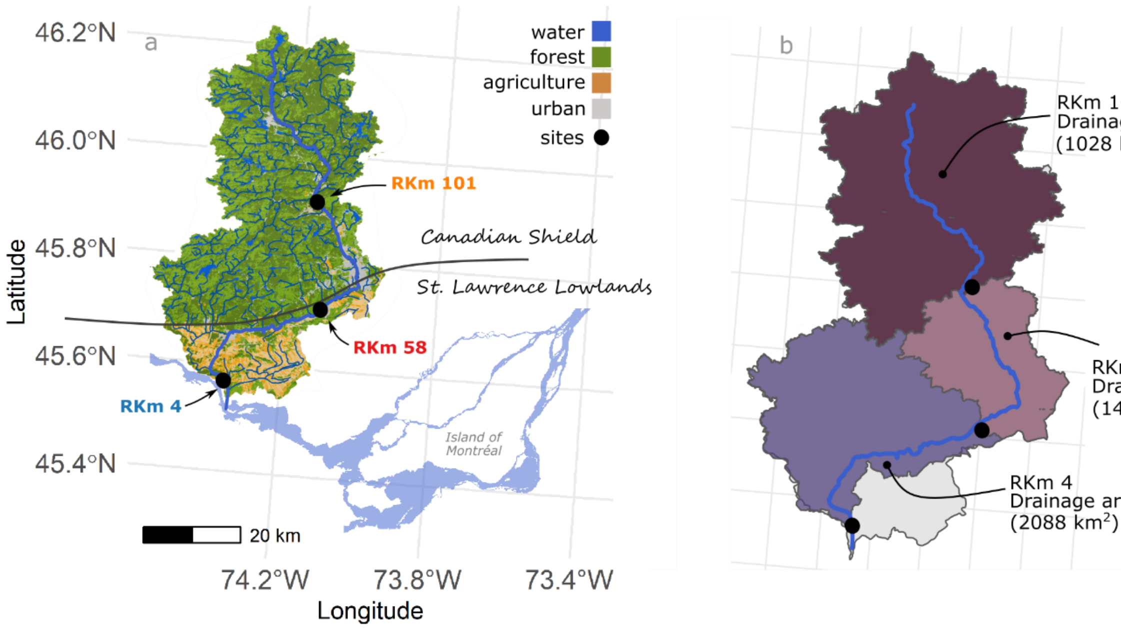

Figure 1 Land use and land cover map of the Rivière du Nord watershed, positioned with regards to the Island of Montreal (panel a). The thick blue line in the watershed shows the river's mainstem. The three water quality sites are River Kilometers 4, 58, and 101. Panel b shows cumulative drainage areas for the three sites. The grey area is not drained by RKm 4.

To quantify human activities on the landscape historically, we used the Net Anthropogenic Nitrogen/Phosphorus Input (NANI, NAPI) mass balance approach following Goyette et al. (2016). Data sources, coefficients, and descriptions can be found in Supplementary Table 1. The N and P budgets were calculated from 1981 to 2016 at a 5-year interval using municipal-level data which was the finest scale available. Municipality surface area ranged from 16 to 485 km^2 (median = 97 km^2, mean 134 km^2, sd = 114 km^2).

To estimate aerial-weighted riverine loads or riverine export (kg km^{-2} yr^{-1}), we used the loadest and loadflex models (Appling et al., 2015; Runkel et al., 2004) and divided by cumulative catchment area (Figure 1b). Briefly, models predict daily solute concentrations based on daily discharge data and measured concentrations (model outputs in Supplementary Table 2). Daily discharge data from 1979 to 2020 was downloaded from the *Saint-Jérôme* gauging station (45.79, -74.01; *Centre d'expertise hydrique du Québec;* (MELCCFP, 2018) and corrected for subwatershed surface area. Historical solute data was downloaded from the BQMA for the three sites, and included our own sampling data (Shousha et al., 2021). On average, for all variables, the frequency of sampling was bi-monthly.

Monthly precipitation data (1980-2020) were downloaded for 19 stations on and around the watershed (Government of Canada, 2021a; Supplementary Figure S1a). We then interpolated annual precipitation as the sum of rain and snow accumulated on land for all years by making a template grid of 0.01-degree resolution (Supplementary Figure S1b). We quantified the annual runoff coefficient as the ratio between streamflow (mm yr^{-1}) to precipitation (mm yr^{-1}). Specifically, we used daily streamflow at the *Saint-Jérôme* gauging station, converted it to yearly discharge (m^3 yr^{-1}), divided it by the area it drains (1163 km^2). Annual precipitation was derived from daily precipitation from *Saint-Jérôme* from 1980 - 2020. While we originally considered temperature and sulfur deposition as other climatic variables, they explained little to no variation and were therefore excluded from the study.

To compare the N and P inputs on land (5-year interval census data) to riverine loads (annual data), we derived a 5-year average of river estimates around the focal census year (census year: 2001, riverine load average: 1999 – 2003). As 2016 was the last census year, we included riverine loads until the last full data year, 2020. Elemental ratios were calculated as the molar ratios of riverine exports. All analyses have been performed in R version 4.1.2 (R Core Team, 2021).

Results

Temporal changes in element exports and links with precipitation

Across sites and years, exports of C, N, and P in the *Rivière du Nord* varied differentially (Figure 2a-c). There was little difference in the patterns of overall riverine C export across sites in the *Rivière du Nord* mainstem, but a slight increase can be observed for all sites over time. Overall, DOC export for the three sites ranged from 1891 to 4890 kg km^{-2} yr^{-1} (mean = 3123, sd = 662), and most variability can be explained by the broad range in annual precipitation (range: 907 to 1364 mm; Figure 2d). Riverine N and P exports were more distinctive among RKm sites. N exports in the two most downstream sites, RKm 58 and RKm 4, ranged from 281 to 881 kg km^{-2} yr^{-1} (mean = 493, sd = 108) and increased steadily from ~1990. Precipitation explained 42% of the interannual variance for both these sites (Figure 2e). N exports in the forested site, RKm 101, ranged from 218 to 406 kg km^{-2} yr^{-1} (mean = 306, sd = 50) and precipitation explained 48% of the variance. Exports were much lower than the two downstream sites for any given amount of precipitation. The trends in riverine P for the two most downstream sites were similar to one another, remaining constant until ~1998 (mean = 49, sd = 10), after which they dropped by more than half and then tended to increase starting in 2010. As a result, mean P exports for both sites across years was 38 kg km^{-2} yr^{-1} whereas they were 18 kg km^{-2} yr^{-1} for forested RKm 101 on average, where they decreased continuously by more than half between 1980 and 2020. Precipitation did not explain significant amounts of variability in P at any site (Figure 2f).

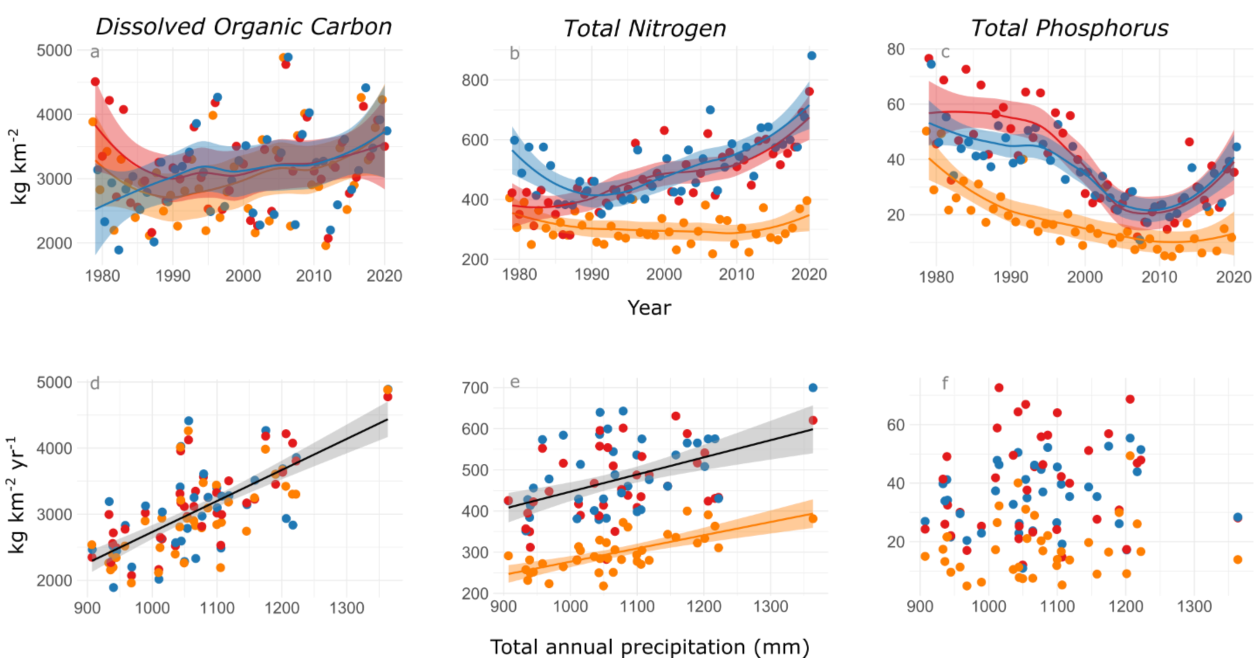

Figure 2 Overall DOC (a), TN (b), and TP (c) riverine export (kg km-2) over four decades for three sites along Rivière du Nord. RKm 101 (yellow) is the most upstream site, followed by RKm 58 (red), and RKm 4 (blue). The larger variations observed at the beginning of the timeframe (~1980-1985) may be an artifact of loadest and loadflex models lacking earlier data points. Annual riverine export as a function of total annual precipitation is shown in d) DOC, e) TN, and f) TP. Linear relation between DOC and total annual precipitation was $y = 4.69x – 1962$ ($R2 = 0.51$, p-value < 0.01) and no significant differences among RKms were observed using an analysis of covariance. TN slopes were not different among RKms, but intercepts between RKms 4-58 and 101 were significantly different ($p < 0.01$). Equation of the RKms 4-58 was $y = 0.42x +$

30 (R2 = 0.21, p-value < 0.01) and equation for RKm 101 was y = 0.32x – 44 (R2 = 0.48, p-value < 0.01). TP loads were twice as high at sites RKm 4 and 58 than 101, but there was no relationship with precipitation.

<u>Changes in land inputs</u>

To quantify the overall change in nutrient inputs, Figure 3 shows the difference in Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI, respectively) between 2016 and 1981. The municipalities for which the inputs increased the most across years (in red) followed urban development along major highways, which followed the river mainstem. Across all years and municipalities, NANI averaged 1332 kg km^{-2} (sd = 1249) and ranged from ~ 500 kg N km^{-2} in Doncaster, a Mohawk First Nations Reserve (Supplementary Figure S2a) to 7827 kg N km^{-2} in the most populated municipality in 2016, *Saint-Jérôme* (805 habitants km^{-2}; Supplementary Figure S2b). The municipality of Doncaster should be largely uninhabited as it serves as a hunting and fishing territory reserved for the Mohawk First Nation (Gouvernement du Québec, 2012), and NANI was estimated as atmospheric N deposition only. Across all years and municipalities, NAPI averaged 141 kg km^{-2} (sd = 354) and ranged from -47 kg P km^{-2} to 1394 kg P km^{-2} (Supplementary Figure S2c, d).

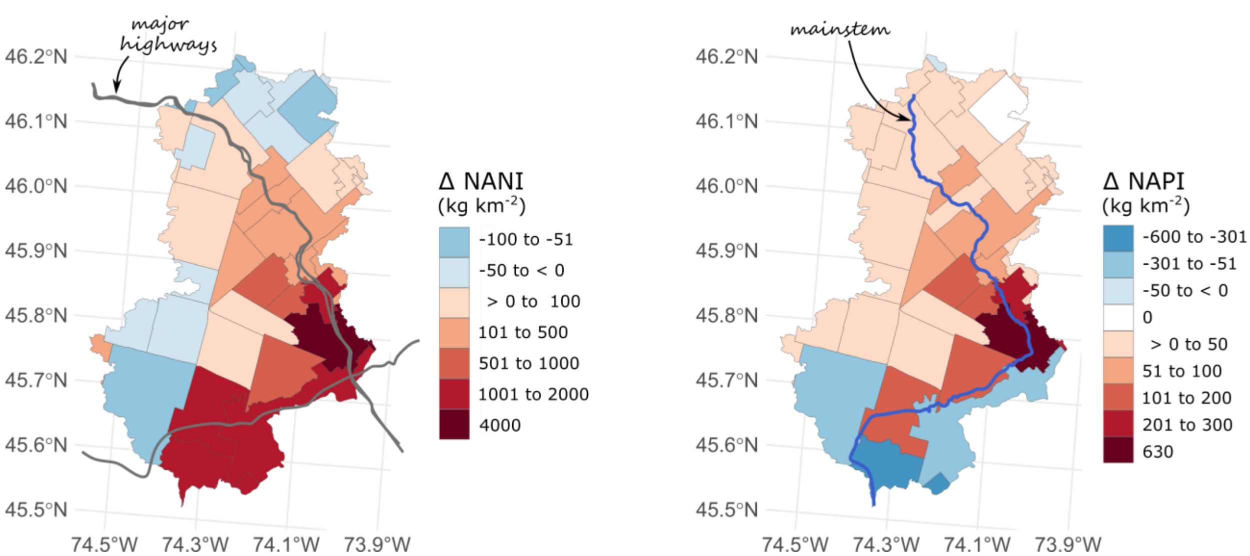

Figure 3 Two *Rivière du Nord* maps showing historical changes in NANI (left) and NAPI (right). Municipalities in red represent an increase from 1981 to 2016, and in blue represent a decrease.

<u>Relationship between anthropogenic inputs and riverine exports</u>

There were large differences between N and P trends, both in terms of anthropogenic landscape inputs and riverine exports (Figure 4). For the most upstream site draining mostly forested landscape, RKm 101, neither NANI (mean = 896, sd = 65 kg km^{-2}) nor NAPI (mean = 57, sd = 7 kg km^{-2}) increased significantly through the years, and TN riverine exports remained rather constant (mean = 305, sd = 20 kg km^{-2}) whereas TP exports dropped by more than half, from 35 ± 14 kg P km^{-2} in 1981 to 13 ± 5 kg P km^{-2} in 2016.

For the two downstream sites, RKms 58 and 4, there was a strong linear relationship between NANI and TN riverine exports ($p < 0.001$, $R^2 = 0.59$). In contrast, while NAPI increased (from 117 to 178 kg km^{-2} at RKm 58, and 122 to 145 kg km^{-2} at RKm 4), riverine TP exports decreased by almost half in both sites (52 to 33 kg P km^{-2}).

On average, for the last 40 years, the fraction of NANI in riverine export has been relatively stable (37 ± 5%, Figure 4c) suggesting that just over a third of the yearly net human inputs on land are exported towards the river. P, however, was more variable. The fractional export of NAPI decreased from 31% in 1996 to 15% in both 2006 and 2011, then increased again in 2016 (23%), resulting in an overall average and standard deviation of 27 ± 10%.

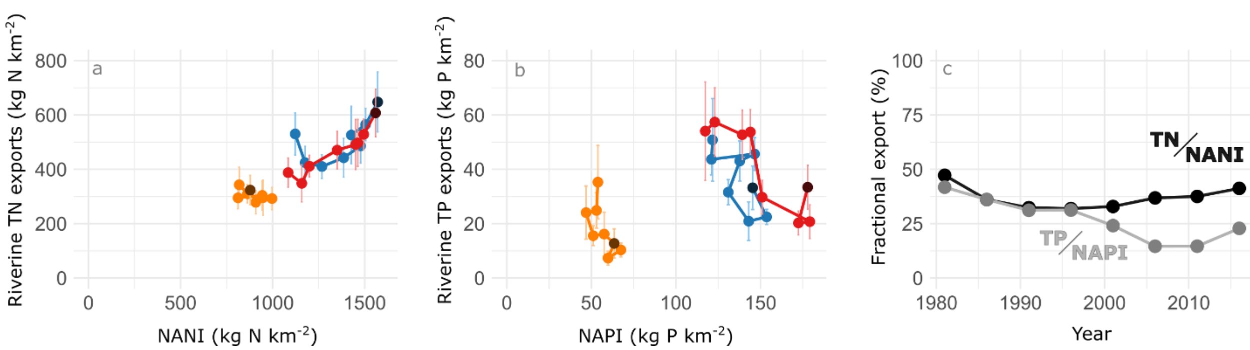

Figure 4 Riverine exports of TN (a) and TP (b) versus NANI and NAPI. Yellow, red and blue colours represent sites at RKm 101, 58, and 4, respectively. The eight census years appear linked in chronological order, the darker circles representing the last census year, 2016. Riverine exports represent a 5 year mean around the focal census year, with vertical bars as the standard deviation. Panel c shows the fraction (%) of NANI and NAPI observed in TN and TP riverine exports, respectively (kg N or P km^{-2}), across years for the most downstream site.

Historical stoichiometry

To characterise how riverine ecosystem stoichiometry varied through time at sites receiving differential anthropogenic inputs, we plotted molar C: N vs C: P ratios (Figure 5a; exact values in Supplementary Table 3). C: P was much more variable in the upstream site (mean = 587: 1, sd = 334, cv = 57), while C: N was more constrained (mean = 11.6, sd = 1.7, cv = 14.9). For the two downstream sites, ratios were typically more constrained, but shifted from a more variable C: N in the first two decades (cv = 22 vs 15 in the last two decades) to a more variable C: P in the last two (cv = 33 vs 22 in the first two). To consider the variability and specific trends in those ratios, we plotted C: P (panel b), N: P (panel c), and C: N (panel d) molar ratios of exports at all three sites across years. C: P and N: P in the most upstream site varied most (587 ± 334, 50 ± 27, respectively), while trends in the two more impacted sites followed an inverse V-shape in response to human interventions. Considering what the river ultimately exports to downstream ecosystems, C: N at RKm 4 had the least variation of all ratios (7.2 ± 1.4) and ranged from 10.6 (in 1991) to 4.7 (in 2013), supporting N-enrichment over time. C: P varied more (251 ± 112), ranging from a low of 109 (in 1979) to a high of 554 (in 2008), largely as a function of decreasing P, whereas N: P (36 ± 17) ranged from 17 (in 1992) to 87 (in 2007) both as a function of decreased P and increased N. From 1980 to 2020, C: N: P exports shifted from 130: 23: 1 to 217: 44: 1, with a C and N peak in 2007-2008 of 554: 87: 1. The decline in N: P and C: P ratios after 2008 appears to largely be driven by an increase in P entering the river over the last 15 years (Figure 2c), that was not fully explained by changes in NAPI.

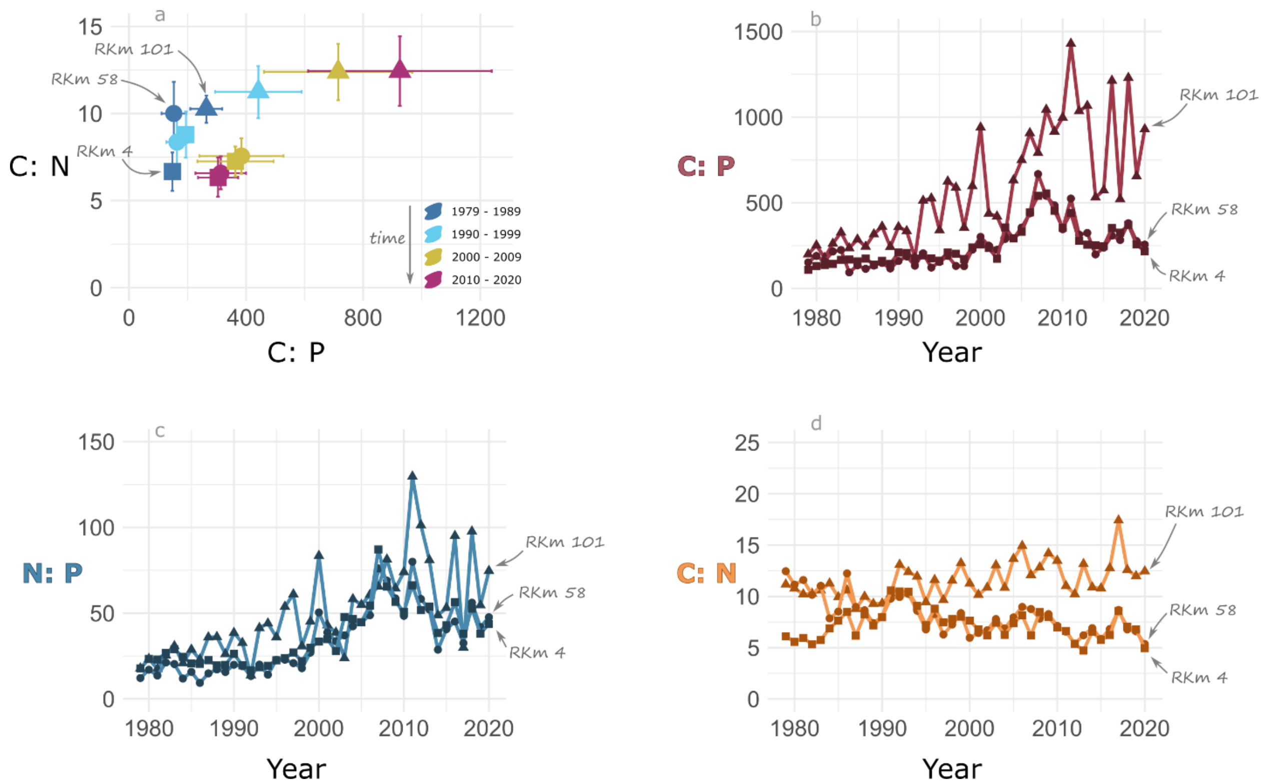

Figure 5 Panel a shows molar C: N vs C: P ratios for all three sites, where RKm 101 is represented by triangles, RKm 58 by squares, and RKm 4 by circles. The ratios are averaged by decade with standard deviations. Panels b, c, and d show molar C: P, N: P, and C: N ratios for riverine exports across years at all sites.

Discussion

<u>Mechanisms underlying trends in riverine C, N, and P</u>

The inputs of the three major elements that influence the base of food webs and ecosystem functioning are being altered across rivers globally (Carpenter et al., 1998; Hong et al., 2017; Xenopoulos et al., 2021), subsequently influencing ecosystem level stoichiometry which is rarely considered. Here we show the differential response of riverine C, N, and P exports to changes in the catchment and precipitation across space over four decades. Urbanisation over the last four decades was the most remarkable anthropogenic change in nutrient inputs to land in this large north temperate river. However, these increased inputs did not necessarily result in higher phosphorus exports over time because of human interventions on the landscape. We found no obvious impact of land use change on C exports with precipitation being the main driver, whereas N was influenced by both. The combined consequences of these differential drivers in the catchment related to exports resulted in changes in riverine ecosystem stoichiometry over time with impacts on functional properties.

The lack of correlation between riverine P exports with precipitation (Figure 2f) and the unexpected negative relationship with NAPI (Figure 4b) supports successful intervention strategies. The most striking was the precipitous drop at RKm 58, by half, from 2000 (76 533 ± 16 445 kg yr-1) to 2010 (32 795 ± 7 390 kg yr-1), following the construction of government-subsidised wastewater treatment plants (WWTPs) designed to retain P in the 1990s (MELCCFP, 2022a). The largest WWTP alone (constructed in 1998 ~10 km upstream from RKm 58; at *Saint-Jérôme* on Supplementary Figure S3 map) could account for up to 24 276 ± 5 230 kg of annual phosphorus removal or 72% of the total reaching its intake (2017 – 2020 average). This management intervention, not considered in NAPI, resulted in a major P retention control point that influenced overall riverine exports. However, riverine P exports have increased in the last 10 years despite the fact that ~70% continues to be removed from wastewater. This increase may be due to a higher sewage throughput because of a continuously growing population reflected in the slight uptick in NAPI in the last years (Figure 4b) or alternatively by a 1.5-fold increase in runoff ratio from 1980 – 2000 to 2010 – 2020 (Supplementary Figure S4c) as a function of urban expansion. Impervious surfaces are known to increase delivery of P to surface waters (Hobbie et al., 2017; Müller et al., 2020), and stormwater runoff often leads to higher P concentrations (Yang & Toor, 2018). Although there is no clear linear trend between TP exports and runoff (Supplementary Figure S4f), we suggest changes in delivery pathways through urbanisation, as well as higher throughput in wastewater, have contributed to the recent increases observed in riverine TP.

N was the only element that seemed to be influenced by both precipitation and anthropogenic inputs. This is not surprising because hydrology is a strong driver of N losses in more forested catchments (Inamdar et al., 2015; Mitchell et al., 1996), and NANI has been extensively used to successfully predict N in rivers (Chen et al., 2016; Goyette et al., 2016; Han et al., 2009; Swaney et al., 2012). Nevertheless, the scale at which we quantified NANI revealed that increased urbanisation was the most probable factor contributing to N exports in the two downstream sites in this river, reflecting wastewater inputs minimally treated for N through holding ponds directly discharged into the mainstem. As the fraction of NANI estimated in the mainstem has been relatively stable over 40 years (Figure 4c), riverine N exports in this specific system could be abated through N removal in wastewater treatment (Rahimi et al., 2020) or a reduction in NANI through large-scale dietary shifts away from meat (Almaraz et al., 2022).

Among the three elements in this study, C was the most strongly influenced by changes in climate drivers, with more than half of the inter-decadal variation in riverine exports being explained by total annual precipitation (Figure 2). The strong relationship between precipitation and area-specific exports suggests that DOC is transport-limited in this watershed, a relatively widespread phenomenon across rivers in the United States (Zarnetske et al., 2018) and northern Europe (Winterdahl et al., 2014). Although we could not fully resolve the temporal increase in DOC with historical precipitation changes (Supplementary Figure S4a), the increase in relative runoff could be contributing to this observed trend. Regardless, our results show how interannual variation in precipitation strongly impacted DOC exports, even more so than other elements, whereas nutrients were more strongly influenced by anthropogenic drivers. This led to clear inter-decadal trends in riverine stoichiometry.

<u>Implications of varying riverine ecosystem stoichiometry</u>

Changes in ecosystem stoichiometry were depicted through the modifications in inputs, retention, and delivery for C, N, and P across the watershed over four decades. Trends in the last three decades of C: N to C: P (Figure 5a) follow the same decreasing trajectory from upstream to downstream as in Shousha et al. (2021), where nutrients increased relative to C as a function of land use change. However, the upstream to downstream shift in C: P has become more remarkable over time, because ratios at the most upstream site increased almost 4-fold due to a concomitant increase in C and decrease in P (triangles in Figure 5a; absolute exports in Figure 2a, c). At this site, there is a surprising 5.8-fold decrease in P, whereas the C increase is considerably more modest (1.2-fold) and driven by changes in precipitation. Indeed, the variability in the C: P and N: P ratios in the forested section is a function of interannual variation in hydrology influencing C and N riverine exports, whereas P is on a steady decline. Several possible reasons could explain the decrease in riverine P at this pristine forested site. One could be the legislation of septic tanks to prevent P leakage across the region (MELCCFP, 2022c; MTESS, 2021). A second possibility is the increased construction of dams, largely for recreational purposes, throughout the watershed over the last decades (MELCCFP, 2023), as increasing lentification is known to retain more P at the watershed scale (Kirchner & Dillon, 1975; Maavara et al., 2015; Soranno et al., 2015). Another potential more regional explanation is the decrease in apatite weathering with acid rain reversal, where TP in streams has been shown to decrease over recent decades in a watershed located in the same geological province (Baker et al., 2015). Although we cannot resolve the exact mechanism behind this trend, our results show how a combination of change in precipitation, human interventions, and potentially atmospheric pollution has induced profound changes in riverine stoichiometry even in the most pristine area of the river. As increases in C: nutrient ratios can favour microbial sequestration of N and P locally or downstream of C-rich inputs (Stutter et al., 2018), the shift towards higher C: P (and C: N to a certain extent) at RKm 101 may increasingly fuel downstream metabolism.

Moving downstream, land use changes impacted the delivery of nutrients to the river, differentially influencing the stoichiometry at RKms 58 and 4. C ratios shifted from those with higher P and lower N in the first two decades to lower P and higher N at these sites in the last two decades. Although we do not have information on historical shifts in C type, composition was shown to change abruptly between the more forested upstream pristine reach as compared to the downstream more impacted one (Shousha et al., 2022). This suggests that there must be a high turnover of terrestrial C likely driven by the land use driven changes in nutrient inputs (Rosemond et al., 2015) that likely also occurred through time. It was interesting to note that the C: P in the upstream site was similar to those downstream in the 1980s. This original C: P upstream was more a result of much higher P than lower C, but this observation was not expressed in the estimated NAPI (Figure 4b). This suggests some other P input such as those potentially related to the forestry industry (Faubert et al., 2016) pervasive in the region at that time (Abrinord, 2022), which was not accounted for. The shift in C: P in downstream sites over time was a direct influence of WWTP P removal. Interestingly, however, the C: N ratio at the downstream site varied little over the four decades, and hovered around Redfield. This constrained C: N downstream could in part be shaping the N: P and C: P imbalances over time (Elser et al., 2022), and act as some sort of emerging ecosystem property, where both C and N can be permanently removed from the system hence converging toward this value metabolically (Maranger et al., 2018). Yet how P influences stoichiometry may more be a function of historical changes in inputs, and geomorphometric settling (Maavara et al., 2015; Soranno et al., 2015).

Absolute nutrient concentrations, however, and their ratios would ultimately shape C type and the fate of terrestrial sources (Rosemond et al., 2015; Shousha et al., 2022).

Management implications for nutrient inputs

Adopting the mass balances at the spatial resolution used here (i.e. the municipality) allowed us to identify areas in the watershed where nutrient inputs were highest and have changed the most over time. Our approach is easily adaptable to rivers globally to identify meaningful places to intervene in the watershed and abate nutrient loadings. This was particularly the case for N exports in this watershed, where urban expansion and the resulting increase in wastewater non-treated for N, entering as a point source, appears to be the most significant portion of NANI entering the river. A likely impact of not reducing N and maintaining high N: P ratios is that when nutrient concentrations are high, toxic cyanobacteria and other harmful algal blooms are favoured (Glibert et al., 2014; Scott et al., 2013), that can result in local issues as well as downstream consequences resulting in coastal degradation (Howarth, 2008; Paerl et al., 2004). As such, where possible, a dual nutrient removal strategy should be supported in systems where WWTPs are the main sources of N inputs (Conley et al., 2009; Paerl et al., 2004). We should note however that due to historical data limitation, the river sections where we were able to evaluate elemental export were mainly pristine or affected by urbanisation, with limited agricultural activity. Abatement choices would be different if we captured the input of the largely agricultural sub-watershed entering downstream of our most downstream site (Figure 1). There, reduction in fertiliser use and landscape level restoration efforts including the targeted wetland restoration (Cheng et al., 2020) and implementing winter cover crops (Hanrahan et al., 2018; Speir et al., 2022) may be the most effective practice. We suggest the broad applicability of our approach, and the relative accessibility of census data around human populations and agricultural practices in many watersheds of the world, could provide the needed guidance to help mitigate the excessive nutrient loadings to many rivers at scales relevant to management.

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Author contributions

SS, RM, and JFL designed the study. SS created the results and wrote the initial draft. SS, JFL, and RM edited subsequent ones.

Open Research

The data used for the figures in the study are available on Zenodo via the DOI 10.5281/zenodo.7806130 with the Creative Commons Attribution 4.0 International license (Shousha et al., 2023).

Global Biogeochemical Cycles

Supporting Information

Decadal Changes in Anthropogenic Inputs and Precipitation Influence Riverine Exports of Carbon, Nitrogen, and Phosphorus, and Alter Ecosystem Level Stoichiometry

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The coefficients used to calculate the Net Anthropogenic Nitrogen and Phosphorus Input (NANI/NAPI) mass balances are listed in Supplementary Table 1 along with their sources.

Supplementary Table 1: List of sources for data and coefficients used to calculate all categories in the NANI and NAPI mass balances at the municipal level in Québec, Canada.

Mass balance sub-category	Source	Details
AGRICULTURAL CENSUS		
	Statistics Canada, 1982a, 1987a, 1992a, 1997a, 2002a, 2007a, 2012a, 2017a	
POPULATION CENSUS		
	Statistics Canada, 1982b, 1987b, 1992b, 1997b, 2002b, 2007b, 2012b, 2017b	
FERTILISER		
	Statistics Canada, 2022d	Metric tonnes of N, P fertiliser at QC level (x1000).
	Statistics Canada, 2013	For 2006 and prior
	Russell et al., 2008	To transform P_2O_5 into P
LIVESTOCK SLAUGHTER		
Number slaughtered cattle, calves	Statistics Canada, 2022b	Number of cattle, calves slaughtered at the national level (Canada)
Number slaughtered hogs, sheep & lamb	Statistics Canada, 2022e	Number of hogs, sheep & lamb slaughtered at the national level (Canada)
Number slaughtered chicken, turkey	Government of Canada, 2021b	Number of chicken, turkeys slaughtered at national level (Canada)
Number slaughtered livestock at provincial level	Census of agriculture > Livestock	Total heads cattle, calves, hogs, sheep, lamb, chicken, turkey at national level (Canada)

	Census of agriculture > Livestock	Total heads cattle, calves, hogs, sheep, lamb, chicken, turkey at provincial level (QC)
LIVESTOCK LIVE WEIGHT		
Weight cold carcass cattle, calves	Statistics Canada, 2022b	Average weight, cold carcass
Weight cold carcass hog, sheep & lamb	Statistics Canada, 2022e	Average weight, cold carcass
Conversion factor carcass to live	Government of Canada, 2022	Conversion factor from live weight to cold carcass
Weight live chicken, turkey	Statistics Canada, 2021b	Total kg for chickens, hens + number of heads
Weight live egg	Statistics Canada, 2021a	Egg number per head of layer
Weight live milk	FAO, 2021	Kg of milk produced per cow
EDIBLE PORTION		
Edible portion of animals as % of live weight	Han et al., 2009	What we can eat of the animal
NP CONTENT		
N content	Han et al., 2009	What % of the edible portion is N
	personal communication with J.-O. Goyette	N % for pork, chicken, broiler (all = 3.648)
P content	Goyette et al., 2016	What % of the edible portion is P
ANIMAL INTAKE		
Consumtion rates N	Han & Allan, 2008	Consumption rates of N for livestock under dynamic model
Consumtion rates P	Han et al., 2011	Consumption rates of P for livestock under dynamic model
Life cycle (days alive per year)	Han et al., 2009	Duration of livestock life on farm (usually less than 1 year)
	Kellogg et al., 2000	" "
	Goyette et al., 2016	" "
Equations to calculate dynamic life cycle	Goyette et al., 2016 Kellogg et al., 2000 Han et al., 2009	
CROP YIELD		
Provincial yield for certain crops	Statistics Canada, 2022c	Crop yields at provincial level (not found at smaller scale)
Provincial yield for potatoes	Statistics Canada, 2022a	Crop yield at provincial level for potatoes
	https://www.potatopro.com/quebec/potato-statistics	PotatoPro
Administrative region crop yield	Institut de la statistique du Québec, 2020	Crop yield at the administrative level for big cultures For the provincial yield, if had no data for region, used average of all instead. Used the provincial average for the following crops to build in missing regional data: For Fodder corn: Saguenay, Abitibi, Côte-Nord, Nord-du-Québec For Grain corn : Bas-Saint-Laurent, Abitibi,Nord-du-Québec,Gaspésie For Barley: Estrie, Outaouais, Laurentides For Soya : Bas-Saint-Laurent, Gaspésie,Abitibi,Nord-du-Québec For Oats : Montréal, Laval,Lanaudière,Montérégie

Understanding agricultural regions in QC	Statistics Canada, 2021c	For mixed grains : Capitale-Nationale, Mauricie, Montréal, Laval, Lanaudière, Outouais, Laurentides, Abitibi, Nord-du-Québec, Montérégie Codes for each region (not to mix up with administrative codes, which are slightly different)
CROP CONTENT		
Kilograms harvested per yield unit (nitrogen)	USDA, 2017	USDA Natural Resources Conservation Service, Technical Resources
Percent Dry Matter, Percent N in Dry Matter (nitrogen)	USDA, 2017	USDA Natural Resources Conservation Service, Technical Resources
Percent N in Dry Matter for Corn grain : updated (nitrogen)	David et al., 2010	% protein in modern corn hybrids is decreasing continuously (from 10 to 8.5% from 1985 to 2006). Assumed 1.36% N for 2006 (assumption: use 2006 data for today too). Toolbox assumes 9.5% protein = 1.5% N (average between 1985 - 2006).
N content for cropland and non cropland pastures (nitrogen)	Hong & Swaney, 2010; Table 5.1.1.1	
P content in crops	MacDonald & Bennett, 2009	P content in crop types (kg / kg of crop)
P content for cropland and non cropland pastures	Schaefer & Alber, 2007	P content for pastures
DISTRIBUTION		
% distributed to humans and animals	Boyer et al., 2002	Partition crop yields to humans and animals
	Jordan & Weller, 1996	
% of crop lost during harvest	Boyer et al., 2002	Losses of crops during harvest
		Missing rice and buckwheat for distribution and loss: For buckwheat, in Yieldbased BNF, buckwheat column notes are in red (10% loss and 90% to humans)
	Swaney et al., 2018; Toolbox v3	Pasture loss : take half leave half
BIOLOGICAL NITROGEN FIXATION		
Yield based for soybean, alfalfa, non-alfalfa	Han & Allan, 2008	Table 4 : proportion of plant N from fixation
Nonalfalfa have 25% leguminous plants	USDA, 2007	Alfalfa fixes nitrogen. Legumes (in non-alfalfa plants) are the ones that fix nitrogen in the non-alfalfa pastures. So, include the legumes from nonalfalfa that fix nitrogen in calculation.
Cropland, area-based	Jordan & Weller, 1996	Named non-wooded pastures, east of Mississippi, eastern pastures
Snap beans, area-based	Boyer et al., 2002,	
Peanuts, area-based	Jordan & Weller, 1996	They have 86 kg N / ha / yr
	Schaefer & Alber, 2007	They have 8000 kg N / km^2 / yr
PROTEIN CONSUMPTION		
Amount of protein consumed per capita, recent average	Hong & Swaney, 2010; Toolbox 3.1	6.21 kg / person / yr is data in toolbox. It's an average, and does not say from what years. Only says that data comes from US censuses.
N content in protein	Jones, 1941	N is 16% of protein
	Hong et al., 2012	Conversion factor used in NANI-PI
P content in protein	Hong et al., 2012	P consumption is equivalent to 20% N consumption

	Russell et al., 2008	Authors do not clearly state in article that N:P is 5, so ref is here because (Hong et al., 2012) based themselves off (Russell et al., 2008) to calculate N:P of 5
DETERGENT		
For laundry detergent :		
Laundry detergent (kg / capita / yr)	Han et al., 2012	Laundry detergent use (USA proxy because unavailable for Canada)
% of P by weight	Litke, 1999	Detergent industry limits phosphate in detergents to 8.7% by weight as phosphorus in 1970 and to 2.2% in 1972 in Canada (for laundry)
	Government of Canada, 2019	Limit goes down to 0.5% in 2009 + when click to see previous versions, find the 2.2% limit website last up to date 2019, so use values there for most recent year
For dishwasher detergent :		
Detergent use (Spoons / capita / yr)	Han et al., 2012	dishwasher detergent use
	Goyette et al., 2016	dishwasher detergent use
P content (kg P / spoons)	Han et al., 2012	Article has kg P per spoon (0.0009687). Assume this is when limit is at 8.7% P content because in same time range of regulations (Litke, 1999)
	Government of Canada, 2019	Limit goes down to 0.5% in 2009
		Rule of 3 : if 0.0009687 is for 8.7, what is kg-P for 0.5% (limit of 2.2% in the 1970s only for laundry)
Proportion of households with automatic washers	Goyette et al., 2016	Proportion of households with dishwasher
	Statistics Canada, 2017c	We are looking for dishwasher information.
		Calculate trendline for 1997-2009 and get proportion for 2011, 2016 (for Canada)
P dishwashing detergent cosumption (kg P / capita / yr)	Equation	= dishwashing detergent use * P content * Proportion of households
ATMOSPHERIC DEPOSITION		
N deposition	www.cmaq-model.org/	Community Multiscale Air Quality model for 2008 (usually kg-N / km^2)
		Used NH_y and NO_x deposition because of small surface areas of municipalities and discrete land use (Boyer et al., 2002; Dentener & Crutzen, 1994)
N emissions, historical	Government of Canada, 2018	Air Pollutant and Black Carbon Emissions Inventories online search (1990 – 2020).
	Asadoorian et al., 2006	Emission trends (Tg) 1890 – 1995.

Supplementary Table 2 summarises the loadflex model outputs for each RKm and variable modelled.

Supplementary Table 2: Example of loadflex model fit for the three sites along the *Rivière du Nord* mainstem, RKms 4, 58, 101. The best models were chosen for their lowest RRMSE and ARIL. They are in bold and are the ones that were used to interpolate concentration predictions for the years of interest, 1980-2020.

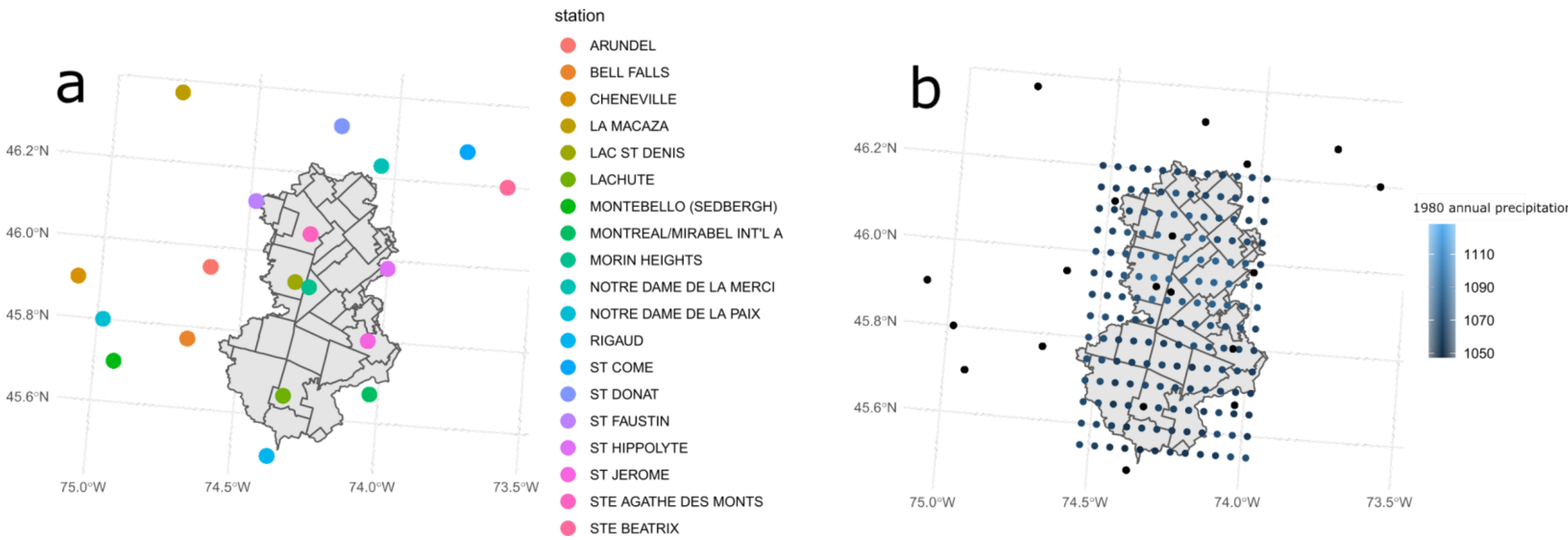
RKm	Variable	Years spanned by data	Model	RRMSE	ARIL
4	TN	1985-2020	interpolation	0	1.1492
			linear model	0.3943	1.3169
			loadReg	0.3389	1.1090
			composite	**0.0006**	**1.1051**
	TP	1979-2020	interpolation	0	2.8505
			linear model	0.9759	3.0094
			loadReg	0.6406	2.1455
			composite	**0.0002**	**1.8968**
	DOC	1984-1990, 1993-2020	**interpolation***	**0**	**0.7636**
			linear model	2.3623	1.2422
			loadReg	2.1029	1.0697
			composite	0.0002	1.1518
58	TN	1985-1986, 1988-2020	interpolation	0	1.2653
			linear model	0.3298	1.1935
			loadReg	0.2736	0.9943
			composite	**0.0009**	**1.0342**
	TP	1979-1986, 1988-2020	interpolation	0	3.2604
			linear model	1.2368	3.7891
			loadReg	0.8605	2.4154
			composite	**0.0007**	**1.8788**
	DOC	1984-1986, 1988-1990, 1993-2020	**interpolation**	**0**	**0.70633**
			linear model	0.2179	0.7174
			loadReg	0.1931	0.6003
			composite	0.0001	0.7288
101	TN	1985-1986, 1988-2020	interpolation	0	1.2745
			linear model	0.2708	1.1115
			loadReg	0.2176	0.8988
			composite	**0.0003**	**0.9723**
	TP	1979-1986, 1988-2020	interpolation	0	6.0454
			linear model	1.9940	5.5106
			loadReg	0.9638	2.8503
			composite	**0.0002**	**2.4020**
	DOC	1984-1986, 1988-1990, 1993-2020	interpolation	0	0.6890
			linear model	0.1957	0.7490
			loadReg	0.1379	0.5257
			composite	**0.0003**	**0.5913**

RRMSE : relative root mean square error, ARIL : average of the relative 95% prediction interval lengths (Appling et al., 2015). Variable acronyms refer to total nitrogen (TN), total phosphorus (TP), and dissolved organic carbon (DOC).

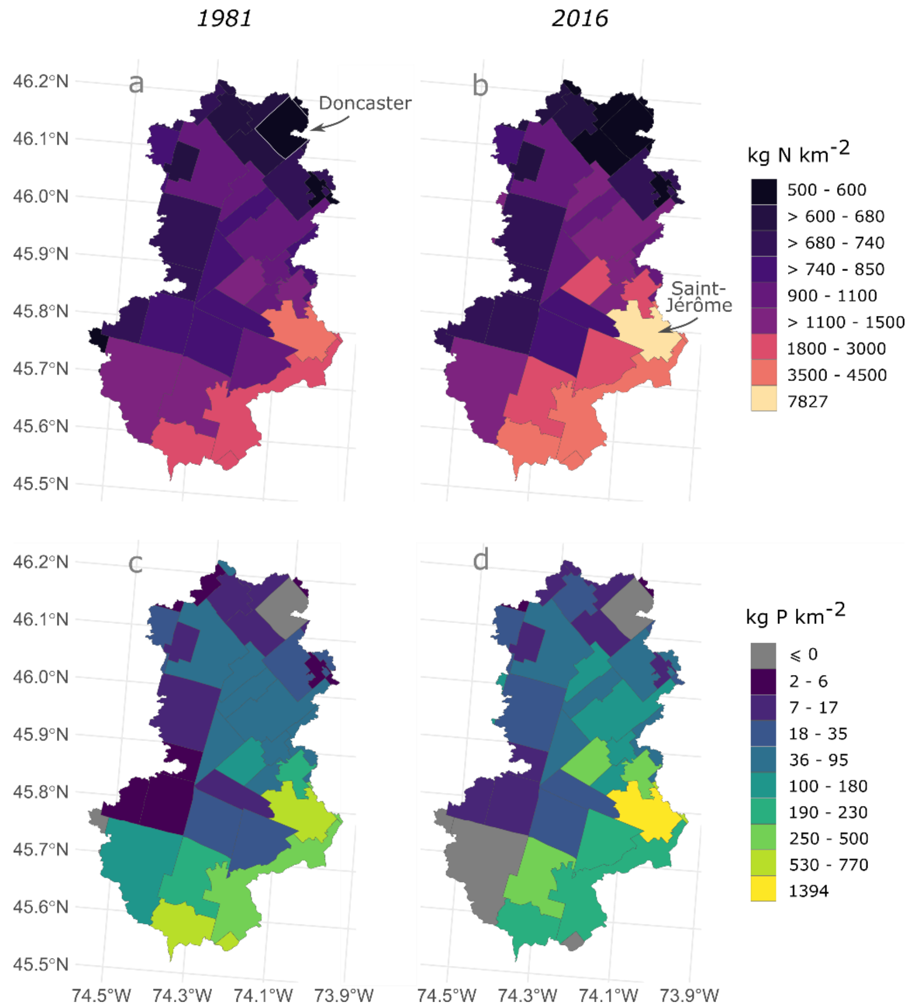
Supplementary Table 3 reports the values for C: N, C: P, and N: P (Figure 5a).

Supplementary Table 3: Decadal averages (± standard deviations) for C: N, C: P, and N: P molar ratios at the three sites along *Rivière du Nord*.

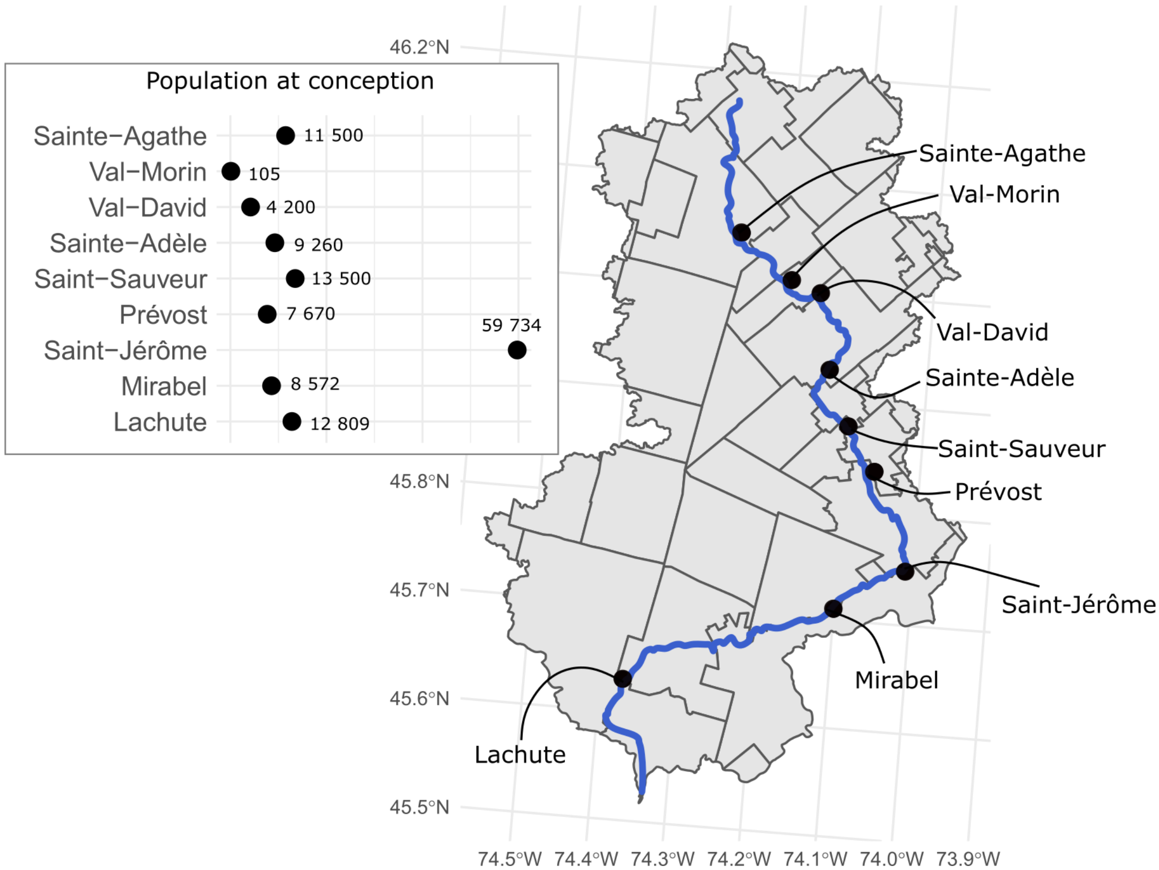
C: N	1979 – 1989	1990 – 1999	2000 – 2009	2010 – 2020
RKm 101	10 ± 0.8	11 ± 1.5	12 ± 1.6	12 ± 2.0
RKm 58	10 ± 1.8	8 ± 1.3	8 ± 1.0	7 ± 0.9
RKm 4	7 ± 1.1	9 ± 1.3	7 ± 0.8	6 ± 1.1
C: P	**1979 – 1989**	**1990 – 1999**	**2000 – 2009**	**2010 – 2020**
RKm 101	264 ± 55	442 ± 148	715 ± 253	926 ± 313
RKm 58	153 ± 42	164 ± 36	384 ± 144	313 ± 86
RKm 4	148 ± 20	194 ± 24	364 ± 130	304 ± 69
N: P	**1979 – 1989**	**1990 – 1999**	**2000 – 2009**	**2010 – 2020**
RKm 101	26 ± 6	40 ± 13	57 ± 18	76 ± 29
RKm 58	15 ± 4	20 ± 4	50 ± 14	48 ± 14
RKm 4	22 ± 3	23 ± 4	50 ± 17	48 ± 9



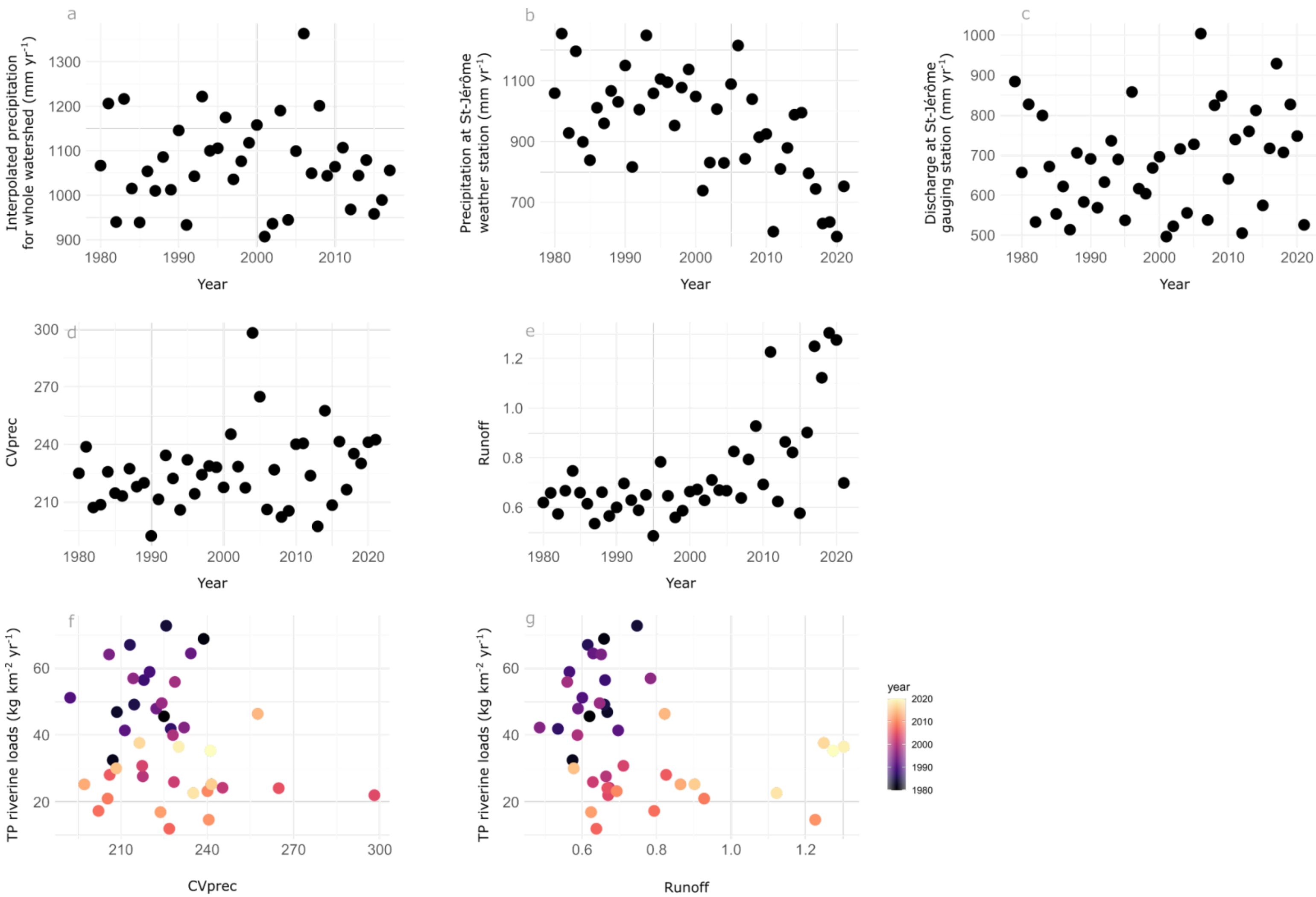
Supplementary Figure S1a) Location of 19 stations where historical precipitation data is recorded, compared to the *Rivière du Nord* watershed and **b)** Inverse Distance Weighting interpolation for 1980. The geospatial interpolation is shown with a resolution of 0.05 degrees for visual representation purposes, but the actual data were interpolated using a 0.01 degree resolution.



Supplementary Figure S2 Four *Rivière du Nord* maps showing historical changes in Net Anthropogenic Nitrogen Inputs (NANI; top) and Net Anthropogenic Phosphorus Inputs (NAPI; bottom). Panels a) and b) show the NANI for 1981 and 2016, respectively. Panels c) and d) are the equivalent of a) and b) but for NAPI, where municipalities in grey represent a net export of P (negative values).



Supplementary Figure S3 Location of wastewater treatment plants in the *Rivière du Nord* watershed with their associated population in the year of conception.



Supplementary Figure S4 Panels a) and b) show precipitation (rain and snow) for each year at the watershed level (interpolated) and at the specific *Saint-Jérôme* weather station. Panel c) shows discharge at the *Saint-Jérôme* gauging station. We use CVprec as a proxy for flashiness, with the intent that if a year had a larger coefficient of variation (CV) for its total precipitation, that year had flashier precipitation. Panel e) shows that runoff (annual discharge over annual precipitation) has increased in the last 10 years. Panels f) and g) show no clear relationship between TP riverine loads (at RKm 58, the closest to *Saint-Jérôme*) and flashiness or runoff.

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Decadal Changes in Anthropogenic Inputs and Precipitation Influence Riverine Exports of Carbon, Nitrogen, and Phosphorus, and Alter Ecosystem Level Stoichiometry

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Key Points:

- 40 years of riverine export data show a differential response for carbon, nitrogen, and phosphorus to climatic and anthropogenic drivers.
- Higher anthropogenic nutrient inputs to land explained nitrogen increases over time, but phosphorus decreased because of human interventions.
- Precipitation drove carbon export variability, which combined with nutrients resulted in variable ratios along the river and over decades.

Abstract

Changes in precipitation and land use influence carbon (C), nitrogen (N) and phosphorus (P) exports from land to receiving waters. However, how these drivers differentially alter elemental inputs and impact subsequent ecosystem stoichiometry over time remains poorly understood. Here we quantified long-term (1979-2020) trends in C, N, and P exports at three sites along the mainstem of a north temperate river, that successively drains forested, urban, and more agriculturally impacted land-use areas. Riverine N and to a lesser degree C exports tended to increase over time, with major inter-annual variation largely resolved by changes in precipitation. Historical increases in net anthropogenic N inputs on land (NANI) also explained increases in riverine N exports, with about 35% of NANI reaching the river annually. Despite higher Net anthropogenic P inputs, NAPI, over time, P exports tended to decrease at all riverine sites. This decrease in P at the forested site was more gradual, whereas a precipitous drop was observed at the downstream urban site, following legislated P removal in municipal wastewater. Changes in historical ecosystem stoichiometry reflected the differential elemental exports due to natural and anthropogenic drivers and ranged from 174: 23: 1 to 547: 76: 1 over the years. Our work shows how C, N, and P have responded to different drivers in the same catchment over the last four decades, and how their differential riverine exports have influenced ecosystem stoichiometry.

Keywords: river, stoichiometry, carbon, nitrogen, phosphorus, decadal trends

Introduction

Carbon (C), nitrogen (N), and phosphorus (P) are at the base of aquatic ecosystem metabolism (von Schiller et al., 2017), but excess loadings of these elements from land to water can adversely impact ecosystem functioning (Stutter et al., 2018). There have been widespread increases in the export of C, N, and P from land to water in response to changing climate and human modifications to the landscape (Ballard et al., 2019; Howarth et al., 1996; Kritzberg et al., 2020), resulting in eutrophication and loss of aquatic ecosystem services (Carpenter et al., 1998; Graeber et al., 2021). However, terrestrial transfers of nutrients and carbon to a river may differ across or within a watershed as a function of different land use practices or physical watershed features affecting the elemental stoichiometries of the receiving systems (Goyette et al., 2019). As such, aquatic ecosystem stoichiometry, defined as the combined elemental gain and loss patterns at the watershed scale is a useful integrative framework to understand global change impacts on receiving waters (Maranger et al., 2018). The approach has been successfully applied along the mainstem of a river, where stark differences were measured as a function of seasonal climate and upstream-downstream land use gradients (Shousha et al., 2021). However, how long-term changes in land use and climate variation may influence C, N, and P on land and in the water, and influence aquatic ecosystem stoichiometry, remains poorly understood.

It is well known that C, N, and P exports have been influenced by land use changes and/or climate variation (Carpenter et al., 1998; Zarnetske et al., 2018). Increasing C loading to freshwaters has been indirectly related to changes in precipitation (Vidon et al., 2008; Zarnetske et al., 2018), recovery from acid rain (Clark et al., 2010; Kritzberg et al., 2020), and reforestation practices (Kritzberg, 2017). Land use change has been shown to influence dissolved riverine C concentrations and composition, but these vary in direction and magnitude (Xenopoulos et al., 2021), and composition often tracks nutrients (Shousha et al., 2022). Anthropogenic N and P inputs to land have increased over time (Carpenter et al., 1998; Steffen et al., 2015) mostly because of urban population growth and intensive agriculture where N has outpaced P inputs (Glibert et al., 2014; Monchamp et al., 2014), influencing ecosystem stoichiometry. Atmospheric N deposition can also be a significant human-derived input on the landscape particularly in remote regions where land use change is limited (McCrackin & Elser, 2010). Historical legislative acts, however, such as the Clean air and Clean water acts in North America for example, have resulted in reductions in N and P respectively to water (Goyette et al., 2016; Keiser & Shapiro, 2019). As such, elemental exports as well as their stoichiometries may be highly variable through time and across space, even within a single system.

In terms of nutrient transfers from land to water, N, as nitrate, is more mobile in the soil matrix (Caraco & Cole, 1999), and precipitation or runoff has been shown to increase the anthropogenic N fraction exported to rivers (Han et al., 2009; Howarth et al., 2012; Howarth et al., 2006). P on the other hand is highly reactive and tends to bind to the soil matrix (Sharpley et al., 2013). P often enters rivers in a particulate form (Holtan et al., 1988; Paytan & McLaughlin, 2011) where increased exports tend to be influenced by flashier discharge patterns rather than annual precipitation (Goyette et al., 2019). In managed watersheds, delivery pathways are also a function of landscape modifications that promote runoff. For example, tile drainage has been shown to accelerate N transport accounting for > 80% of inputs loaded to waters (McIsaac & Hu, 2004), whereas stormwater runoff from even moderately urbanised regions have higher P loads than less managed regions (Yang & Toor, 2018). However, understanding how these three elements respond to different drivers of change that influence riverine exports remains limited.

Quantifying Net Anthropogenic N and P Inputs (NANI/NAPI) to land using a simple mass balance approach (Howarth et al., 1996) has successfully tracked historic and stoichiometric changes on the catchment and in riverine exports (Goyette et al., 2016, 2019). The NANI and NAPI mass balances have been done extensively in the United States (Hong et al., 2011), the Baltic Sea watershed (Hong et al., 2017), the United Kingdom (Howarth et al., 2012), Europe (using a similar approach, GRAFS; Billen et al., 2021), China (Gao et al., 2014; Han et al., 2013), India (Swaney et al., 2015), and certain parts of Canada (Goyette et al., 2016; Van Staden et al., 2021), but at relatively broad spatial scales. Anthropogenic inputs are estimated using census data compiled at different administrative scales (for example: country vs municipality), and applying this approach at the finest scale possible could enable scientists and managers to target precise areas for intervention. However, applying changes in input type at finer scales over time remains to be explored. Here we combined historical changes in NANI and NAPI at the finest scale available (the municipality) together with precipitation to disentangle riverine C, N, and P export and consequences on aquatic ecosystem stoichiometry along the mainstem through time. We quantify these changes at three sites along a river's mainstem with an increasing gradient of human pressure in the sub-watersheds over a 40-year period to understand the differential sources and fates of these essential elements.

Methods

The *Rivière du Nord* watershed is situated north-west of Montreal, in the Laurentians region of Québec, Canada. The mainstem, a 140 km-long river of Strahler order 5, initially drains a largely forested landscape, then an urban, and finally an agricultural one (Figure 1a). Agricultural land use is constrained to fertile plains of the St. Lawrence Lowlands located in the southern-most third of the watershed. North of the St. Lawrence Lowlands is the Canadian Shield, a geological province covered with very little topsoil, a mix of conifer and deciduous trees, lakes and rivers. Most urban development occurred along the river banks.

Three sites along the *Rivière du Nord* mainstem have been sampled periodically by the *Ministère de l'Environnement et de la Lutte contre les changements climatiques, Forêt faune et parc* (MELCCFP, 2022b) since ~1980, with measurements available for dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP) in the *Banque de données sur la qualité du milieu aquatique* (BQMA). Data were available for three sites, named based on their location along the mainstem, using the outlet as river kilometer 0 (RKm 0, Figure 1a). These sites coincided with major changes in land cover and land use (Natural Resources Canada, 2009; Shousha et al., 2021).

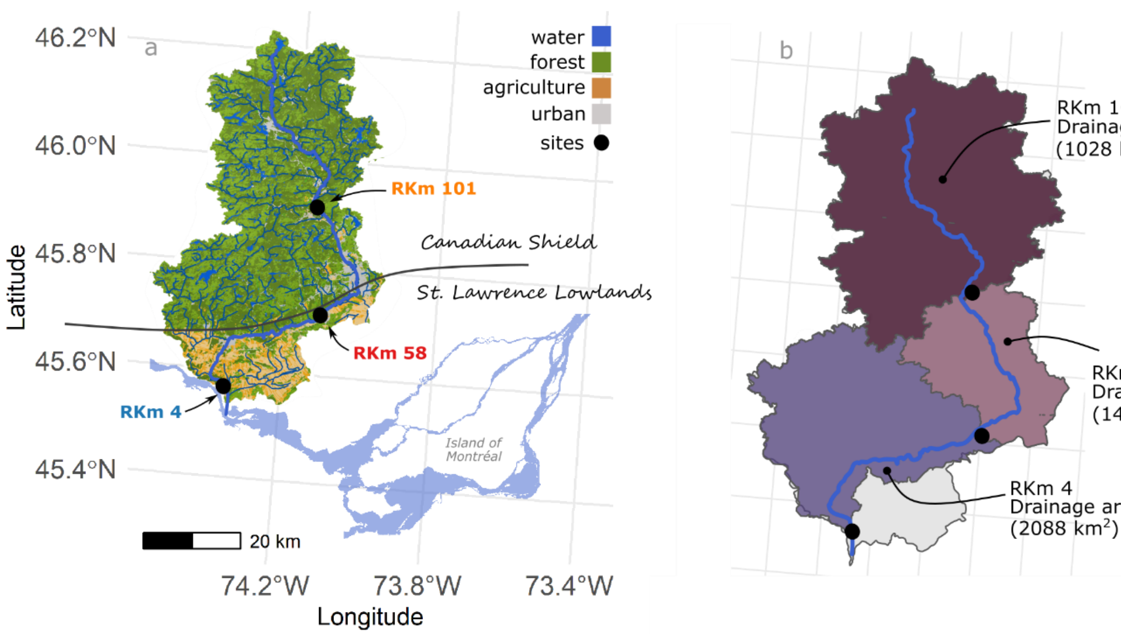

Figure 1 Land use and land cover map of the Rivière du Nord watershed, positioned with regards to the Island of Montreal (panel a). The thick blue line in the watershed shows the river's mainstem. The three water quality sites are River Kilometers 4, 58, and 101. Panel b shows cumulative drainage areas for the three sites. The grey area is not drained by RKm 4.

To quantify human activities on the landscape historically, we used the Net Anthropogenic Nitrogen/Phosphorus Input (NANI, NAPI) mass balance approach following Goyette et al. (2016). Data sources, coefficients, and descriptions can be found in Supplementary Table 1. The N and P budgets were calculated from 1981 to 2016 at a 5-year interval using municipal-level data which was the finest scale available. Municipality surface area ranged from 16 to 485 km^2 (median = 97 km^2, mean 134 km^2, sd = 114 km^2).

To estimate aerial-weighted riverine loads or riverine export (kg km^{-2} yr^{-1}), we used the loadest and loadflex models (Appling et al., 2015; Runkel et al., 2004) and divided by cumulative catchment area (Figure 1b). Briefly, models predict daily solute concentrations based on daily discharge data and measured concentrations (model outputs in Supplementary Table 2). Daily discharge data from 1979 to 2020 was downloaded from the *Saint-Jérôme* gauging station (45.79, -74.01; *Centre d'expertise hydrique du Québec;* (MELCCFP, 2018) and corrected for subwatershed surface area. Historical solute data was downloaded from the BQMA for the three sites, and included our own sampling data (Shousha et al., 2021). On average, for all variables, the frequency of sampling was bi-monthly.

Monthly precipitation data (1980-2020) were downloaded for 19 stations on and around the watershed (Government of Canada, 2021a; Supplementary Figure S1a). We then interpolated annual precipitation as the sum of rain and snow accumulated on land for all years by making a template grid of 0.01-degree resolution (Supplementary Figure S1b). We quantified the annual runoff coefficient as the ratio between streamflow (mm yr^{-1}) to precipitation (mm yr^{-1}). Specifically, we used daily streamflow at the *Saint-Jérôme* gauging station, converted it to yearly discharge (m^3 yr^{-1}), divided it by the area it drains (1163 km^2). Annual precipitation was derived from daily precipitation from *Saint-Jérôme* from 1980 - 2020. While we originally considered temperature and sulfur deposition as other climatic variables, they explained little to no variation and were therefore excluded from the study.

To compare the N and P inputs on land (5-year interval census data) to riverine loads (annual data), we derived a 5-year average of river estimates around the focal census year (census year: 2001, riverine load average: 1999 – 2003). As 2016 was the last census year, we included riverine loads until the last full data year, 2020. Elemental ratios were calculated as the molar ratios of riverine exports. All analyses have been performed in R version 4.1.2 (R Core Team, 2021).

Results

<u>Temporal changes in element exports and links with precipitation</u>

Across sites and years, exports of C, N, and P in the *Rivière du Nord* varied differentially (Figure 2a-c). There was little difference in the patterns of overall riverine C export across sites in the *Rivière du Nord* mainstem, but a slight increase can be observed for all sites over time. Overall, DOC export for the three sites ranged from 1891 to 4890 kg km^{-2} yr^{-1} (mean = 3123, sd = 662), and most variability can be explained by the broad range in annual precipitation (range: 907 to 1364 mm; Figure 2d). Riverine N and P exports were more distinctive among RKm sites. N exports in the two most downstream sites, RKm 58 and RKm 4, ranged from 281 to 881 kg km^{-2} yr^{-1} (mean = 493, sd = 108) and increased steadily from ~1990. Precipitation explained 42% of the interannual variance for both these sites (Figure 2e). N exports in the forested site, RKm 101, ranged from 218 to 406 kg km^{-2} yr^{-1} (mean = 306, sd = 50) and precipitation explained 48% of the variance. Exports were much lower than the two downstream sites for any given amount of precipitation. The trends in riverine P for the two most downstream sites were similar to one another, remaining constant until ~1998 (mean = 49, sd = 10), after which they dropped by more than half and then tended to increase starting in 2010. As a result, mean P exports for both sites across years was 38 kg km^{-2} yr^{-1} whereas they were 18 kg km^{-2} yr^{-1} for forested RKm 101 on average, where they decreased continuously by more than half between 1980 and 2020. Precipitation did not explain significant amounts of variability in P at any site (Figure 2f).

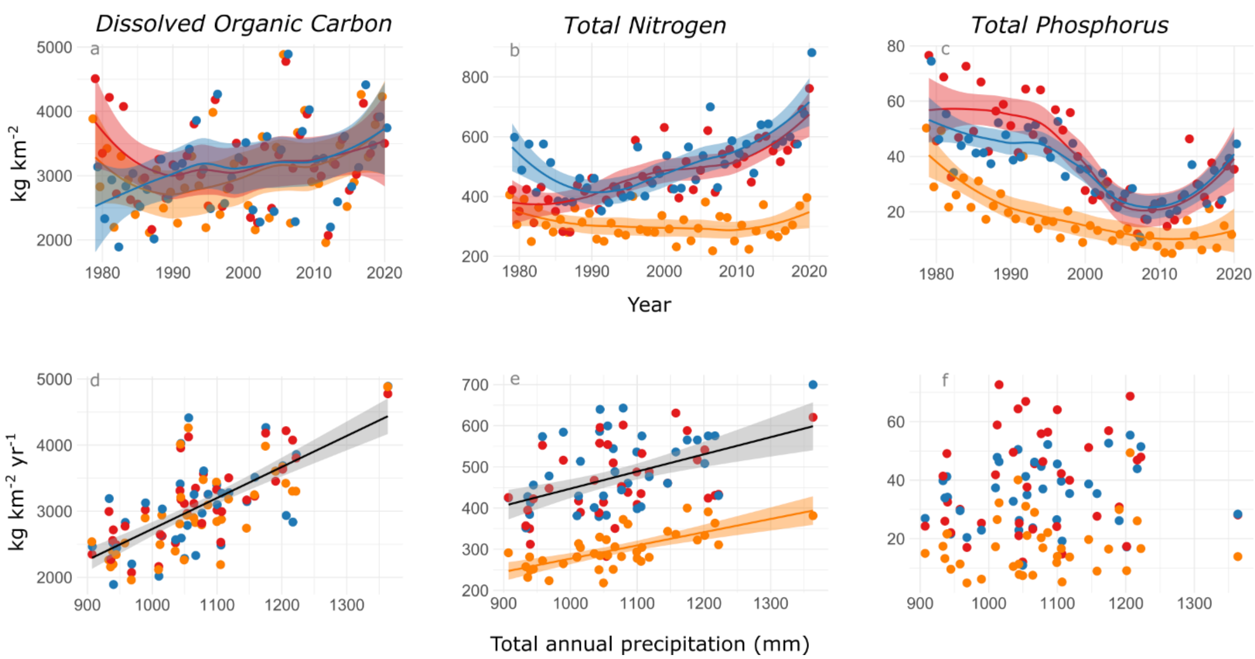

Figure 2 Overall DOC (a), TN (b), and TP (c) riverine export (kg km-2) over four decades for three sites along Rivière du Nord. RKm 101 (yellow) is the most upstream site, followed by RKm 58 (red), and RKm 4 (blue). The larger variations observed at the beginning of the timeframe (~1980-1985) may be an artifact of loadest and loadflex models lacking earlier data points. Annual riverine export as a function of total annual precipitation is shown in d) DOC, e) TN, and f) TP. Linear relation between DOC and total annual precipitation was $y = 4.69x - 1962$ ($R2 = 0.51$, p-value < 0.01) and no significant differences among RKms were observed using an analysis of covariance. TN slopes were not different among RKms, but intercepts between RKms 4-58 and 101 were significantly different ($p < 0.01$). Equation of the RKms 4-58 was $y = 0.42x +$

30 (R2 = 0.21, p-value < 0.01) and equation for RKm 101 was y = 0.32x – 44 (R2 = 0.48, p-value < 0.01). TP loads were twice as high at sites RKm 4 and 58 than 101, but there was no relationship with precipitation.

<u>Changes in land inputs</u>

To quantify the overall change in nutrient inputs, Figure 3 shows the difference in Net Anthropogenic Nitrogen and Phosphorus Inputs (NANI and NAPI, respectively) between 2016 and 1981. The municipalities for which the inputs increased the most across years (in red) followed urban development along major highways, which followed the river mainstem. Across all years and municipalities, NANI averaged 1332 kg km^{-2} (sd = 1249) and ranged from ~ 500 kg N km^{-2} in Doncaster, a Mohawk First Nations Reserve (Supplementary Figure S2a) to 7827 kg N km^{-2} in the most populated municipality in 2016, *Saint-Jérôme* (805 habitants km^{-2}; Supplementary Figure S2b). The municipality of Doncaster should be largely uninhabited as it serves as a hunting and fishing territory reserved for the Mohawk First Nation (Gouvernement du Québec, 2012), and NANI was estimated as atmospheric N deposition only. Across all years and municipalities, NAPI averaged 141 kg km^{-2} (sd = 354) and ranged from -47 kg P km^{-2} to 1394 kg P km^{-2} (Supplementary Figure S2c, d).

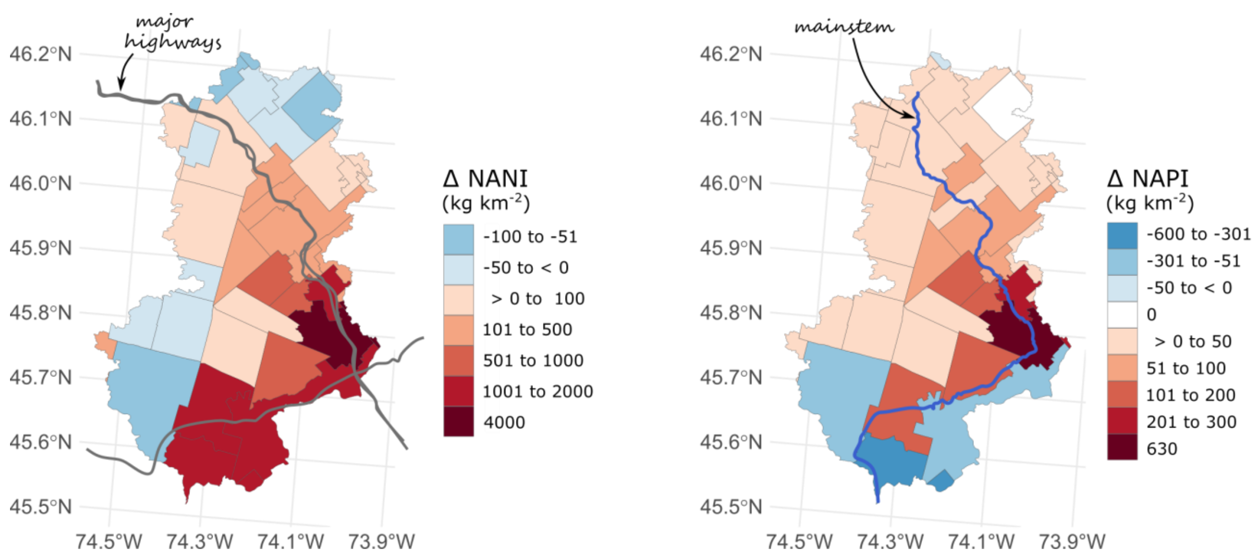

Figure 3 Two *Rivière du Nord* maps showing historical changes in NANI (left) and NAPI (right). Municipalities in red represent an increase from 1981 to 2016, and in blue represent a decrease.

<u>Relationship between anthropogenic inputs and riverine exports</u>

There were large differences between N and P trends, both in terms of anthropogenic landscape inputs and riverine exports (Figure 4). For the most upstream site draining mostly forested landscape, RKm 101, neither NANI (mean = 896, sd = 65 kg km^{-2}) nor NAPI (mean = 57, sd = 7 kg km^{-2}) increased significantly through the years, and TN riverine exports remained rather constant (mean = 305, sd = 20 kg km^{-2}) whereas TP exports dropped by more than half, from 35 ± 14 kg P km^{-2} in 1981 to 13 ± 5 kg P km^{-2} in 2016.

For the two downstream sites, RKms 58 and 4, there was a strong linear relationship between NANI and TN riverine exports ($p < 0.001$, $R^2 = 0.59$). In contrast, while NAPI increased (from 117 to 178 kg km^{-2} at RKm 58, and 122 to 145 kg km^{-2} at RKm 4), riverine TP exports decreased by almost half in both sites (52 to 33 kg P km^{-2}).

On average, for the last 40 years, the fraction of NANI in riverine export has been relatively stable (37 ± 5%, Figure 4c) suggesting that just over a third of the yearly net human inputs on land are exported towards the river. P, however, was more variable. The fractional export of NAPI decreased from 31% in 1996 to 15% in both 2006 and 2011, then increased again in 2016 (23%), resulting in an overall average and standard deviation of 27 ± 10%.

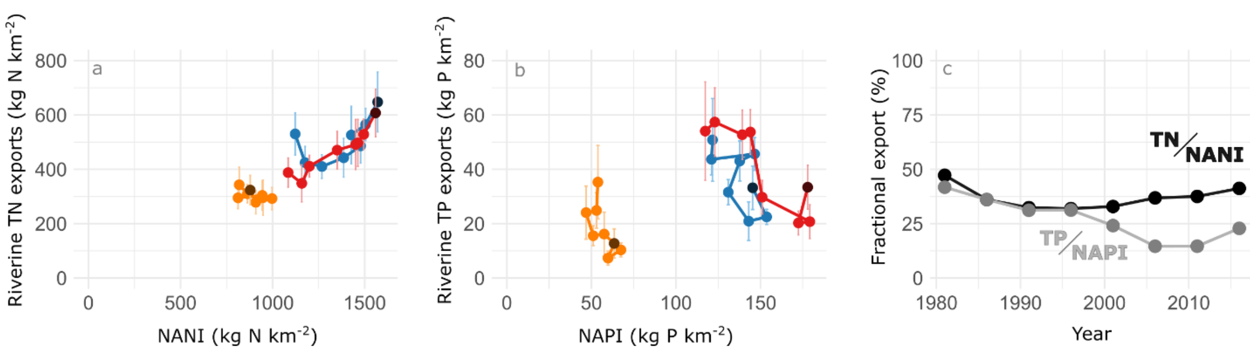

Figure 4 Riverine exports of TN (a) and TP (b) versus NANI and NAPI. Yellow, red and blue colours represent sites at RKm 101, 58, and 4, respectively. The eight census years appear linked in chronological order, the darker circles representing the last census year, 2016. Riverine exports represent a 5 year mean around the focal census year, with vertical bars as the standard deviation. Panel c shows the fraction (%) of NANI and NAPI observed in TN and TP riverine exports, respectively (kg N or P km^{-2}), across years for the most downstream site.

Historical stoichiometry

To characterise how riverine ecosystem stoichiometry varied through time at sites receiving differential anthropogenic inputs, we plotted molar C: N vs C: P ratios (Figure 5a; exact values in Supplementary Table 3). C: P was much more variable in the upstream site (mean = 587: 1, sd = 334, cv = 57), while C: N was more constrained (mean = 11.6, sd = 1.7, cv = 14.9). For the two downstream sites, ratios were typically more constrained, but shifted from a more variable C: N in the first two decades (cv = 22 vs 15 in the last two decades) to a more variable C: P in the last two (cv = 33 vs 22 in the first two). To consider the variability and specific trends in those ratios, we plotted C: P (panel b), N: P (panel c), and C: N (panel d) molar ratios of exports at all three sites across years. C: P and N: P in the most upstream site varied most (587 ± 334, 50 ± 27, respectively), while trends in the two more impacted sites followed an inverse V-shape in response to human interventions. Considering what the river ultimately exports to downstream ecosystems, C: N at RKm 4 had the least variation of all ratios (7.2 ± 1.4) and ranged from 10.6 (in 1991) to 4.7 (in 2013), supporting N-enrichment over time. C: P varied more (251 ± 112), ranging from a low of 109 (in 1979) to a high of 554 (in 2008), largely as a function of decreasing P, whereas N: P (36 ± 17) ranged from 17 (in 1992) to 87 (in 2007) both as a function of decreased P and increased N. From 1980 to 2020, C: N: P exports shifted from 130: 23: 1 to 217: 44: 1, with a C and N peak in 2007-2008 of 554: 87: 1. The decline in N: P and C: P ratios after 2008 appears to largely be driven by an increase in P entering the river over the last 15 years (Figure 2c), that was not fully explained by changes in NAPI.

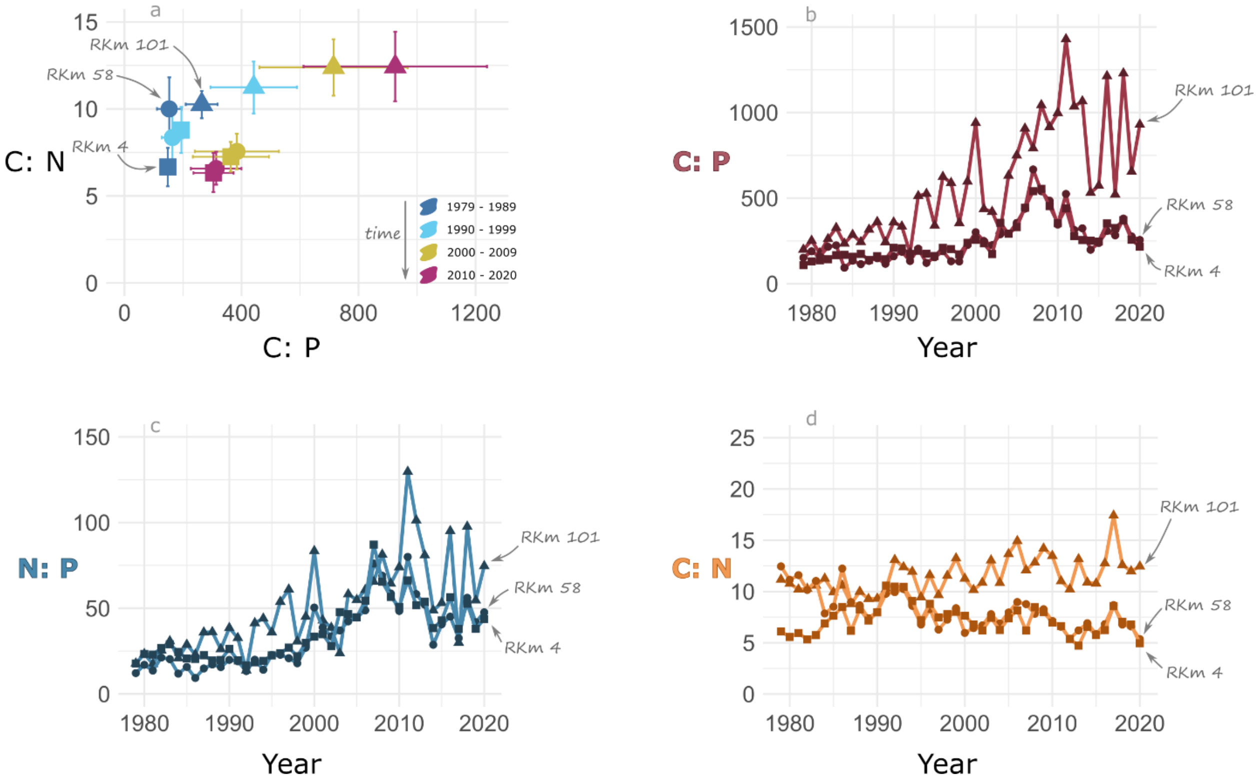

Figure 5 Panel a shows molar C: N vs C: P ratios for all three sites, where RKm 101 is represented by triangles, RKm 58 by squares, and RKm 4 by circles. The ratios are averaged by decade with standard deviations. Panels b, c, and d show molar C: P, N: P, and C: N ratios for riverine exports across years at all sites.

Discussion

<u>Mechanisms underlying trends in riverine C, N, and P</u>

The inputs of the three major elements that influence the base of food webs and ecosystem functioning are being altered across rivers globally (Carpenter et al., 1998; Hong et al., 2017; Xenopoulos et al., 2021), subsequently influencing ecosystem level stoichiometry which is rarely considered. Here we show the differential response of riverine C, N, and P exports to changes in the catchment and precipitation across space over four decades. Urbanisation over the last four decades was the most remarkable anthropogenic change in nutrient inputs to land in this large north temperate river. However, these increased inputs did not necessarily result in higher phosphorus exports over time because of human interventions on the landscape. We found no obvious impact of land use change on C exports with precipitation being the main driver, whereas N was influenced by both. The combined consequences of these differential drivers in the catchment related to exports resulted in changes in riverine ecosystem stoichiometry over time with impacts on functional properties.

The lack of correlation between riverine P exports with precipitation (Figure 2f) and the unexpected negative relationship with NAPI (Figure 4b) supports successful intervention strategies. The most striking was the precipitous drop at RKm 58, by half, from 2000 (76 533 ± 16 445 kg yr-1) to 2010 (32 795 ± 7 390 kg yr-1), following the construction of government-subsidised wastewater treatment plants (WWTPs) designed to retain P in the 1990s (MELCCFP, 2022a). The largest WWTP alone (constructed in 1998 ~10 km upstream from RKm 58; at *Saint-Jérôme* on Supplementary Figure S3 map) could account for up to 24 276 ± 5 230 kg of annual phosphorus removal or 72% of the total reaching its intake (2017 – 2020 average). This management intervention, not considered in NAPI, resulted in a major P retention control point that influenced overall riverine exports. However, riverine P exports have increased in the last 10 years despite the fact that ~70% continues to be removed from wastewater. This increase may be due to a higher sewage throughput because of a continuously growing population reflected in the slight uptick in NAPI in the last years (Figure 4b) or alternatively by a 1.5-fold increase in runoff ratio from 1980 – 2000 to 2010 – 2020 (Supplementary Figure S4c) as a function of urban expansion. Impervious surfaces are known to increase delivery of P to surface waters (Hobbie et al., 2017; Müller et al., 2020), and stormwater runoff often leads to higher P concentrations (Yang & Toor, 2018). Although there is no clear linear trend between TP exports and runoff (Supplementary Figure S4f), we suggest changes in delivery pathways through urbanisation, as well as higher throughput in wastewater, have contributed to the recent increases observed in riverine TP.

N was the only element that seemed to be influenced by both precipitation and anthropogenic inputs. This is not surprising because hydrology is a strong driver of N losses in more forested catchments (Inamdar et al., 2015; Mitchell et al., 1996), and NANI has been extensively used to successfully predict N in rivers (Chen et al., 2016; Goyette et al., 2016; Han et al., 2009; Swaney et al., 2012). Nevertheless, the scale at which we quantified NANI revealed that increased urbanisation was the most probable factor contributing to N exports in the two downstream sites in this river, reflecting wastewater inputs minimally treated for N through holding ponds directly discharged into the mainstem. As the fraction of NANI estimated in the mainstem has been relatively stable over 40 years (Figure 4c), riverine N exports in this specific system could be abated through N removal in wastewater treatment (Rahimi et al., 2020) or a reduction in NANI through large-scale dietary shifts away from meat (Almaraz et al., 2022).

Among the three elements in this study, C was the most strongly influenced by changes in climate drivers, with more than half of the inter-decadal variation in riverine exports being explained by total annual precipitation (Figure 2). The strong relationship between precipitation and area-specific exports suggests that DOC is transport-limited in this watershed, a relatively widespread phenomenon across rivers in the United States (Zarnetske et al., 2018) and northern Europe (Winterdahl et al., 2014). Although we could not fully resolve the temporal increase in DOC with historical precipitation changes (Supplementary Figure S4a), the increase in relative runoff could be contributing to this observed trend. Regardless, our results show how interannual variation in precipitation strongly impacted DOC exports, even more so than other elements, whereas nutrients were more strongly influenced by anthropogenic drivers. This led to clear inter-decadal trends in riverine stoichiometry.

Implications of varying riverine ecosystem stoichiometry

Changes in ecosystem stoichiometry were depicted through the modifications in inputs, retention, and delivery for C, N, and P across the watershed over four decades. Trends in the last three decades of C: N to C: P (Figure 5a) follow the same decreasing trajectory from upstream to downstream as in Shousha et al. (2021), where nutrients increased relative to C as a function of land use change. However, the upstream to downstream shift in C: P has become more remarkable over time, because ratios at the most upstream site increased almost 4-fold due to a concomitant increase in C and decrease in P (triangles in Figure 5a; absolute exports in Figure 2a, c). At this site, there is a surprising 5.8-fold decrease in P, whereas the C increase is considerably more modest (1.2-fold) and driven by changes in precipitation. Indeed, the variability in the C: P and N: P ratios in the forested section is a function of interannual variation in hydrology influencing C and N riverine exports, whereas P is on a steady decline. Several possible reasons could explain the decrease in riverine P at this pristine forested site. One could be the legislation of septic tanks to prevent P leakage across the region (MELCCFP, 2022c; MTESS, 2021). A second possibility is the increased construction of dams, largely for recreational purposes, throughout the watershed over the last decades (MELCCFP, 2023), as increasing lentification is known to retain more P at the watershed scale (Kirchner & Dillon, 1975; Maavara et al., 2015; Soranno et al., 2015). Another potential more regional explanation is the decrease in apatite weathering with acid rain reversal, where TP in streams has been shown to decrease over recent decades in a watershed located in the same geological province (Baker et al., 2015). Although we cannot resolve the exact mechanism behind this trend, our results show how a combination of change in precipitation, human interventions, and potentially atmospheric pollution has induced profound changes in riverine stoichiometry even in the most pristine area of the river. As increases in C: nutrient ratios can favour microbial sequestration of N and P locally or downstream of C-rich inputs (Stutter et al., 2018), the shift towards higher C: P (and C: N to a certain extent) at RKm 101 may increasingly fuel downstream metabolism.

Moving downstream, land use changes impacted the delivery of nutrients to the river, differentially influencing the stoichiometry at RKms 58 and 4. C ratios shifted from those with higher P and lower N in the first two decades to lower P and higher N at these sites in the last two decades. Although we do not have information on historical shifts in C type, composition was shown to change abruptly between the more forested upstream pristine reach as compared to the downstream more impacted one (Shousha et al., 2022). This suggests that there must be a high turnover of terrestrial C likely driven by the land use driven changes in nutrient inputs (Rosemond et al., 2015) that likely also occurred through time. It was interesting to note that the C: P in the upstream site was similar to those downstream in the 1980s. This original C: P upstream was more a result of much higher P than lower C, but this observation was not expressed in the estimated NAPI (Figure 4b). This suggests some other P input such as those potentially related to the forestry industry (Faubert et al., 2016) pervasive in the region at that time (Abrinord, 2022), which was not accounted for. The shift in C: P in downstream sites over time was a direct influence of WWTP P removal. Interestingly, however, the C: N ratio at the downstream site varied little over the four decades, and hovered around Redfield. This constrained C: N downstream could in part be shaping the N: P and C: P imbalances over time (Elser et al., 2022), and act as some sort of emerging ecosystem property, where both C and N can be permanently removed from the system hence converging toward this value metabolically (Maranger et al., 2018). Yet how P influences stoichiometry may more be a function of historical changes in inputs, and geomorphometric settling (Maavara et al., 2015; Soranno et al., 2015).

Absolute nutrient concentrations, however, and their ratios would ultimately shape C type and the fate of terrestrial sources (Rosemond et al., 2015; Shousha et al., 2022).

Management implications for nutrient inputs

Adopting the mass balances at the spatial resolution used here (i.e. the municipality) allowed us to identify areas in the watershed where nutrient inputs were highest and have changed the most over time. Our approach is easily adaptable to rivers globally to identify meaningful places to intervene in the watershed and abate nutrient loadings. This was particularly the case for N exports in this watershed, where urban expansion and the resulting increase in wastewater non-treated for N, entering as a point source, appears to be the most significant portion of NANI entering the river. A likely impact of not reducing N and maintaining high N: P ratios is that when nutrient concentrations are high, toxic cyanobacteria and other harmful algal blooms are favoured (Glibert et al., 2014; Scott et al., 2013), that can result in local issues as well as downstream consequences resulting in coastal degradation (Howarth, 2008; Paerl et al., 2004). As such, where possible, a dual nutrient removal strategy should be supported in systems where WWTPs are the main sources of N inputs (Conley et al., 2009; Paerl et al., 2004). We should note however that due to historical data limitation, the river sections where we were able to evaluate elemental export were mainly pristine or affected by urbanisation, with limited agricultural activity. Abatement choices would be different if we captured the input of the largely agricultural sub-watershed entering downstream of our most downstream site (Figure 1). There, reduction in fertiliser use and landscape level restoration efforts including the targeted wetland restoration (Cheng et al., 2020) and implementing winter cover crops (Hanrahan et al., 2018; Speir et al., 2022) may be the most effective practice. We suggest the broad applicability of our approach, and the relative accessibility of census data around human populations and agricultural practices in many watersheds of the world, could provide the needed guidance to help mitigate the excessive nutrient loadings to many rivers at scales relevant to management.

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Author contributions

SS, RM, and JFL designed the study. SS created the results and wrote the initial draft. SS, JFL, and RM edited subsequent ones.

Open Research

The data used for the figures in the study are available on Zenodo via the DOI 10.5281/zenodo.7806130 with the Creative Commons Attribution 4.0 International license (Shousha et al., 2023).

Global Biogeochemical Cycles

Supporting Information

Decadal Changes in Anthropogenic Inputs and Precipitation Influence Riverine Exports of Carbon, Nitrogen, and Phosphorus, and Alter Ecosystem Level Stoichiometry

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The coefficients used to calculate the Net Anthropogenic Nitrogen and Phosphorus Input (NANI/NAPI) mass balances are listed in Supplementary Table 1 along with their sources.

Supplementary Table 1: List of sources for data and coefficients used to calculate all categories in the NANI and NAPI mass balances at the municipal level in Québec, Canada.

Mass balance sub-category	Source	Details
AGRICULTURAL CENSUS		
	Statistics Canada, 1982a, 1987a, 1992a, 1997a, 2002a, 2007a, 2012a, 2017a	
POPULATION CENSUS		
	Statistics Canada, 1982b, 1987b, 1992b, 1997b, 2002b, 2007b, 2012b, 2017b	
FERTILISER		
	Statistics Canada, 2022d	Metric tonnes of N, P fertiliser at QC level (x1000).
	Statistics Canada, 2013	For 2006 and prior
	Russell et al., 2008	To transform P_2O_5 into P
LIVESTOCK SLAUGHTER		
Number slaughtered cattle, calves	Statistics Canada, 2022b	Number of cattle, calves slaughtered at the national level (Canada)
Number slaughtered hogs, sheep & lamb	Statistics Canada, 2022e	Number of hogs, sheep & lamb slaughtered at the national level (Canada)
Number slaughtered chicken, turkey	Government of Canada, 2021b	Number of chicken, turkeys slaughtered at national level (Canada)
Number slaughtered livestock at provincial level	Census of agriculture > Livestock	Total heads cattle, calves, hogs, sheep, lamb, chicken, turkey at national level (Canada)

	Census of agriculture > Livestock	Total heads cattle, calves, hogs, sheep, lamb, chicken, turkey at provincial level (QC)
LIVESTOCK LIVE WEIGHT		
Weight cold carcass cattle, calves	Statistics Canada, 2022b	Average weight, cold carcass
Weight cold carcass hog, sheep & lamb	Statistics Canada, 2022e	Average weight, cold carcass
Conversion factor carcass to live	Government of Canada, 2022	Conversion factor from live weight to cold carcass
Weight live chicken, turkey	Statistics Canada, 2021b	Total kg for chickens, hens + number of heads
Weight live egg	Statistics Canada, 2021a	Egg number per head of layer
Weight live milk	FAO, 2021	Kg of milk produced per cow
EDIBLE PORTION		
Edible portion of animals as % of live weight	Han et al., 2009	What we can eat of the animal
NP CONTENT		
N content	Han et al., 2009	What % of the edible portion is N
	personal communication with J.-O. Goyette	N % for pork, chicken, broiler (all = 3.648)
P content	Goyette et al., 2016	What % of the edible portion is P
ANIMAL INTAKE		
Consumtion rates N	Han & Allan, 2008	Consumption rates of N for livestock under dynamic model
Consumtion rates P	Han et al., 2011	Consumption rates of P for livestock under dynamic model
Life cycle (days alive per year)	Han et al., 2009	Duration of livestock life on farm (usually less than 1 year)
	Kellogg et al., 2000	" "
	Goyette et al., 2016	" "
Equations to calculate dynamic life cycle	Goyette et al., 2016 Kellogg et al., 2000 Han et al., 2009	
CROP YIELD		
Provincial yield for certain crops	Statistics Canada, 2022c	Crop yields at provincial level (not found at smaller scale)
Provincial yield for potatoes	Statistics Canada, 2022a	Crop yield at provincial level for potatoes
	https://www.potatopro.com/quebec/potato-statistics	PotatoPro
Administrative region crop yield	Institut de la statistique du Québec, 2020	Crop yield at the administrative level for big cultures For the provincial yield, if had no data for region, used average of all instead. Used the provincial average for the following crops to build in missing regional data: For Fodder corn: Saguenay, Abitibi, Côte-Nord, Nord-du-Québec For Grain corn : Bas-Saint-Laurent, Abitibi,Nord-du-Québec,Gaspésie For Barley: Estrie, Outaouais, Laurentides For Soya : Bas-Saint-Laurent, Gaspésie,Abitibi,Nord-du-Québec For Oats : Montréal, Laval,Lanaudière,Montérégie

Understanding agricultural regions in QC	Statistics Canada, 2021c	For mixed grains : Capitale-Nationale, Mauricie, Montréal, Laval, Lanaudière, Outouais, Laurentides, Abitibi, Nord-du-Québec, Montérégie Codes for each region (not to mix up with administrative codes, which are slightly different)
CROP CONTENT		
Kilograms harvested per yield unit (nitrogen)	USDA, 2017	USDA Natural Resources Conservation Service, Technical Resources
Percent Dry Matter, Percent N in Dry Matter (nitrogen)	USDA, 2017	USDA Natural Resources Conservation Service, Technical Resources
Percent N in Dry Matter for Corn grain : updated (nitrogen)	David et al., 2010	% protein in modern corn hybrids is decreasing continuously (from 10 to 8.5% from 1985 to 2006). Assumed 1.36% N for 2006 (assumption: use 2006 data for today too). Toolbox assumes 9.5% protein = 1.5% N (average between 1985 - 2006).
N content for cropland and non cropland pastures (nitrogen)	Hong & Swaney, 2010; Table 5.1.1.1	
P content in crops	MacDonald & Bennett, 2009	P content in crop types (kg / kg of crop)
P content for cropland and non cropland pastures	Schaefer & Alber, 2007	P content for pastures
DISTRIBUTION		
% distributed to humans and animals	Boyer et al., 2002	Partition crop yields to humans and animals
	Jordan & Weller, 1996	
% of crop lost during harvest	Boyer et al., 2002	Losses of crops during harvest
		Missing rice and buckwheat for distribution and loss: For buckwheat, in Yieldbased BNF, buckwheat column notes are in red (10% loss and 90% to humans)
	Swaney et al., 2018; Toolbox v3	Pasture loss : take half leave half
BIOLOGICAL NITROGEN FIXATION		
Yield based for soybean, alfalfa, non-alfalfa	Han & Allan, 2008	Table 4 : proportion of plant N from fixation
Nonalfalfa have 25% leguminous plants	USDA, 2007	Alfalfa fixes nitrogen. Legumes (in non-alfalfa plants) are the ones that fix nitrogen in the non-alfalfa pastures. So, include the legumes from nonalfalfa that fix nitrogen in calculation.
Cropland, area-based	Jordan & Weller, 1996	Named non-wooded pastures, east of Mississippi, eastern pastures
Snap beans, area-based	Boyer et al., 2002,	
Peanuts, area-based	Jordan & Weller, 1996	They have 86 kg N / ha / yr
	Schaefer & Alber, 2007	They have 8000 kg N / km^2 / yr
PROTEIN CONSUMPTION		
Amount of protein consumed per capita, recent average	Hong & Swaney, 2010; Toolbox 3.1	6.21 kg / person / yr is data in toolbox. It's an average, and does not say from what years. Only says that data comes from US censuses.
N content in protein	Jones, 1941	N is 16% of protein
	Hong et al., 2012	Conversion factor used in NANI-PI
P content in protein	Hong et al., 2012	P consumption is equivalent to 20% N consumption

	Russell et al., 2008	Authors do not clearly state in article that N:P is 5, so ref is here because (Hong et al., 2012) based themselves off (Russell et al., 2008) to calculate N:P of 5
DETERGENT		
For laundry detergent :		
Laundry detergent (kg / capita / yr)	Han et al., 2012	Laundry detergent use (USA proxy because unavailable for Canada)
% of P by weight	Litke, 1999	Detergent industry limits phosphate in detergents to 8.7% by weight as phosphorus in 1970 and to 2.2% in 1972 in Canada (for laundry)
	Government of Canada, 2019	Limit goes down to 0.5% in 2009 + when click to see previous versions, find the 2.2% limit website last up to date 2019, so use values there for most recent year
For dishwasher detergent :		
Detergent use (Spoons / capita / yr)	Han et al., 2012	dishwasher detergent use
	Goyette et al., 2016	dishwasher detergent use
P content (kg P / spoons)	Han et al., 2012	Article has kg P per spoon (0.0009687). Assume this is when limit is at 8.7% P content because in same time range of regulations (Litke, 1999)
	Government of Canada, 2019	Limit goes down to 0.5% in 2009
		Rule of 3 : if 0.0009687 is for 8.7, what is kg-P for 0.5% (limit of 2.2% in the 1970s only for laundry)
Proportion of households with automatic washers	Goyette et al., 2016	Proportion of households with dishwasher
	Statistics Canada, 2017c	We are looking for dishwasher information.
		Calculate trendline for 1997-2009 and get proportion for 2011, 2016 (for Canada)
P dishwashing detergent cosumption (kg P / capita / yr)	Equation	= dishwashing detergent use * P content * Proportion of households
ATMOSPHERIC DEPOSITION		
N deposition	www.cmaq-model.org/	Community Multiscale Air Quality model for 2008 (usually kg-N / km^2)
		Used NH_y and NO_x deposition because of small surface areas of municipalities and discrete land use (Boyer et al., 2002; Dentener & Crutzen, 1994)
N emissions, historical	Government of Canada, 2018	Air Pollutant and Black Carbon Emissions Inventories online search (1990 – 2020).
	Asadoorian et al., 2006	Emission trends (Tg) 1890 – 1995.

Supplementary Table 2 summarises the loadflex model outputs for each RKm and variable modelled.

Supplementary Table 2: Example of loadflex model fit for the three sites along the *Rivière du Nord* mainstem, RKms 4, 58, 101. The best models were chosen for their lowest RRMSE and ARIL. They are in bold and are the ones that were used to interpolate concentration predictions for the years of interest, 1980-2020.

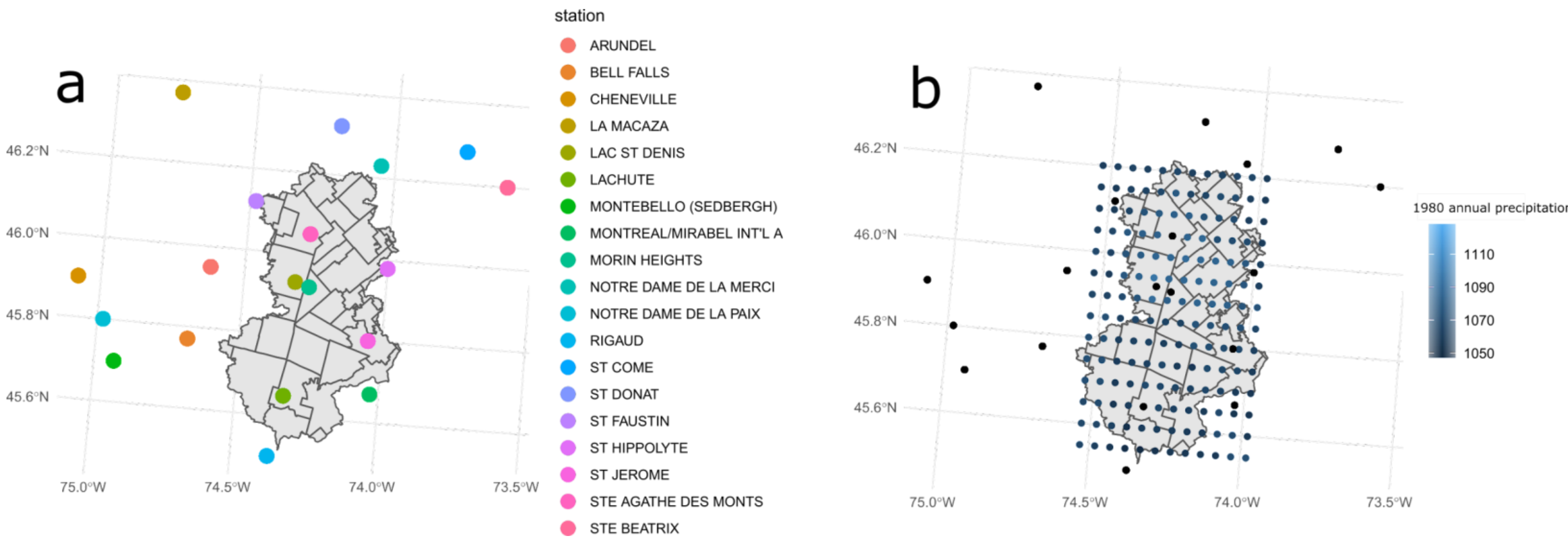
RKm	Variable	Years spanned by data	Model	RRMSE	ARIL
4	TN	1985-2020	interpolation	0	1.1492
			linear model	0.3943	1.3169
			loadReg	0.3389	1.1090
			composite	**0.0006**	**1.1051**
	TP	1979-2020	interpolation	0	2.8505
			linear model	0.9759	3.0094
			loadReg	0.6406	2.1455
			composite	**0.0002**	**1.8968**
	DOC	1984-1990, 1993-2020	**interpolation***	**0**	**0.7636**
			linear model	2.3623	1.2422
			loadReg	2.1029	1.0697
			composite	0.0002	1.1518
58	TN	1985-1986, 1988-2020	interpolation	0	1.2653
			linear model	0.3298	1.1935
			loadReg	0.2736	0.9943
			composite	**0.0009**	**1.0342**
	TP	1979-1986, 1988-2020	interpolation	0	3.2604
			linear model	1.2368	3.7891
			loadReg	0.8605	2.4154
			composite	**0.0007**	**1.8788**
	DOC	1984-1986, 1988-1990, 1993-2020	**interpolation**	**0**	**0.70633**
			linear model	0.2179	0.7174
			loadReg	0.1931	0.6003
			composite	0.0001	0.7288
101	TN	1985-1986, 1988-2020	interpolation	0	1.2745
			linear model	0.2708	1.1115
			loadReg	0.2176	0.8988
			composite	**0.0003**	**0.9723**
	TP	1979-1986, 1988-2020	interpolation	0	6.0454
			linear model	1.9940	5.5106
			loadReg	0.9638	2.8503
			composite	**0.0002**	**2.4020**
	DOC	1984-1986, 1988-1990, 1993-2020	interpolation	0	0.6890
			linear model	0.1957	0.7490
			loadReg	0.1379	0.5257
			composite	**0.0003**	**0.5913**

RRMSE : relative root mean square error, ARIL : average of the relative 95% prediction interval lengths (Appling et al., 2015). Variable acronyms refer to total nitrogen (TN), total phosphorus (TP), and dissolved organic carbon (DOC).

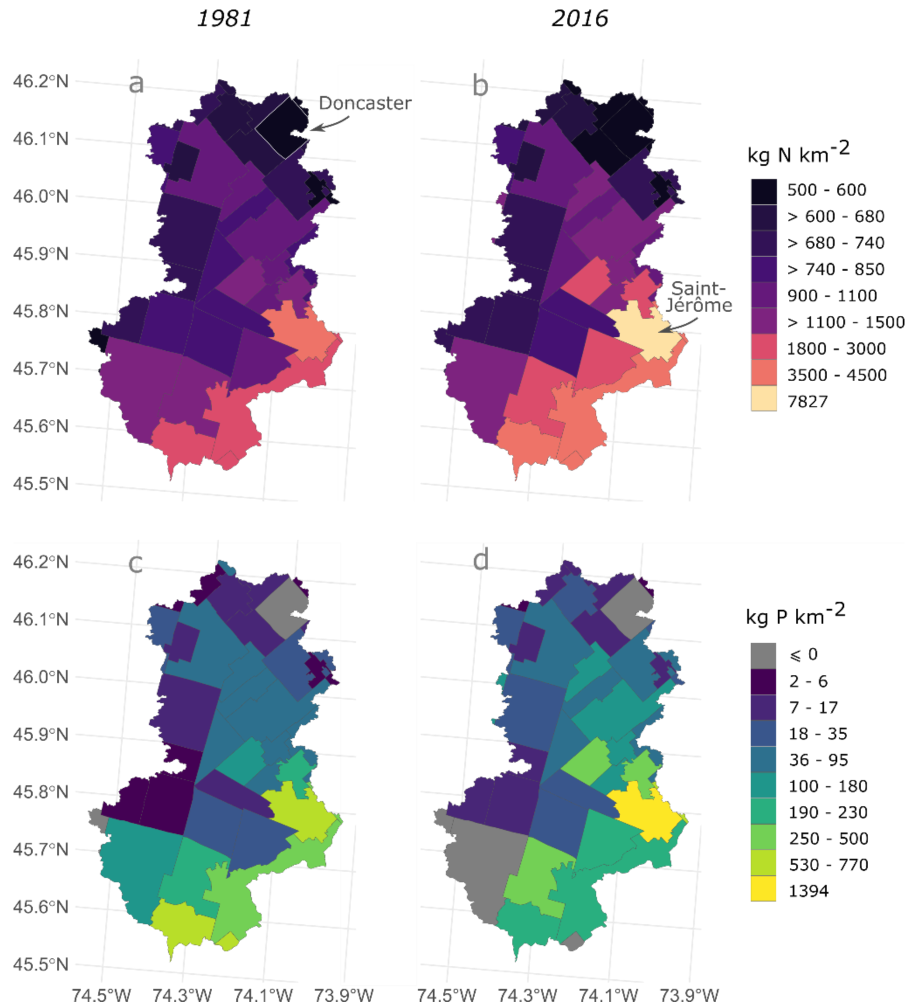
Supplementary Table 3 reports the values for C: N, C: P, and N: P (Figure 5a).

Supplementary Table 3: Decadal averages (± standard deviations) for C: N, C: P, and N: P molar ratios at the three sites along *Rivière du Nord*.

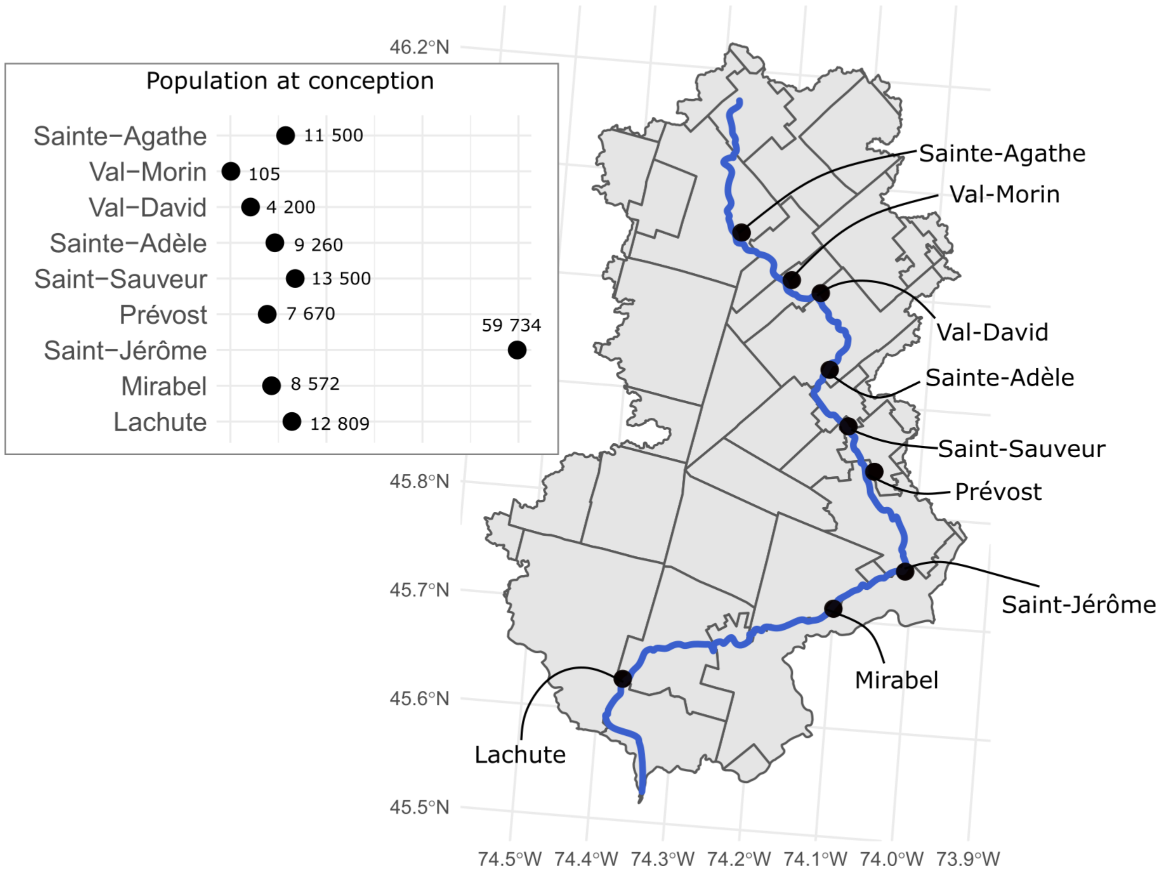
C: N	1979 – 1989	1990 – 1999	2000 – 2009	2010 – 2020
RKm 101	10 ± 0.8	11 ± 1.5	12 ± 1.6	12 ± 2.0
RKm 58	10 ± 1.8	8 ± 1.3	8 ± 1.0	7 ± 0.9
RKm 4	7 ± 1.1	9 ± 1.3	7 ± 0.8	6 ± 1.1
C: P	1979 – 1989	1990 – 1999	2000 – 2009	2010 – 2020
RKm 101	264 ± 55	442 ± 148	715 ± 253	926 ± 313
RKm 58	153 ± 42	164 ± 36	384 ± 144	313 ± 86
RKm 4	148 ± 20	194 ± 24	364 ± 130	304 ± 69
N: P	1979 – 1989	1990 – 1999	2000 – 2009	2010 – 2020
RKm 101	26 ± 6	40 ± 13	57 ± 18	76 ± 29
RKm 58	15 ± 4	20 ± 4	50 ± 14	48 ± 14
RKm 4	22 ± 3	23 ± 4	50 ± 17	48 ± 9



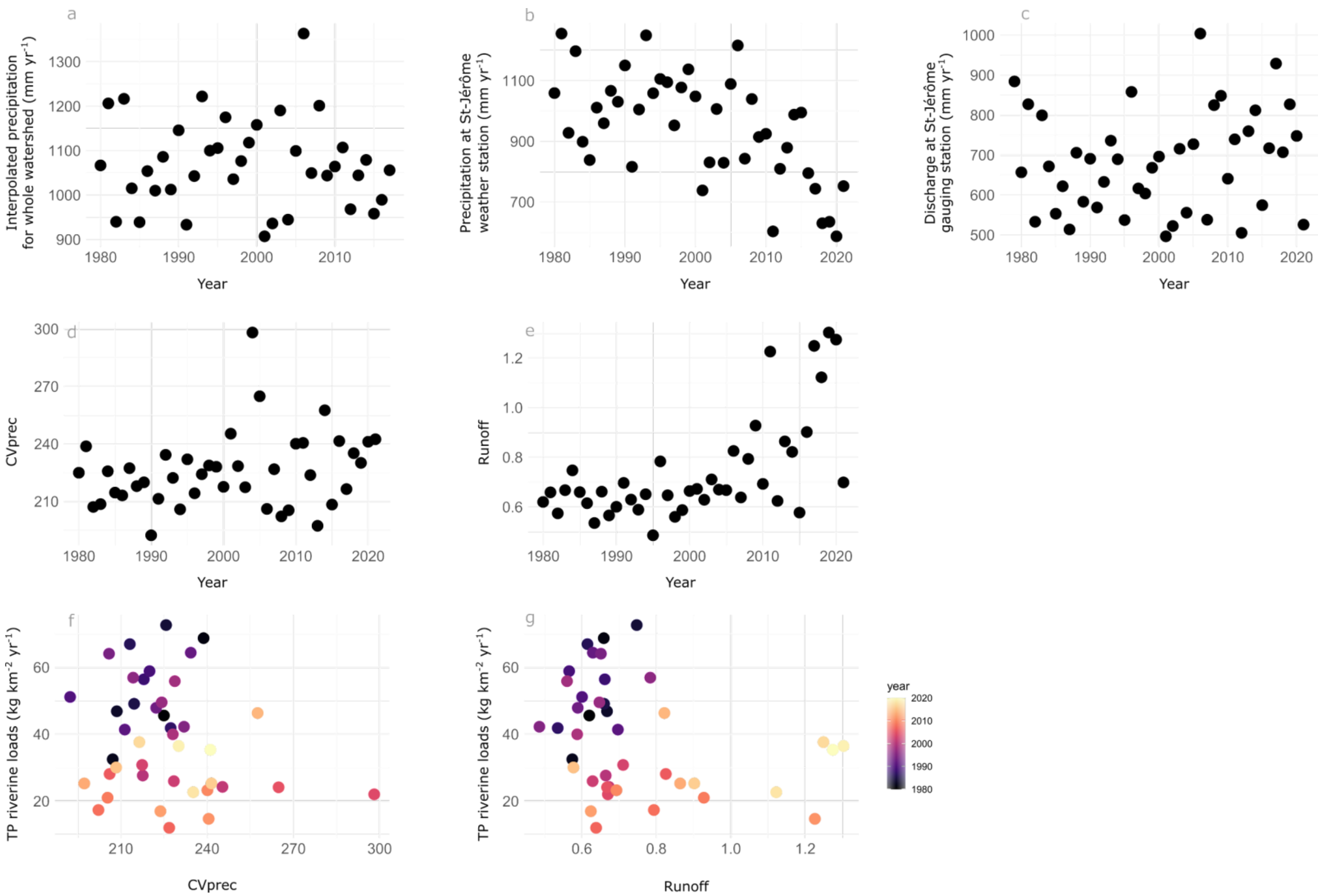
Supplementary Figure S1a) Location of 19 stations where historical precipitation data is recorded, compared to the *Rivière du Nord* watershed and **b)** Inverse Distance Weighting interpolation for 1980. The geospatial interpolation is shown with a resolution of 0.05 degrees for visual representation purposes, but the actual data were interpolated using a 0.01 degree resolution.



Supplementary Figure S2 Four *Rivière du Nord* maps showing historical changes in Net Anthropogenic Nitrogen Inputs (NANI; top) and Net Anthropogenic Phosphorus Inputs (NAPI; bottom). Panels a) and b) show the NANI for 1981 and 2016, respectively. Panels c) and d) are the equivalent of a) and b) but for NAPI, where municipalities in grey represent a net export of P (negative values).



Supplementary Figure S3 Location of wastewater treatment plants in the *Rivière du Nord* watershed with their associated population in the year of conception.



Supplementary Figure S4 Panels a) and b) show precipitation (rain and snow) for each year at the watershed level (interpolated) and at the specific *Saint-Jérôme* weather station. Panel c) shows discharge at the *Saint-Jérôme* gauging station. We use CVprec as a proxy for flashiness, with the intent that if a year had a larger coefficient of variation (CV) for its total precipitation, that year had flashier precipitation. Panel e) shows that runoff (annual discharge over annual precipitation) has increased in the last 10 years. Panels f) and g) show no clear relationship between TP riverine loads (at RKm 58, the closest to *Saint-Jérôme*) and flashiness or runoff.

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