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Influence des flux anthropiques de nutriments et des caractéristiques du territoire sur la qualité de l'eau: une perspective historique du bassin du Saint-Laurent

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Résumé

L'azote (N) et le phosphore (P) sont au coeur des défis visant à concilier production alimentaire et qualité d'eau. Si N et P sont essentiels à la production agricole, l'enrichissement des écosystèmes aquatiques par ces éléments nutritifs peut occasionner une perte d'oxygène dans le milieu, une perturbation des réseaux trophiques, la prolifération d'algues nuisibles toxiques et une perte de biodiversité. Ce processus d'eutrophisation entraîne donc d'importantes conséquences sur la santé humaine et les économies locales. L'objectif de cette thèse est d'améliorer notre compréhension des facteurs anthropiques et naturels régissant les flux de N et P à l'échelle des bassins hydrographiques, et ce en voie d'une meilleure gestion des nutriments au nexus eau-alimentation.

D'abord, nous nous penchons sur l'impact des activités humaines sur les flux de N et P dans 76 bassins versants du Saint-Laurent, et ce dans une perspective historique couvrant le dernier siècle. Nous montrons que depuis 1901 les surplus de N et P au bassin du Saint-Laurent (BSL) ont augmenté respectivement de 4,5 fois et 3,8 fois, avec un pic en 1991 principalement dû aux dépôts de N atmosphérique et à l'application d'engrais phosphatés. Ces apports nets anthropiques au territoire sont fortement liés aux charges fluviales où ~22% des surplus de N et ~17% des surplus de P sont exportés par les rivières. En suivant les principales sources d'intrants au territoire à travers le temps, cette étude souligne que les stratégies devront être spécifiques à chaque région, bien qu'elle montre aussi clairement l'impact positif de législations à grande échelle (Goyette et al. 2016).

Si nous savons que les apports anthropiques de N et P au territoire favorisent l'export fluvial, notre compréhension d'autres facteurs contrôlant ces transferts demeure limitée. Aussi, au-delà des apports absolus au milieu aquatique, les concentrations relatives de N et P influencent la qualité de l'eau. Nous montrons que les précipitations et la capacité de rétention d'eau du territoire agissent comme principales forces de contrôle et de découplage des flux de N et P et que les lacs et réservoirs jouent un rôle second, mais significatif. Nous observons un effet de legs historique, et ce particulièrement lors de précipitations extrêmes, et concluons que face aux changements climatiques, l'augmentation de capacité de rétention d'eau des territoires sera essentielle à l'atténuation de l'eutrophisation (Goyette et al. in review a).

L'effet de legs en P est une problématique majeure de l'eutrophisation. Cependant, les décalages temporels des flux de P encourus par cet effet demeurent incertains. Aussi, l'existence d'un seuil d'accumulation au-delà duquel un bassin dépasse sa capacité optimale de rétention de P est inconnue. Nous nous penchons donc sur la capacité tampon en P des bassins versants, tant durant la phase d'accumulation que celle d'épuisement des stocks accumulés. Nous montrons que le seuil d'accumulation pour une rétention optimale de P par les bassins versants est particulièrement bas et qu'il peut être atteint en moins de 10 ans aux taux actuels d'intrants dans les régions fortement agricoles. À l'inverse, le retour aux conditions initiales pourrait prendre plusieurs siècles. L'étude présente pour la première fois un seuil de saturation en P à l'échelle du bassin versant et met en lumière la nécessité d'exploiter les stocks de P accumulés dans les sols (et sédiments) afin de concilier production alimentaire et qualité d'eau (Goyette et al. in review b).

Parmi différentes mesures d'atténuation de pollution par les nutriments, l'augmentation d'efficience d'utilisation de N et P dans le secteur agricole apparaît comme une stratégie clé. Nous dressons donc un portrait des tendances temporelles d'efficience d'utilisation de N et P dans la filière agroalimentaire du BSL au cours du dernier siècle. Nous montrons que l'agriculture de cette région était non durable entre 1901 et 1960 épuisant graduellement les sols de leurs nutriments, et que par l'utilisation de fertilisants, le système a rapidement basculé vers un système inefficient où ~70% et ~90% des apports en N et P respectivement sont aujourd'hui perdus vers l'environnement. Nous observons que la simple augmentation d'efficience au sein du système agroalimentaire n'est pas garante d'une diminution des pertes en nutriments vers l'environnement et concluons donc, qu'en parallèle aux gains d'efficience, un seuil maximal de pertes vers l'environnement doit être quantifié et imposé, afin de respecter la capacité de support des écosystèmes (Goyette et al. in prep).

En quantifiant l'effet différentiel des activités humaines, du climat et de certaines caractéristiques du territoire sur les flux de N et P, cette thèse dégage de l'information pertinente à une meilleure gestion de ces nutriments au sein des systèmes socio-écologiques.
Mots-clés : azote, phosphore, eutrophisation, anthropique, charges fluviales, qualité d'eau, territoire, lacs, barrages, climat, bassin du Saint-Laurent, historique.

Abstract

Nitrogen (N) and phosphorus (P) are at the heart of the challenges of reconciling food production and water quality. If N and P are essential nutrients for agricultural production, nutrient enrichment of aquatic ecosystems can lead to loss of oxygen in the water, disruption of food webs, proliferation of toxic algae, and loss of biodiversity. This eutrophication process therefore has important consequences for human health and local economies. The aim of this thesis is to improve our understanding of anthropogenic and natural factors governing N and P fluxes at the watershed scale, in order to foster a better nutrient management at the Food-Water Nexus.

First, we examine the impacts of human activities on N and P fluxes in 76 watersheds of the St. Lawrence, from a historical perspective covering important social transitions of the last century. We show that since 1901, the N and P surpluses in the St. Lawrence basin have increased by 4.5 and 3.8 times respectively, with a peak in 1991 mainly due to atmospheric N deposition and the application of phosphate fertilizer. These net anthropogenic inputs to the landscape are strongly related to riverine loads where ~ 22% of N and ~ 17% of P surpluses are exported by rivers. By tracking the main sources of inputs to the landscape over time, this study emphasizes that strategies will need to be region-specific, although it also clearly shows the positive impact of large-scale legislation (Goyette et al. 2016).

While the anthropogenic inputs of N and P to the landscape favor riverine exports, our understanding of other factors controlling the transfers remains limited. Also, beyond absolute nutrient loads to aquatic ecosystems, the relative concentrations of N and P influences water quality. We thus explore the role of different land and climate characteristics in controlling and decoupling N and P fluxes along the aquatic network. We show that precipitation and water retention capacity of the landscape act as the main controlling forces on these fluxes, and that lakes and reservoirs play a secondary but significant role. We also identify a legacy effect, especially during extreme precipitation events. We conclude that, in the face of climate change, increasing the water retention capacity of the landscape is essential to mitigating eutrophication (Goyette et al. in review a).

Legacy P is known as a major water quality issue, yet time lags incurred by this effect remain uncertain. Moreover, the existence of an accumulation threshold beyond which a basin exceeds its optimal P retention capacity is unknown. We show that the accumulation threshold for optimal P retention by watersheds is particularly low and can be achieved in less than 10 years at current input rates in highly agricultural regions. Conversely, a return to initial conditions in terms of water quality could take several centuries. Our study presents for the first time a threshold of P buffering capacity at the watershed scale and highlights the need to exploit residual P stocks in soils (and sediments) in order to reconcile food production and water quality (Goyette et al. in review b).

Among various measures to mitigate nutrient pollution, increasing nutrient use efficiency in the agricultural sector is emerging as a key strategy. We therefore draw a portrait of temporal trends in N and P use efficiency in the agro-food sector of the St. Lawrence basin during the last century. We show that agriculture in this region was unsustainable between 1901 and 1960, gradually depleting soils of nutrients, and that through the use of fertilizers, the system rapidly tipped to an inefficient system where ~70% of N and ~90% and P resources are lost to the environment. We observe that an increase in efficiency within the agro-food system does not guarantee a decline in nutrient pollution and thus conclude that, in parallel with gains in efficiency, there is an urgent need to identify and constrain human activities to the carrying capacity of ecosystems (Goyette et al. in prep).

By quantifying the different effects of N and P transport and retention by human activities and key climate and landscape features, this thesis provides relevant information to a better understanding of the dynamics of N and P within socio-ecological systems. **Keywords** : nitrogen, phosphorus, eutrophication, anthropogenic, riverine loads, water quality, land use, lakes, dams, climate, St. Lawrence basin, historical

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Annexe V

Liste des abréviations

(Les caractères en italiques indiquent les termes en anglais)

$CAN: dollar canadien

ADN: acide désoxyribonucléique

AICc: Akaike information criterion

BNF: biological N fixation

BQMA: Banque de qualité du milieu aquatique

BSL: bassin du Saint-Laurent

CEHQ: Centre d'expertise hydrique du Québec

CMAQ: *Community Multiscale Air Quality Modeling System*

CV: *coefficient of variation*

CWG: *clustered within groups*

DIN: *dissolved inorganic nitrogen*

Dv: *Development volume*

FAO: *Food and Agriculture Organization of the United Nations*

FNB: fixation d'azote biologique

FRQNT: Fond de Recherche du Québec Nature et Technologies

Gg: *Gigagrams*

GMO: *Genetically modified organisms*

GRAFS: *generalized representation of agro-food systems*

GRIL: Groupe de recherche en limnologie et environment aquatique

ha: *hectare*

HABs: *harmful algal blooms*

HANPP: *human appropriation of net primary production*

kg: *kilograms*

km: *kilometers*

LMMs: *linear mixed models*

Log: *logarithmic*

LU: *livestock units*

m: *meter*

max: *maximum*

MDDEFP: Ministèere du développement durable, de la faune et des parcs

MEA: *millenium ecosystem assessment*

min: *minimum*

mm: *millimeter*

N: *nitrogen*; azote

N_2: *atmospheric nitrogen*

N_2O: *nitrous oxide*

NANI: *Net Anthropogenic Nitrogen Inputs*

NAPI:*Net Anthropogenic Phosphorus Inputs*

NH_3: *ammonia*

NO: *nitrogen oxide*

NO_2: *nitrogen dioxide*

NSERC: *Natural Sciences and Engineering Research Council of Canada*

NUE: *nutrient use efficiency*

ON: *organic nitrogen*

P: *phosphorus*

ResZ: *reservoir mean depth*

SD: *standard deviation*

SLB: *St. Lawrence Basin*

Tg: *teragrams*

TN: *total nitrogen*

TP: *total phosphorus*

TSP: *total suspended phosphorus*

UK: *United Kingdom*

USA: *United States of America*

VIF: *variance inflation factor*

yr: *year*

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Introduction

L’azote et le phosphore, une question d’équilibre

L’azote (N) et le phosphore (P) sont des éléments d’intérêts pour les populations humaines depuis des milliers d’années (Ashley et al. 2011). L’apport en N et P aux champs stimule la croissance des plantes cultivées. En tant qu'importants constituants des protéines, des membranes cellulaires et de l’ADN, N et P sont indispensables à la vie sur Terre (Reece et al. 2014). Si les humains ont d’abord fait bon usage de ces éléments par diverses pratiques agricoles telles que l’agriculture sur brulis (Flannery 2002), le recyclage de déjections animales ou humaines (Ashley et al. 2011; Mårald 1998), et l’utilisation d’os broyés ou de guano (Cordell et al. 2009), la révolution industrielle aura permis de dégager un potentiel énergétique considérable afin d’accélérer l’extraction minière de roche phosphatée (Smil 2000b) et de synthétiser des engrais azotés par des méthodes à haute température et haute pression (Hager 2009). Ces avancées technologiques ont ainsi permis une forte augmentation de l’utilisation de ces nutriments en agriculture, et donc des rendements céréaliers. Bien que cette « révolution verte » ait permis de nourrir une population en constante croissance depuis le milieu du dernier siècle, elle a aussi induit une diminution dans l’efficience d’utilisation de ces deux éléments nutritifs au sein des systèmes agricoles et des sociétés en général (Bouwman et al. 2013; Lassaletta et al. 2014a), et ainsi participé à une hausse des pertes de N et P dans l’environnement.

Si N et P sont essentiels à la production agricole, ils présentent aussi un risque majeur pour la qualité des sols, de l’air et de l’eau lorsque présents en excès dans l'environnement (Carpenter et al. 1998; Vitousek et al. 1997a). La menace que N et P posent pour les écosystèmes aquatiques est particulièrement préoccupante. Lorsque lessivés par les pluies ou déversés directement aux eaux de surface à la sortie d’usines d'épuration, N et P sont assimilés par les plantes aquatiques et les algues, entraînant l'eutrophisation du système, un enrichissement en éléments nutritifs menant à une production excessive de biomasse végétale et une dégradation de la qualité de l'eau (Galloway et al. 2002; Schindler et al. 1971). L’enrichissement en matière organique qui s’ensuit peut mener à des conditions d'hypoxie ou d'anoxie (appauvrissement en oxygène) suite à la décomposition de restes végétaux par les microorganismes (Rabalais et al. 2010), pouvant ainsi induire la mortalité d’organismes aquatiques et l’effondrement de ressources halieutiques (Diaz and Rosenberg 2008). De plus, l'eutrophisation favorise la prolifération d'algues nuisibles toxiques (Scott et al. 2013), une perturbation des réseaux trophiques (Sterner and Elser 2002), et une perte de biodiversité au sein de l'écosystème (Cloern 2001; Vitousek et al. 1997a). L'eutrophisation affecte donc grandement le fonctionnement des écosystèmes aquatiques menant à d'importantes conséquences sur la santé humaine et les économies locales (Dodds et al. 2009; Le et al. 2010).

N et P : un tandem le long du continuum aquatique

La plupart des efforts de gestion liés aux problèmes d'eutrophisation ont porté sur la réduction d'apport en P aux systèmes. Le P est généralement considéré comme élément limitant (Liebig 1841) en eaux douces (Schindler, 1977, 2012), où des apports nouveaux stimuleront drastiquement l'augmentation de la productivité primaire. Cependant, plusieurs cas de limitation en N ou de co-limitation par N et P ont aussi été observés (Elser et al. 2007; Harpole et al. 2011). Aussi, N contrôle généralement la production primaire en milieux marins côtiers (Howarth and Marino 2006). En ce sens, plusieurs chercheurs préconisent une double stratégie comprenant la réduction de N et P (Conley et al. 2009; Howarth et al. 2011; Paerl 2009), considérant ainsi l'ensemble du réseau hydrographique de façon holistique. En effet, un apport de N en eaux douces aura des effets potentiels tant *in situ* qu'en aval, par son transport le long du continuum aquatique, entraînant ainsi la dégradation des sites estuariens et côtiers (Howarth et al. 2011; Paerl 2009). Toutefois, que N influence ou non la production primaire dans les eaux douces n'est pas la seule préoccupation; la charge absolue en N, les formes chimiques de N et le ratio N: P (stoechiométrie des formes biodisponibles) peuvent avoir des impacts importants sur la qualité de l'eau en modifiant les patrons de limitation et la structure des communautés au sein des systèmes aquatiques (Sterner and Elser 2002) et jouer un rôle central dans la toxicité des cyanobactéries en eau douce (Dolman et al. 2012; Giani et al. 2005; Lee et al. 2000).

Compte tenu de l'importance de N et P au nexus eau-alimentation, et donc au maintien d'un développement socio-économique prospère et durable, il est essentiel de mieux comprendre comment les cycles biogéochimiques de N et P sont régis par les écosystèmes naturels et comment l'activité humaine les modifie.

Perturbations anthropiques des cycles N et P

Depuis les temps préindustriels, les activités humaines ont augmenté les flux annuels de N et P biodisponibles sur les continents par deux et trois fois respectivement (Bennett et al., 2001; Galloway et al., 2004). Dans le cas de N, les apports naturels annuels vers les écosystèmes terrestres sont estimés à ~ 132 Tg N an^{-1} (Galloway et al., 2004), la majorité provenant de la fixation biologique de N_2 (FNB, 97%), et le reste par la foudre (3%). Au début des années 1990, le flux de N avait atteint ~270 Tg N an^{-1}, où ~156 Tg N an^{-1} provenaient d'activités anthropiques (Galloway et al., 2004). L'augmentation de la fixation anthropique de N se produit principalement par le procédé industriel Haber-Bosh (Hager 2009) permettant la conversion de N atmosphérique (N_2) en ammoniac (NH_3), et ce pour l'utilisation d'engrais principalement, mais aussi pour la fabrication de fibres synthétiques, de frigorigènes, d'explosifs et de plastiques. La culture répandue de plantes fixant le N_2 (légumineuses telles que le soya) et l'utilisation de combustibles fossiles sont également des sources majeures de N biodisponible additionnel aux écosystèmes (Galloway et al., 2004).

Les activités humaines ont également modifié les flux de P sur Terre principalement par l'extraction de roches phosphatées inorganiques (Cordell 2009). La disponibilité naturelle de P dans l'environnement (sans intervention humaine) provient d'un dénudement mécanique et chimique de la croûte terrestre relativement lent causé par les intempéries (Cordell 2009). Cependant, l'extraction minière introduit des quantités considérables de P supplémentaires dans les écosystèmes via son utilisation dans les engrais, les compléments alimentaires, les détergents ainsi que d'autres produits industriels (Bennett et al., 2001). Globalement, l'activité humaine a augmenté les flux de P sur les continents de 12,5 Tg P an^{-1} aux temps préindustriels à 37,3 Tg P an^{-1} en 1996 (Bennett et al., 2001).

Les apports en N et P excédentaires aux besoins des plantes peuvent s'accumuler dans les sols, être lixivié vers les eaux de surface et souterraines ou être éliminés vers l'atmosphère par dénitrification dans le cas du N (Knowles, 1982). Aussi, bien que minime dans le cas du P, la volatilisation de formes inorganiques et organiques de ces nutriments offre une voie additionnelle de transport entre les écosystèmes (Bennett et al., 2001; Smith et al., 1999). D'un point de vue mondial, le flux de P aux océans est passé de 9 à 23 Tg P an^{-1} (Howarth et al. 1995) alors que N a augmenté de 43 à 81 Tg N an^{-1} (Galloway et al., 2004). Une nouvelle augmentation d'utilisation de N devrait atteindre 370 Tg N an^{-1} d'ici 2050 dont 270 Tg N an^{-1} proviendraient de sources anthropiques (Galloway et al., 2004, MEA, 2005). L'exportation fluviale de P devrait également augmenter dans les années à venir (Seitzinger, 2010). Les flux de ces deux éléments varieront de façon importante entre pays et régions, et ce avec des augmentations relatives plus élevées anticipées dans les régions aux économies émergentes (Le et al., 2010).

Transfert de N et P vers les systèmes aquatiques

Un défi majeur dans la prédiction des charges en nutriments à la sortie de bassins hydrographiques est de tenir compte des nombreuses sources et processus de rétention (ou d'élimination dans le cas de N) par le système. Pendant leur passage dans les sols et les cours d'eau, la plupart des excédents anthropiques de N et P sont retenus en amont pour une période indéterminée (Hamilton 2012; Jarvie et al. 2013a; Sharpley et al. 2013; Van Meter et al. 2016) ou, dans le cas de N, peuvent être éliminés vers l'atmosphère par dénitrification (Knowles, 1982). Cependant, la capacité de rétention/élimination des nutriments par les bassins hydrographiques varie considérablement selon les années et les régions (Hong et al., 2012, Howarth et al., 2012). Bien qu'un certain consensus existe pour dire qu'en moyenne, 25% des surplus anthropiques de N au territoire semblent être exporté vers les rivières, le reste (75%) étant retenue ou dénitrifié (Boyer et al., 2002; Han et al., 2009; Hayakawa et al. 2009, Howarth et al., 2012; Howarth et al., 1996), il existe une grande variabilité dans ces taux de transfert aux eaux de surface, tant au niveau spatial (~10% à 60%) (Hong et al., 2012; Kimura et al., 2012; Schaefer et Alber, 2007a; Sutton et al., 2011; Swaney et al., 2012), que temporel (Chen et al. 2015; Han et al. 2012). Compte tenu des propriétés lithophiles de P (Holtan et al.

1988), les charges fluviales de cet élément à l'exutoire des bassins hydrographiques sont plus variables et moins prévisibles (Green and Finlay 2010). La fraction des surplus de P exportée à l'exutoire semble varier entre 1 et 15% (Han et al., 2011; Hong et al., 2012; Russell et al., 2008), bien que des transferts plus élevés aient également été observés (25% dans le cas du lac Erie; Han et al., 2012).

Découplage des cycles de N et P par le territoire et le climat

La rétention de N et P dans le territoire et l'export fluvial de ces nutriments à l'exutoire du bassin versant résultent de différents facteurs climatiques, géomorphologiques, ou d'utilisation du territoire. Par exemple, des précipitations annuelles élevées favorisent le transfert de nutriments en aval (Howarth et al. 2006, Zhou et al. 2014), tandis que les bandes riveraines (Lowrance et al., 1997, Correll 2005) et la présence de lacs et de réservoirs le long du réseau fluvial (Saunders et Kalff 2001, Harrison et al. 2009, Van Cappellen et Maavara 2016) semblent généralement améliorer leur rétention dans le territoire (et/ou élimination dans le cas du N). Cependant, les voies de transport de N et P diffèrent considérablement (Wetzel 2001, Kalff 2002) de sorte que la géomorphologie, le climat et l'utilisation des terres pourraient modifier leur transfert relatif à l'exutoire des bassins hydrographiques. Si, tel que mentionné, les changements dans les rapports N: P peuvent avoir un impact considérable sur l'intégrité de l'écosystème aquatique (Sterner and Elser 2002), peu d'études ont identifié comment les différentes caractéristiques du climat et du territoire, qu'elles soient naturelles ou anthropiques, agissent sur la rétention ou le transfert relatif de ces deux éléments (Alexander et al. 2008; Seitzinger et al., 2010).

Effet de legs historique

Si N et P sont partiellement retenus dans les différents compartiments du territoire, et ce pour une durée indéterminée, ils peuvent aussi être remobilisés ou recyclés créant ainsi des sources chroniques et continues pour les masses d'eau en aval, et ce pendant des années, voire des décennies (Carpenter 2005; Hamilton, 2012; Meals et al., 2010; Sharpley et al. , 2013). Ces décalages temporels entre l’apport anthropique de N et P au territoire et leurs sorties à l’exutoire (Sharpley et al 2013; Van Meter 2015) créent un effet de legs qui complexifie l’enjeu des nutriments à l’échelle du bassin versant. Malgré des diminutions de surplus en nutriment au territoire, de nombreux programmes de conservation ont échoué à l'amélioration de la qualité de l'eau dans les délais prévus par les scientifiques (Sharpley 2013). Il est suggéré que ces programmes n'aient pas suffisamment pris en compte cet effet de legs lié aux apports d'années antérieures (Kleinman et al., 2011). Bien que des études aient exploré la capacité de rétention du P dans les sols agricoles (Maguire and Sims 2002; Nair 2014), très peu d’études ont approché cette question à l’échelle du bassin versant. En effet, notre compréhension de la capacité de rétention en nutriment par les bassins versants et du temps de réponse à l'implantation de plans de gestion demeure limitée. Pour que les plans de conservation réussissent dans les délais prescrits, des études historiques au niveau régional sont nécessaires afin de mieux évaluer les effets de legs en N et P.

Cadre conceptuel et objectifs généraux de la thèse

Dans le cadre de cette thèse, je me suis intéressé aux flux d’azote et de phosphore dans le bassin du Saint-Laurent (BSL) et aux facteurs, tant naturels qu’anthropiques, régissant leur export à l’exutoire des bassins hydrographiques. Les objectifs et les principaux résultats des différents chapitres de la thèse sont présentés ici-bas.

Le **Chapitre I** se penche sur l’impact des activités humaines sur les flux de ces nutriments à l’échelle du bassin versant. Si les activités humaines ont été identifiées comme cause majeure d’apports accrus en nutriments aux eaux de surface, nous avons voulu vérifier leur importance relative dans le BSL, et ce dans une perspective historique. Les objectifs de ce chapitre étaient de 1) quantifier les sources d'intrants anthropiques de N et P dans 76 bassins hydrographiques du Saint-Laurent tout au long du XX^{e} siècle afin d’identifier les sources dominantes, leurs tendances temporelles et les «points chauds » en termes de surplus au territoire, ainsi que 2) d'identifier la relation entre ces surplus en nutriments et les charges fluviales à l'exutoire.

En utilisant une approche par bilan de masse basée sur des données historiques publiquement accessibles telles que les recensements agricoles et d'autres archives, nous montrons que depuis 1901, les surplus de N et P au BSL ont augmenté respectivement de 4,5 fois et 3,8 fois, avec un pic en 1991 principalement en raison du dépôt élevé d'azote atmosphérique et de l'application d'engrais phosphatés. Cependant, l'augmentation au cours du siècle fut beaucoup plus élevée dans certains sous-bassins versants, en particulier ceux ayant connu une forte urbanisation. De plus, les surplus au territoire sont fortement liés aux charges fluviales. Nos résultats suggèrent que 22% des surplus en N et 17% des surplus en P sont exportés aux rivières, et que la capacité de rétention par les bassins versants semble plus variable pour P que pour N. En suivant les principales sources d'intrants au territoire à travers le temps, cette étude fournit des informations pertinentes à la gestion de l'azote et du phosphore à l'échelle du bassin versant. Les stratégies devront probablement être spécifiques à chaque région, même si nos résultats montrent aussi clairement l'impact positif de législations à grande échelle.

Bien que les nutriments rejoignent les eaux de surface par ruissellement, une portion importante est néanmoins retenue dans le bassin versant, et ce de façon différentielle pour N et P. Or, si les concentrations relatives de N et P (stœchiométrie) influencent grandement la qualité de l'eau, notre compréhension des facteurs contrôlant l'export relatif de N et P par les rivières demeure limitée. Le **Chapitre II** se penche sur les différentes caractéristiques du territoire et du climat expliquant la variabilité spatiale et temporelle des transferts de N et P aux eaux de surfaces et sur la capacité de ces facteurs à découpler les flux relatifs de ces deux éléments. Les objectifs de ce chapitre étaient d'abord 1) d'identifier l'importance relative de caractéristiques climatiques et territoriales sur le transfert des différentes formes chimiques de

N et P (soit particulaires et dissoutes) au long du réseau aquatique, et ce au niveau temporel et spatial, puis 2) de quantifier l'effet relatif de ces facteurs sur la rétention de N et P.

D'abord nous montrons que les facteurs de transport de nutriment, tels que les précipitations et la capacité de rétention d'eau du territoire, agissent comme principales forces de contrôle sur les flux de N et P et que les systèmes aquatiques lentiques (lacs et réservoirs) jouent un rôle second, mais significatif, dans le contrôle de ces flux en favorisant des processus de sédimentation, ou de dénitrification dans le cas de N. Les bassins présentant une plus grande capacité de rétention d'eau à l'échelle annuelle favorisent la rétention de P par rapport à N. Cet effet relatif est aussi observé pour la présence de lacs et la morphométrie des réservoirs. Nous observons que les réservoirs hydriques présents dans les bassins versants de cette étude semblent agir comme des sources nettes de nutriments, et ce particulièrement pour N, suggérant une remobilisation de nutriments ayant été stockés dans les sédiments. En ce sens, certains résultats de cette étude témoignent d'un effet de legs, où des nutriments provenant d'apports d'années antérieures seraient remobilisés suite à leur stockage dans les sols, les sédiments ou les aquifères, et ce de façon particulièrement prononcée lors d'évènements de précipitations extrêmes. Cette étude souligne l'effet différentiel de différentes caractéristiques naturelles et anthropiques sur les flux de N et P et fournit des informations importantes pour une meilleure compréhension des dynamiques N:P dans les eaux de surface.

Si, comme nous l'avons vu, différents compartiments du territoire ont la capacité de retenir une partie des surplus de P d'origine anthropique, l'existence d'un seuil d'accumulation au-delà duquel un bassin dépasse sa capacité optimale de rétention de P est inconnue. De plus, si nous savons que les stocks de P accumulés dans le territoire sont transférés graduellement aux eaux de surface, pouvant ainsi maintenir l'eutrophisation aquatique sur le long terme (Jarvie et al. 2013a), l'envergure de ces décalages temporels demeure incertaine. Le **Chapitre III** se penche donc sur la capacité tampon en P des bassins versants, tant durant la phase d'accumulation lors de surplus au territoire, que durant la phase d'épuisement des stocks accumulés. Les objectifs de ce chapitre étaient d'abord 1) d'identifier l'existence d'un seuil d'accumulation (ou de saturation) en P à l'échelle du bassin versant au-delà duquel les exports fluviaux seraient accrus, 2) de quantifier ce seuil d'accumulation pour les bassins du Saint-Laurent, puis 3) d'estimer l'ampleur des décalages temporels pour un retour aux conditions initiales suite à une accumulation sur plus d'un siècle, et ce dans un scénario « idéal » de recyclage complet des pertes en P aux usines d'épuration et en agriculture.

En utilisant des reconstitutions historiques de flux de P dans plusieurs bassins versants du Saint-Laurent, nous avons quantifié pour la première fois le point de rupture à l'échelle du bassin versant, au-delà duquel des apports additionnels en P au bassin accentuent drastiquement le transfert de P à l'exutoire. Nous montrons que ce seuil d'accumulation pour une rétention optimale de P est étonnamment bas et qu'il peut être atteint en moins d'une décennie aux taux actuels d'intrants en P dans la plupart des régions fortement agricoles. À l'inverse, nous estimons que le retour aux conditions initiales pourrait prendre plusieurs siècles dans certains cas. Ces résultats soulignent l'impact rapide des activités humaines sur le fonctionnement des écosystèmes et les conséquences à long terme des pertes en P vers l'environnement. L'étude met aussi en lumière la nécessité d'exploiter les stocks de P résiduel accumulé dans les sols (et sédiments) afin de concilier production alimentaire et qualité d'eau.

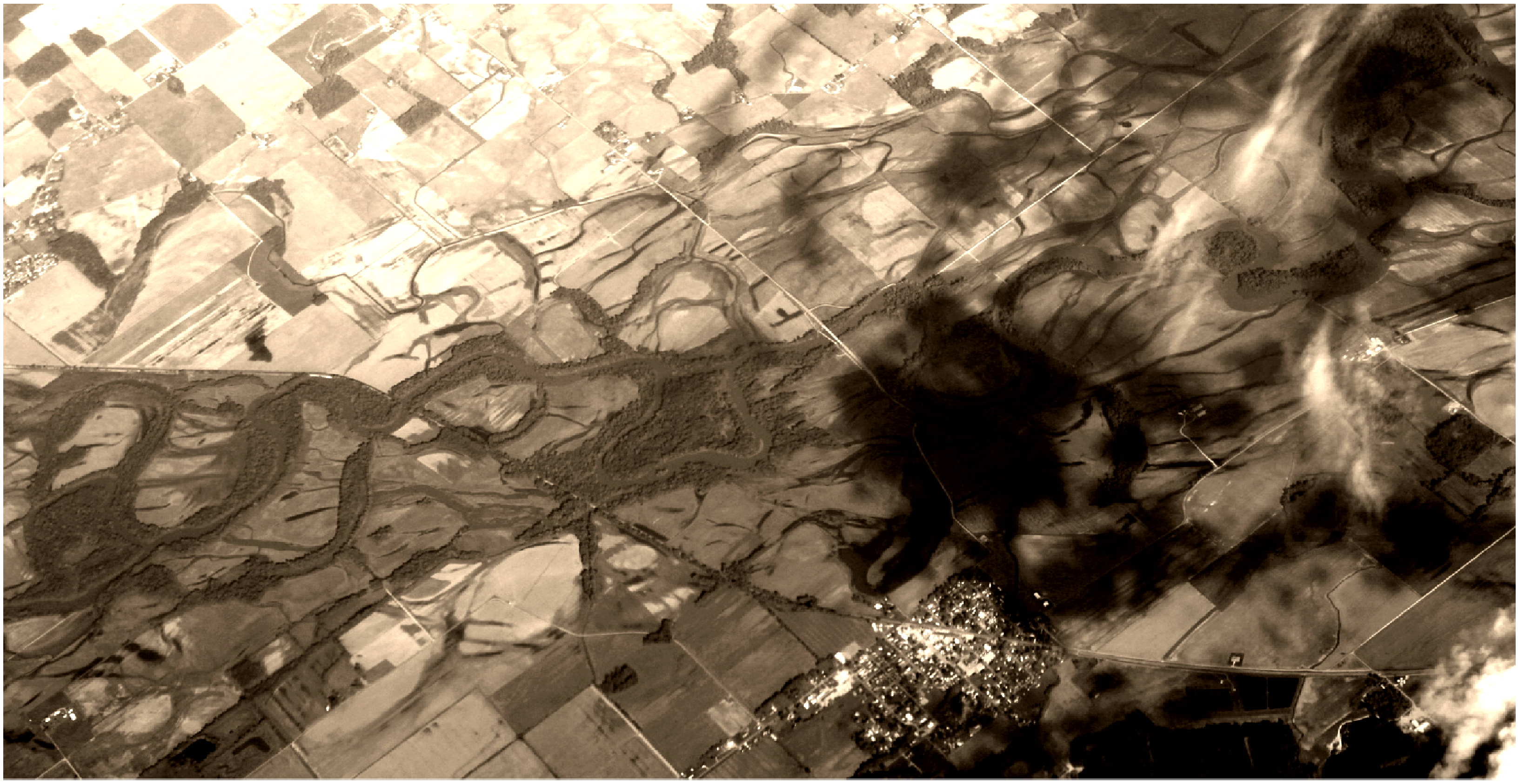
En ce sens, les plans stratégiques de gestion de N et P au nexus eau-alimentation proposent différentes mesures d'atténuation de pollution aquatique par les nutriments (Foley et al. 2011; Sutton et al. 2013) . Parmi celles-ci, l'augmentation d'efficience d'utilisation de N et P dans le secteur agricole apparaît comme stratégie clé tant pour la sécurité alimentaire que pour la protection de l'environnement (Godfray et al. 2010). Le **Chapitre IV** se veut donc une exploration des tendances temporelles d'efficience d'utilisation de N et P dans la production céréalière et animale dans le BSL au cours du dernier siècle. Les objectifs de ce chapitre étaient de 1) dresser un portrait des flux de N et P dans le système agroalimentaire du BSL durant le dernier siècle et 2) de quantifier les changements d'efficience d'utilisation des nutriments à différents niveaux de la chaîne de production agricole tout en considérant le cycle de vie complet des nutriments. Nous montrons que l'agriculture dans le BSL était non durable entre 1901 et 1960 puisque N et P étaient extraits des sols par les cultures en quantité plus importantes que l'étaient leurs retours sous forme d'engrais. Par l'utilisation de fertilisants, le système a rapidement basculé vers un système inefficient occasionnant de larges pertes de N et P vers l'environnement. Nous observons une transition tant dans les cultures que dans le type d'élevage permettant d'expliquer les tendances divergentes d'efficience d'utilisation de N et P à travers le temps. En considérant l'ensemble du système de production de nourriture à destination humaine, et en considérant les pertes encourues à l'étranger par l'importation de nourriture animale, nous observons une énorme diminution dans l'efficience d'utilisation des nutriments et soulignons l'importance de considérer le cycle de vie complet des nutriments dans l'évaluation des performances des systèmes agroalimentaires.

Cette thèse comporte également 4 articles en annexe qui ont été réalisés au cours de ce doctorat et qui se rattachent aux chapitres présentés ici. L'**Annexe I** est un article découlant d'un projet multidisciplinaire, le « Great Lakes Futures project », portant sur l'état du système socio-écologique des Grands Lacs d'Amérique du Nord et du fleuve Saint-Laurent, et auquel j'ai eu la chance de participé en tant que membre du groupe responsable de la qualité de l'eau. L'article dresse une revue historique des tendances des contaminants au cours des 50 dernières années (1963-2013), décrit leurs interactions avec différents facteurs socio-écologiques du bassin et présente trois scénarios concernant les contaminants pour les 50 prochaines années (jusqu'en 2063). En mettant en évidence certains outils nécessaires au suivi des contaminants et en explorant les scénarios futurs plausibles, l'article vise à souligner la nécessité de développer et renforcer des accords et des initiatives binationales pour restaurer et protéger l'écosystème. En tant que 1er auteur à parts égales avec deux autres personnes, ma contribution à cet article a été de participer à la synthèse d'information et à l'écriture de l'article (Cromwell, Goyette et al., 2015).

L'**Annexe II** est une étude paléolimnologique portant sur l'effet historique de rabattage hivernal des niveaux d'eau dans les réservoirs sur la qualité de l'eau (concentration en P). Nous montrons que l'effet semble négligeable en comparaison à ceux de la température et des apports anthropiques de P aux bassins versants. En tant que coauteur, ma contribution à cet article a été de reconstituer les apports anthropiques de P au bassin versant au cours des 110 dernières années, et ce en empruntant la méthodologie développée dans le **Chapitre I** de cette thèse (Elchyshyn et al. 2018).

L'**Annexe III** est un article découlant des **Chapitres III et IV**, et présente les différentes caractéristiques socio-écologiques du territoire affectant la capacité de rétention du P à court et long terme. En tant que second auteur, ma contribution a été de participer à l'élaboration du modèle conceptuel, de la question de recherche et de la méthodologie ainsi qu'à générer les données de surplus historique en P au territoire (Kusmer et al. 2018).

Finalement, l'**Annexe IV** est un article portant sur les causes du déclin des populations de perchaude dans le lac Saint-Pierre dans une perspective historique. Nous montrons que l'apport en P au système depuis 1960 est fortement relié au déclin de la population et posons l'hypothèse que l'effet d'eutrophisation aurait détérioré l'habitat des poissons. En tant que coauteur, ma contribution à cet article fut de reconstituer les charges fluviales historiques de P provenant des cinq principaux tributaires du fleuve Saint-Laurent à la hauteur du lac Saint-Pierre (Giacomazzo et al. in prep, 2018).



Chapitre 1. Changements des apports anthropiques d'azote et de phosphore dans le bassin du Saint-Laurent sur 110 ans et impacts sur les charges fluviales

Changes in anthropogenic nitrogen and phosphorus inputs to the St. Lawrence sub-basin over 110 years and impacts on riverine export

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Abstract

Human activities have increased the flow of nitrogen (N) and phosphorus (P) over much of the Earth, leading to increased agricultural production, but also the degradation of air, soil, and water quality. Here, we quantify the sources of anthropogenic N and P inputs to 76 watersheds of the St. Lawrence Basin (SLB) throughout the 20th century using NANI/NAPI (net anthropogenic N/P input to watersheds), a mass balance modeling approach, and estimate the fraction of these inputs exported to adjacent rivers. Our results show that since 1901, NANI and NAPI increased 4.5- and 3.8-fold respectively with a peak in 1991 mainly due to high atmospheric N deposition and P fertilizer application. However the relative increase over the course of the last century was much higher in certain watersheds, particularly those where there was greater urbanization. Ranges in NANI and NAPI vary greatly among watersheds (110 to 9351 kg N km^{-2} yr^{-1} and 0.16 to 1938 kg P km^{-2}yr^{-1}, respectively in 2011) and are strongly related to riverine fluxes (R^2 = 0.87 and 0.71 for N and P, respectively). Our results suggest that 22% of NANI (ranging from 11% to 68% across watersheds) and 17% of NAPI (ranging from 3% to 173%) are exported to rivers. Predominant sources of inputs vary spatially and through time largely due to changes in farming practices. By tracking the main sources of inputs to specific watersheds and through time, our work provides insights for N and P management. Reduction strategies will likely need to be watershed specific, although through time, our results clearly show the large-scale impact of targeted legislation.

Introduction

Human activities have greatly increased the annual fluxes of bio-available nitrogen (N) and phosphorus (P) on the continents (Bennett et al. 2001; Galloway et al. 2004), primarily since the industrialization of agriculture (Cordell et al. 2009; Galloway and Cowling 2002). The use of N and P fertilizers has enabled the feeding of a growing human population by increasing crop yields substantially (Smil 2001). However, excessive use of nutrients has also caused the degradation of aquatic ecosystems through eutrophication (Galloway and Cowling 2002; Howarth and Malone 2000; Rabalais et al. 2002a; Schindler 2012), which can result in the formation of toxic algal blooms (HABs), fish kills due to oxygen depletion in bottom waters, and loss of biodiversity (Cloern 2001; Vitousek et al. 1997b) with devastating consequences on human health and local economies (Dodds et al. 2009; Le et al. 2010).

Although eutrophication of inland waters is thought to be regulated by P inputs (Schindler 1977; Schindler 2012), several researchers advocate for a dual nutrient reduction strategy including reducing N (Conley et al. 2009; Howarth et al. 2011; Paerl 2009). Whether or not N limits growth of primary producers in freshwaters is not the only concern but N load and N chemical form may play a pivotal role in freshwater cyanobacterial toxicity and therefore in human health (Dolman et al. 2012; Giani et al. 2005; Lee et al. 2000; Monchamp et al. 2014). N load to freshwaters will also have downstream effects along the aquatic continuum when transport into N limited estuaries and coastal sites results in ecosystem degradation (Howarth and Marino 2006; Paerl 2009; Rabalais et al. 2002b).

Identifying the sources of N and P loading to the landscape is an essential first step to improving nutrient management because it can point to the primary sources of pollution for possible reduction strategies. Net Anthropogenic Nitrogen Input (NANI) [*Howarth et al.*, 1996] is a mass balance modelling approach that estimates the anthropogenic movement of N to watersheds and is considered very robust since it can also accurately predict the amount exported to rivers (Alexander et al. 2002). Indeed a global average of 25% of NANI is generally accepted as being exported to rivers, although substantial variability is observed across regions (Howarth et al. 2012; Schaefer et al. 2009; Swaney et al. 2012). Net Anthropogenic Phosphorus Input (NAPI), a recently adapted version of the model for P, presents a more variable pattern of fractional export [*Russell et al.*, 2008] that ranges between ~1 and 15% (Han et al. 2011; Hong et al. 2012).

Sources of inputs vary not only in space but also in time due to changes in technology (e.g. synthetic fertilizers, P mining), land use (Kleinman et al. 2011), diets (Metson et al. 2012), economies [*Galloway et al.,* 2007] and issues related to governance (Maki et al. 1984). A historical perspective is thus critical to portrait the impacts of these social drivers on N and P cycles. Although NANI and NAPI have been widely used to characterize N and P sources and fractional riverine export across watersheds (Billen et al. 2013b; Boyer et al. 2002; Han et al. 2011; Han et al. 2009; Hong et al. 2012; Howarth et al. 1996), few studies have explored temporal changes in land use across multiple sub-watersheds in a single a region (Gao et al. 2015; Han and Allan 2012).

The St. Lawrence sub-basin (SLB, Figure 1) is a region of eastern North America with heterogeneous land use that has experienced significant and often localized social transformations throughout the last century [*MacDonald and Bennett,* 2009]. Sub-watersheds range from densely forested to intensively farmed and the region is dotted with major urban areas. Receiving waters in the region are becoming more eutrophied and are experiencing an increased incidence of cyanobacteria blooms [*Campeau*, 2010; *Glibert et al.,* 2014; *MDDEP* 2011, 2012] . Hypoxic conditions are also prevalent in the deep waters of the St. Lawrence Estuary, with up to 33-50% likely due to increased load of organic matter, N and P via freshwater inputs (Gilbert et al. 2005). The vulnerability of the St. Lawrence estuary to nutrient loading may also be enhanced due to global warming (Altieri and Gedan 2014) and to changes in oceanic currents bringing warmer waters promoting O_2 depletion through greater microbial activity (Gilbert et al. 2005). It is thus imperative to have a better understanding of the current and historical impacts of human activities on the fate of N and P in this landscape.

In this study, we characterized the sources of N and P and their changing dynamics across the SLB throughout the 20th century by calculating the net anthropogenic N and P inputs in 76 watersheds of the SLB over the last 110 years. This allowed for the assessment of total NANI and NAPI, including the relative importance of differential input terms, across space and through time. Furthermore, we calculated annual N and P riverine loads at several outlets over 3 decadal years and compared those with the watershed inputs in order to calculate fractional export. This served as a cross-check validation of our human-induced N and P input model.

Methods

Study area

The SLB (574 000 km^2) is part of the Great Lakes-St. Lawrence Basin that drains the Great Lakes into the Atlantic Ocean (Figure 1; St. Lawrence Centre 1996). Almost 75% of the SLB is located in Canada within the province of Quebec and eastern Ontario, with the remainder residing in northern New York State, and Vermont, USA. The SLB was sub-divided in 76 watersheds [*Natural Resources Canada,* 2003] ranging in size from 1818 to 21 112 km^2. Three major physiographic divisions characterize the SLB: the Canadian Shield, Appalachian Highlands and Interior Plains, which promote differential land use. For example, the Interior Plain located to the south and east of Montreal (Figure 1) on the right bank side of the St-Lawrence is a prime location for agriculture. Precipitation is spread relatively evenly throughout the year with an average of 924 mm in Montreal.

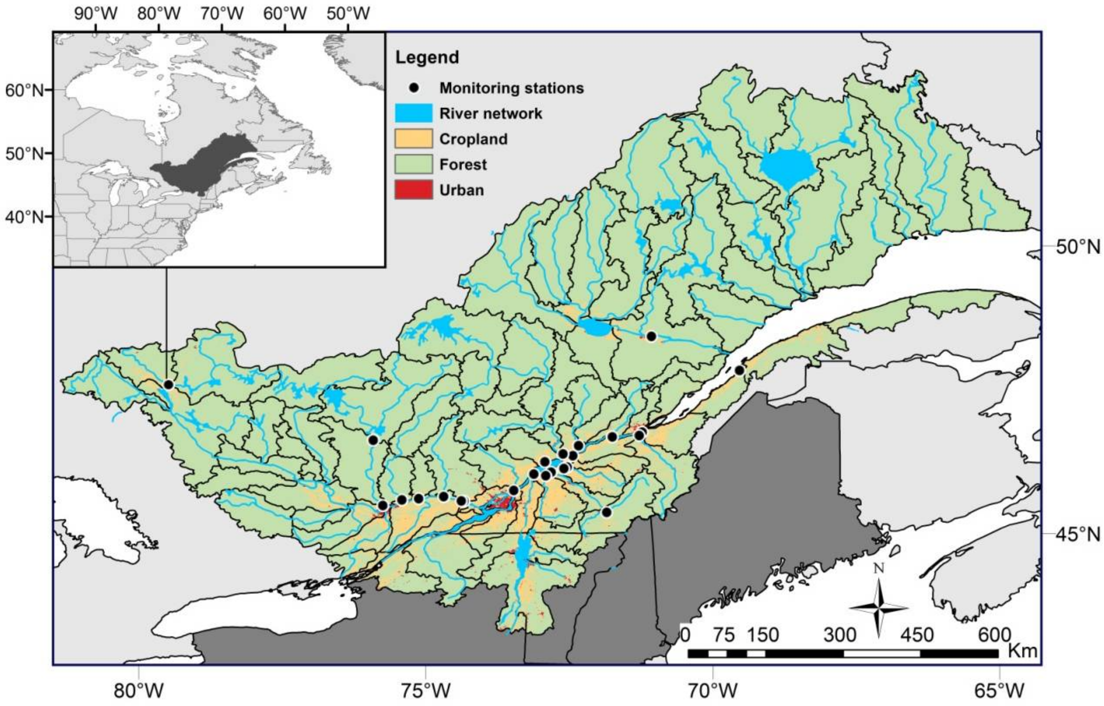

Figure 1. The St. Lawrence sub-basin and its 76 watersheds located in the provinces of Quebec and Ontario, Canada as well as in northern New York State, and Vermont, USA. The sub-basin extends from the outlet of Lake Ontario to the Gulf of St. Lawrence. Light and dark grey areas delineate Canada and US territories, respectively. Black dots show the locations of the monitoring stations used in this study to calculate annual TN and TP riverine loads. Land cover was retrieved from North American Land Cover at 250 m spatial resolution available at : ftp://ccrs.nrcan.gc.ca/NALCMS/

N and P budget construction

N and P budgets were constructed for each of the 76 watersheds of the SLB (Figure 1) at a 10-year time interval from 1901 to 2011. We quantified all known anthropogenic N and P inputs (synthetic N and mined P fertilizers, biological N fixation, atmospheric N deposition, P in detergents and imports of N and P in food and feed), and outputs (exports of N and P in food and feed) and used these to calculate NANI and NAPI budgets (Figure 2) [Howarth et al., 1996; Russel et al., 2008]. NANI and NAPI do not include sewage and manure since these terms are already embedded in the balance of other terms. For example, manure does not represent "new" N or P to the watershed because it originates from the animals consuming feed that is either imported or produced locally using synthetic fertilizers and both of these terms are already considered as inputs in NANI or NAPI (Figure 2). Similarly, NANI includes only oxidized atmospheric inputs (NOy) and excludes reduced forms (NHx) because the latter largely originate from agricultural sources and tends to be re-deposited within the same watershed it was emitted with no net input of N.

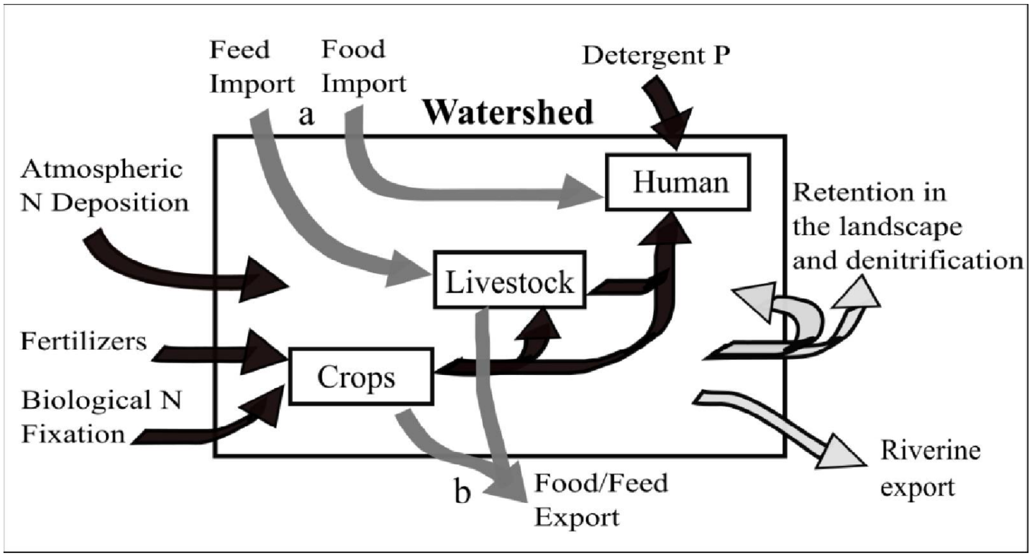

Figure 2. Diagram of major components of Net Anthropogenic Nitrogen/Phosphorus Inputs (NANI/NAPI) and exports from a watershed (adapted from Swaney et al., 2012). The approach assumes that animal and human demand is initially satisfied by local production. Black arrows are thus taken into account in initial calculations. Dark grey arrows serve to balance animal and human N and P demand through feed and food imports when in deficit (a) or if production in a watershed is larger than local demand, as food or feed exports (b). Once these terms are estimated, surplus N and P in a watershed (NANI and NAPI) can either be exported to rivers, lost to the atmosphere through denitrification (N only) or retained in the landscape (light grey arrows).

The NANI and NAPI budgets were first calculated using county-level data retrieved from agricultural censuses [*Canada Department of Agriculture,* 1901; *Canada*

Census and Statistics Office, 1911; *Canada Dominion Bureau of Statistics,* 1922, 1932, 1942, 1952, 1962; *Statistics Canada,* 1972, 1982, 1992, 2003, 2011a; *U.S. Census Office,* 1902; U.S. *Bureau of the Census,* 1913, 1922, 1933, 1942, 1952, 1961, 1972, 1984; *USDA-NASS,* 1994, 2004, 2014]. Since Canadian and US census years differ, budgets in US counties were interpolated linearly to match Canadian census years. Budgets at the county-level were then partitioned to the watershed-level using ArcGIS 10.0. Data sources and calculation methods for each input and output terms are presented hereafter.

Fertilizers

Fertilizer N and P inputs were estimated using provincial and state N and P fertilizer tonnage sales data [*Statistics Canada*, 2014a; *Terry and Kirby,* 1992, 2003; *USDA-CRB*, 1954, 1959, 1969, 1982; *US EPA*, 2014a] as well as county-level fertilizer expenditures reported in each census year. The tonnage of fertilizers sold in each province or state was disaggregated to counties by using the proportion of county to province (or state) of fertilizer expenditures reported in censuses. Details are provided in supplementary material and described in MacDonald and Bennett (2009).

Biological N fixation

Estimates of agricultural N fixation rates vary widely in the literature, particularly for legume-grass mixtures (Smil 1999). In this study, five fixing crops were considered: soybeans, alfalfa hay, non-alfalfa hay, pastures, and snap beans. Agricultural N fixation has often been estimated from area-based N fixation coefficients per crop (Boyer et al. 2002). However, the amount of N fixed from the atmosphere likely depends on N availability in the soil and on crop yields (Meisinger and Randall 1991). A yield-based approach corrects for this by estimating the fraction of N acquired from the soil [Han and Allan 2008]. We followed Hong et al. (2013) and applied the average values attributed to N fixation per plant type reported in Han and Allan (2008) (74% for soybeans and 82% for alfalfa and other fixing crops in non-alfalfa hay mixtures). The non-alfalfa hay areas reported in censuses were assumed to have 25% leguminous plants such as clovers. Like previous reports, our study considers only the fraction of N derived from atmospheric fixation in shoots and does not consider belowground fixation. Although this latter term may be significant, we do not account for it here as there is a large degree of uncertainty in rates across fields, climates and agricultural practices (Anglade et al. 2015). For snap beans and pastures, we applied the area-based approach (Boyer et al. 2002) since the Agricultural Census does not report yields. We compared the area- and the yield-based approaches throughout the century since the latter may be more relevant in longer-term assessments particularly where legume-grass mixtures are dominant crops that may change over time.

Atmospheric N deposition

Atmospheric N deposition was estimated from the 12 km × 12 km grid map containing N deposition estimates generated by the Community Multiscale Air Quality (CMAQ) model [*www.cmaq-model.org/*]. As mentioned above, only oxidized forms were considered as "new" N to the watersheds. Atmospheric deposition of reactive inorganic N oxides (NOy) were retrieved from the CMAQ model for year 2008 and apportioned to watersheds using ArcGIS. NOy deposition in each watershed was extrapolated to 2011 and back to 1901 by using the NOy deposition to NOx (NO +NO_2) emission ratio in 2008 and the historical trends in national NOx emission of both countries [*Statistics Canada*, 2014b; *US EPA*, 2000, 2014b]. Emissions from Canada and the US nearly follow the same trend although a peak in the 1980's occurred only in the US. Changes in NOx emissions in both countries were averaged as a proxy to account for trans-boundary transport. Atmospheric wet organic nitrogen was estimated as 15% of total wet N deposition (also retrieved from CMAQ) and added to each watershed in each decadal year (Hill et al. 2005; Keene et al. 2002; Neff et al. 2002).

P in detergent

We estimated P consumption from historical laundry and dishes detergent use. Following Han et al. (2011), we assumed that there was no phosphorus in detergent until

1935, because traditional bar soaps and liquid detergents used then for laundry and hand-washing of dishes contained little phosphate (Litke 1999). After 1935 we took into account changes in P content of detergent and the timing of bans on P content, which differed between Canada and the US [*Han et al.*, 2011; *Litke,* 1999; *Statistic Canada*, 2014c; Table S1].

Data on the amount of per capita laundry detergent use in Canada was unavailable so US data for years 1954 to 2011 were used as a proxy (Han et al. 2011). Use of laundry detergent was interpolated linearly between 1935 and 1954 to estimate the amounts in years 1941 and 1951. The use of P by automatic dishwashers was estimated from human population, the proportion of households equipped with automatic washers, their increasing efficiency and the P content of dishwasher detergent. Detergent use per capita, P content per spoon and proportion of households equipped with dishwashers were first retrieved from Han et al. (2011) and applied for US counties. The proportion of households equipped with dishwashers in Canada was retrieved for years 1997 to 2009 [*Statistic Canada*, 2014d] and previous years were estimated proportional to the changes in the US. Additionally, we considered the regulations from 2010 in Canada and Vermont limiting P content to 0.5% of total soap mass [*Washington Department of Ecology*, 2014; *Environment Quality Act,* 2014] by adjusting P per spoon in 2011 relative to the value reported in *Han et al.* [2012] when detergent content was 8.7% P [*Knud-Hansen,* 1994; SI, Table S2].

Net imports of N and P in food and feed

Net food import is calculated by subtracting human demand of N and P from N and P in crops and animal products (meat, milk and eggs) grown for humans. Similarly, net feed import is the subtraction of animal demand for N and P from nutrient content in crops grown for feed. Human and animal requirements are assumed to be met initially by local agricultural production, with excess demand being satisfied by imports. Prior to calculations of net imports of N and P in food and feed, livestock populations were adjusted to account for their residence time on the farm, and changes in animal weights and food product yields over time were tracked to account for evolving agricultural practices.

Adjusted livestock populations

Since some livestock groups do not reside yearlong on the farm, year-end inventories from censuses can misrepresent annual livestock populations and may result in biased estimates of N and P traded in livestock. Thus, we followed Han and Allan (2008) to adjust annual livestock populations of 18 animal classes by accounting for their life cycle (i.e. residence time on the farm to the point of animal sales). Canadian censuses do not report animal sales, so data for slaughtered animals were used instead. The span of available historical data on slaughtered animals at the provincial level differed across livestock groups. Sources and methods of estimation for these missing years are presented in SI. Slaughtered animals were then disaggregated to counties using county inventories from censuses and the slaughtered animal to inventory ratios available for each province.

Animal weights and product yields over time

To account for the evolving agricultural practices since 1901 and to get a more realistic account of N and P contained in animal food products throughout the century, we tracked the changes in average animal weights and production rates over time (Table 1). Animal live weights in Quebec were used for the whole basin. Live weights of beef, veal, pork and lamb were obtained for 2001 [*Institut de la Statistique du Québec,* 2013] and scaled through time based on changes in carcass weights in Quebec for years 1981 to 2011 [*Statistics Canada,* 2013c, d] and at the national level for years 1961 and 1971 [*FAO*, 2013]. Live weights of chickens and turkeys in Quebec were obtained for years 1941 to 2011 [*Statistics Canada,* 2013b]. Yields of milk and eggs were obtained at the national level for years 1961 to 2011 and 1921 to 2011, respectively [*FAOSTATS*;

Statistics Canada, 2013e] . For years prior to available data on animal weights and production rates, values were kept constant back to 1901.

Tableau I Animal live weights and product yields over time

years	beef[a]	veal[a]	Hogs[a]	Sheeps[a]	Chicken[b]	Turkey[b]	Eggs[b]	milk[c]
	Kg						eggs/head	(Kg/animal)
2011	619.6	236.4	124.1	46.9	1.7	7.3	269.9	8699.3
2006	616.8	231.2	120.0	46.7	1.6	7.5	262.2	8187.6
2001	613.0	234.0	112.0	44.0	1.6	7.2	267.2	7429.9
1996	539.5	220.2	108.4	42.5	1.5	6.6	270.2	6647.9
1991	524.4	200.2	102.5	41.5	1.5	6.0	273.3	5866.0
1986	487.6	144.2	101.8	41.9	1.5	5.4	257.6	5071.7
1981	460.4	125.0	99.4	37.3	1.5	4.9	242.0	4277.4
1971	431.6	105.8	96.1	37.3	1.5	4.9	205.3	3513.5
1961	-	-	-	-	1.5	4.4	194.9	2787.4
1951	-	-	-	-	2.2	5.9	163.4	-
1941	-	-	-	-	2.3	5.4	148.5	-
1931	-	-	-	-	-	-	111.5	-
1921	-	-	-	-	-	-	74.9	-

[a] Live weights obtained for 2001 [*Institut de la statistique du Quebec,* 2014] and changes through time approximated based on changes in carcass weights at provincial or national levels (see text for details)
[b] Live weights through time obtained from [*Statistics Canada*, 2013e]; For further calculations, eggs were converted to Kg (0.058 Kg Egg^{-1}) [*Han et al.,* 2009]
[c] Yields from *FAOSTATS* (*http://faostat3.fao.org/)*

Animal demand and food products

To estimate N and P consumption in feed, adjusted livestock populations were multiplied by annual N and P consumption coefficients specific to animal classes following Han and Allan (2008) for N and Han et al. (2011) for P. To estimate N and P in food products, we multiplied slaughtered livestock populations with the N and P content of their edible portion [Han et al., 2011; Han and Allan, 2008; Table S3 for P coefficients].The edible portion includes lean meat only and excludes hair, skin, bones, fat and viscera.

Human demand

Human N demand was estimated by multiplying annual county population, retrieved from censuses, with per capita annual N consumption. Values for per capita N consumption were estimated based on annual per capita protein consumption at the national level [*Statistic Canada*, 2013a] and multiplied by 0.16 (the N percentage of protein). Protein consumption in Canada was only available from 1976 to 2009, so US values were used for both countries prior to 1976 [*USDA-CNPP*, 2015]. Protein consumption of 2010 and 1909 were used as proxies for 2011 and 1901, respectively. Human P consumption was estimated as a constant of 20% of N consumption (Hong et al. 2012; Russell et al. 2008).

Crop production

We identified 14 major crops produced in this study region (MacDonald and Bennett 2009). Additionally, cropland pastures and non-cropland pastures were considered. Pastures represent a large amount of local feed available to animals and so are essential in the accounting of the net imports of food and feed. Crop and grass production in each county was obtained from agricultural censuses. Production was not available in Canada after 1951 so area was multiplied by regional yields to estimate annual production for Quebec and Ontario counties [*Bureau de la Statistique du Québec*, 1972, 1983, 1992; *Institut de la Statistique du Quebec*, 2014; *OMAFRA,* 1962, 1982, 1992, 2007, 2013]. Where county or regional data were unavailable, provincial average yields were used [*Statistics Canada*, 2014e]. N and P content in the harvested portion of crop and grass were multiplied by yields in each county and partitioned between human and animals accounting for losses in processing, spoilage and pest following Boyer et al. (2002).

Riverine N and P exports

Annual riverine N and P exports were estimated at the outlet of 23 watersheds in 1991, 2001 and 2011 (Figure 1). Loads were calculated from daily discharge [*Centre d'Expertise Hydrique du Quebec*; *Environment Canada*, 2014a] and monthly total N (TN) and P (TP) concentrations [*MDDEFP-BQMA*; *Environment Canada*, 2014b] , using the U.S. Army Corps of Engineers' software Flux32 (Walker 1996). Flux 32 is a regression-based approach that allows for flow-weighted interpolations of the discrete measurements of the concentration and so, reduces bias by accounting for exceptionally high or low daily discharge events. When a monitoring station integrated the drainage area of multiple watersheds, the total drained area was considered to calculate specific riverine loads (kg N or P km^{-2} yr^{-1}) and the associated NANI or NAPI values (kg N or P km^{-2} yr^{-1}). Discharge gauging stations were not necessarily located where water chemistry (TN and TP) was monitored. In such cases, discharge at the monitoring site was estimated by multiplying the specific discharge (m^3 km^{-2}) at gauging station by the drainage area (km^2) at the monitoring site. NANI and NAPI were used as predictors of annual riverine N and P exports in simple linear regressions using ordinary least squares (OLS) analyses in R [*R development Core Team*, 2012].

Results

NANI and NAPI over time and space

Overall, net anthropogenic N inputs to the SLB increased ~4.5 fold between 1901 and its peak in 1991, from 212 to 919 kg N km^{-2} yr^{-1} for a total load of 115 to 497 Gigagrams (Gg) in the basin as a whole, respectively (Figure 3a). To better understand temporal dynamics of N sources, we assess four different time frames across the century. At the beginning of the century, net feed import was the main source of N contributing to ~45% of total inputs. Anthropogenic biological N fixation, assessed using the yield-based approach, and atmospheric deposition were also important sources contributing ~30%

each of total inputs. From 1921 to 1941, enhanced dairy farming led to the initial marked increase in total net inputs (Figure 3a; SI, Table S4). The second phase of marked increase, observed between 1951 and 1991, was mainly driven by high atmospheric deposition and more intensive synthetic fertilizer use. Since 1991, NANI decreased slightly due to a better control of NOx emissions; however, continued increases in agricultural biological N fixation and fertilizer application have partially counterbalanced this trend. In 2011, NANI was estimated at 866 kg N Km^{-2} yr^{-1} (468 Gg) with fertilizers and atmospheric deposition contributing ~33% of net inputs and biological fixation and net food and feed import ~17%.

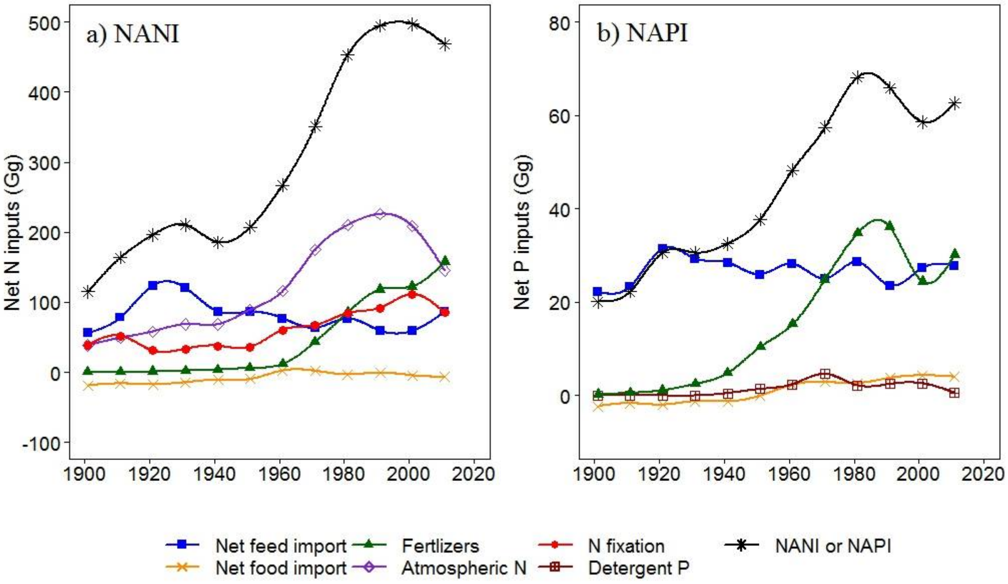

Figure 3. Temporal variation of total and the different terms estimated for a) NANI and b) NAPI over a 110-year time-span for the SLB. Note the difference in scale on y axes.

In the case of NAPI, we report an overall increase of ~3.8 fold from 1901 to a peak in 1981 with rates going from 37 to 125 Kg P Km^2 yr^{-1} (20 to 68 Gg) respectively and declined thereafter to 116 Kg P Km^2 yr^{-1} (63 Gg) by 2011 (Figure 3b). P inputs through net feed imports contributed nearly 100% to NAPI in the early 20th century and have, since the enhancement of dairy farming in the 1920's, remained fairly constant over time. The dynamic changes in NAPI since the 1940's are due to increased P fertilizer application (Figure 3b). Other input terms are relatively minor.

The temporal changes of both NANI and NAPI vary in a similar way spatially across different watersheds (Figure 4). This is largely due to the impact of agricultural intensification focused primarily in the lower St-Lawrence and central regions, which influences both elements. Indeed these areas were already hotspots of N and P inputs in the early part of the 20th century (Figure 4) and intensified over time. Both NANI and NAPI increased ~6 fold in these heavily impacted watersheds. A shift in the hotspots for both nutrients was also observed from the south west of the SBL more towards the south central areas in the second half of the century, where the highest rates went from 1586 to 9351 Kg N Km^2 yr^{-1} for NANI and 341 to 1938 Kg P Km^2 yr^{-1} for NAPI. In the northern region there is barely any change in NAPI over the study period while NANI sees a near three-fold increase due to the regional expanse of atmospheric N deposition (Figure 3a and 4). In the less impacted watershed, NANI went from 29 to 110 Kg N Km^2 yr^{-1}.

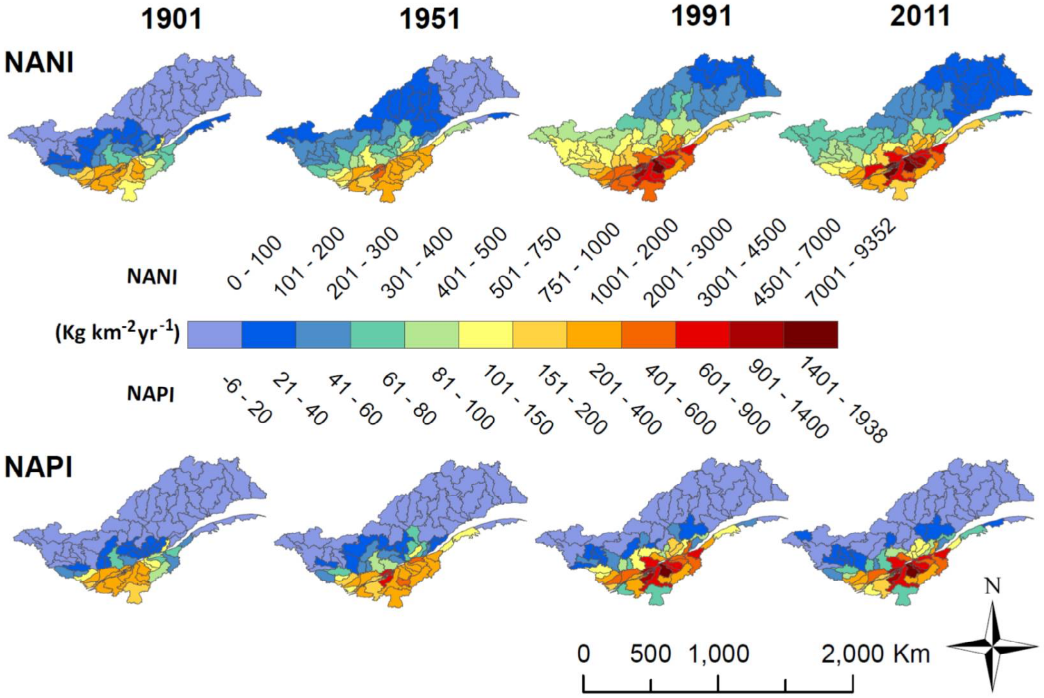

Figure 4. Spatial variation of NANI (top) and NAPI (bottom) for the 76 watersheds of the SLB throughout the study period. Data shown for 1901, 1951 (transition in trends), 1991 (peak of inputs), and 2011.

Net food and feed imports

As noted above, animal farming was already playing an important role in agricultural activities by the early 20th century. Figure 5 shows that animal demand for N and P in feed in 1901 already exceeded what was locally available in the southern watersheds of the SLB (resulting in net imports through feed; for P see Figure S1). This intensive animal production also translates into net N and P export through food from these same watersheds (Figure 5 and S1). Despite the rise of synthetic fertilizers and crop yields in the second half of the century, the intensification of animal farming in the southern and central regions have led to increased net imports of N and P through feed to supply production demands (Figure 5 and S1). The hotspot of net feed imports reached a peak in 2011 of 5450 Kg N km^{-2} and 1315 Kg P km^{-2} in the most intensively farmed watershed. Not surprisingly, the Montreal Island watershed which includes the city of Montreal (population of ~1,7 million in 2011) has been the major N and P importer of food beginning in 1911, with rates increasing from 88 to 2906 Kg N Km^{-2} yr^{-1} and 42 to 592 Kg P km^{-2} yr^{-1} between 1911 and 2011.

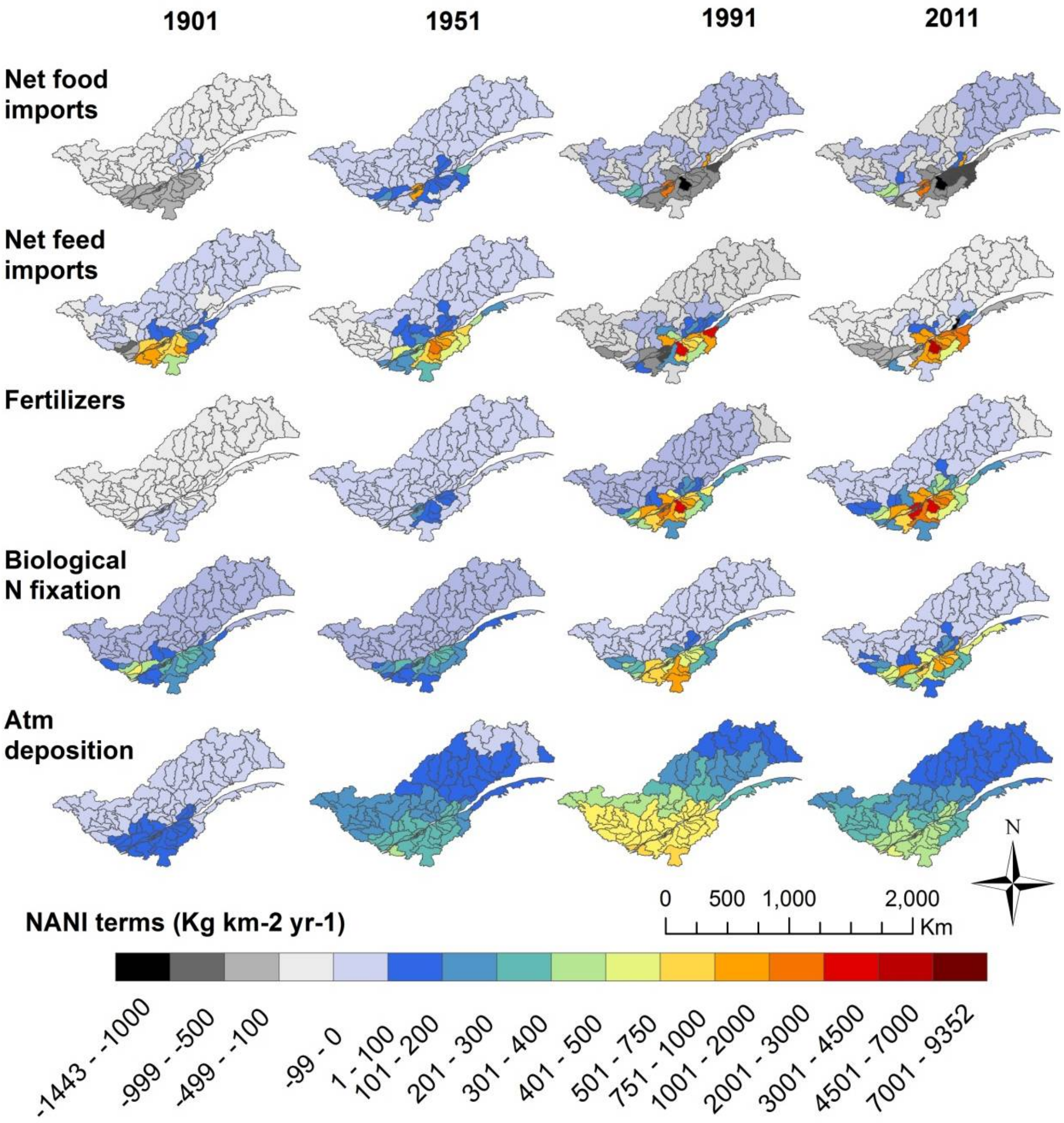

Figure 5. NANI terms in 1901, 1951, 1991 and 2011. Negative values signify net exports of N through food and feed (or zero fertilizer application). A similar map for P can be found in SI, figure S1.

Fertilizers

N inputs to the SLB from synthetic fertilizers increased over the century, but a marked 20-fold overall increase occurred between 1951 and 1991 (Figure 3a). Regionally, these trends are even more impressive (Figure 5). P fertilizer application followed approximately the same pattern over space but increased use started 20 to 30 years earlier (Figure 3b, 4 and S1). P inputs from fertilizers went from ~0 to 67 Kg P Km^{-2} (in the basin as a whole) between 1901 and 1991 but then decreased to 45 Kg P Km^{-2} in 2001 before increasing up again to 56 Kg P Km^{-2} in 2011 (Figure 1) whereas N continuously increased since the last half century.

Biological N Fixation

We observed a large difference between the biological fixation estimates derived from the yield- versus area-based approaches (see Supplementary Information Figure S2 and S3). Estimates using the yield-based approach appear more accurate (Hong et al 2013; this study Figure S3) and are therefore the ones reported in Figures 2 through 4. Figure 3a shows that biological fixation was an important N source to the SLB in 1901 contributing to 72 Kg N Km^{-2} on average (39 Gg N in total). This remained relatively stable through to 1951 and was mainly driven by fixing crops in non-alfalfa hay mixtures (clovers) and pasture. Since 1951, biological N fixation increased to a peak of 206 Kg N Km^{2} (111 Gg N in total) in 2001 due to intensive cultivation of alfalfa and, more recently, soya.

Atmospheric N deposition

Atmospheric deposition played a major role in N inputs to the SLB, especially between 1951 and 1991 (Figure 3a). From 1901 to 1991, atmospheric deposition in the SLB increased nearly 6-fold going from 91 to 418 Kg N Km^{-2} yr^{-1} (38 to 226 Gg) after which it declined to 269 Kg N Km^{-2} yr^{-1} (145 Gg) by 2011 (Figure 3a). Atmospheric N deposition has been an ubiquitous source of N input in the SLB affecting even remote regions in the north mainly characterized by forested areas (Figure 5). Even though absolute atmospheric N deposition in those watersheds is small, it often represents the dominant source of input (up to ~100%). At its peak in 1991, atmospheric N deposition ranged from 161 Kg N Km^{-2} in northern watersheds to 795 Kg N Km^{-2} yr^{-1} in southwestern watersheds. In 2011, deposition rates had decreased to a range of 103 to 511 Kg N Km^{2} yr^{-1}. With fairly high rates in the south, atmospheric deposition can play a large role in total N inputs even in watersheds with important agricultural activities. For example, deposition in the last 4 decades contributed ~18% in the Lake Champlain watershed.

Riverine export

NANI and NAPI explain 87% and 71%, respectively, of the variance in riverine N and P export across space and time (Figure 6). The intercepts of the linear relationships suggest that under pristine watershed conditions, 105 kg N Km^{-2} yr^{-1} and 15 kg P Km^{-2} yr^{-1} would be exported to rivers. Similarly, the slopes suggest that on average, ~15% of NANI and ~5% of NAPI in the watersheds of the SLB are exported to rivers (Figure 6). However, these slopes seem to be largely driven by watersheds with high NANI and NAPI. Indeed, fractional N export across the 23 watersheds for which we had riverine data varies between 11% and 68% with a median of 22%. Fractional P export shows a median of 17% and a much more variable pattern with a range of 3% to 173%.

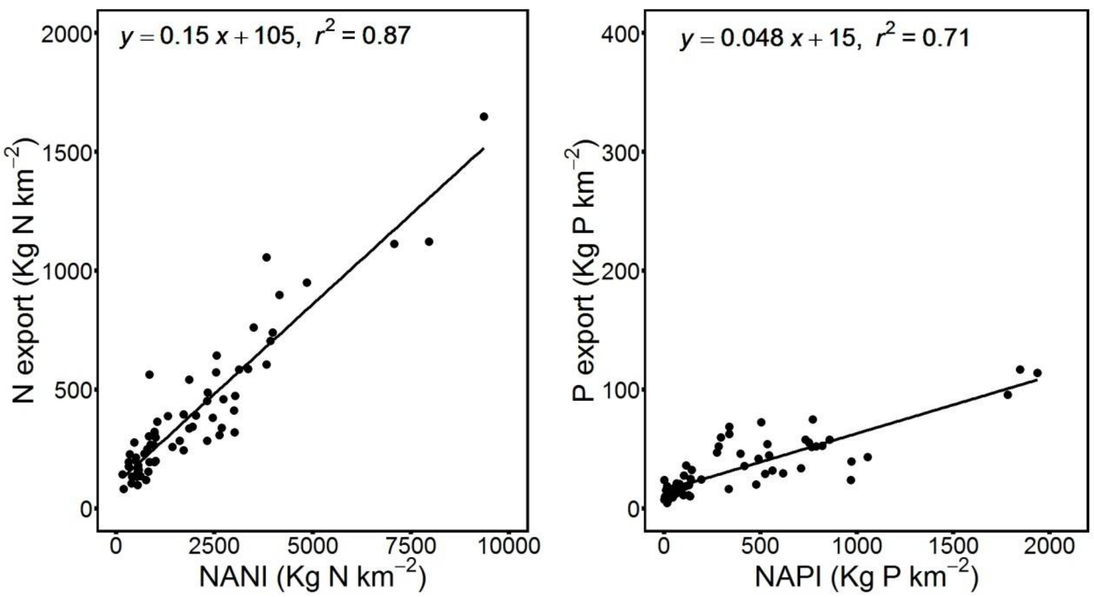

Figure 6. N and P riverine export at the outlet of 23 watersheds of the SLB in 1991, 2001 and 2011 relative to NANI and NAPI. *N=62.*

Discussion

In this study, we track the N and P use and changes in multiple watersheds of the SLB over the last century. We observed that some watersheds were already sites of intensive N and P use even at the beginning of the 1900's, that wide-scale legislation had immense positive repercussions on reducing nutrient fluxes, and that changes in farming practices (to more intensive animal production) influenced spatial trends in N and P inputs the most. Overall we found a 4.5- and 3.8-fold increase of N and P inputs in the entire SLB over the last 110 years, which is similar to global trends (Beusen et al. 2016; Glibert et al. 2014). However, there is a vast range in the relative increase across watersheds, from ~0 to 12-fold for N, and ~0 to 34-fold for P, as a function of the different practices and influences over this time frame. The highest rates of change in NAPI mainly occurred in northern watersheds where absolute inputs were very low in 1901, so that any increase led to a large relative change. For NANI, highest rates of change occurred in agricultural watersheds in the south central region. The watershed with most elevated inputs for NANI and NAPI in the SBL (9351 Kg N Km^{-2} yr^{-1} and

1938 Kg P Km^{-2} yr^{-1} respectively) is the highest reported from studies conducted on similarly sized watersheds in the American Northeast and around the Great Lakes [*Boyer et al.,* 2002; *Han et al.,* 2011]. However reports of NANI estimates on smaller watersheds in the UK and China have shown higher inputs (up to 25 000 Kg N Km^{-2} yr^{-1}) (Gao et al. 2014; Swaney et al. 2012).

The most dynamic shifts in NANI were the increases in atmospheric deposition and fertilizer use, which began in the 1950's and 60's respectively. Overall rates of atmospheric N deposition in the SLB follow the same trend as observed in other regions of the world (Boyer et al. 2002; Hägg et al. 2012; Han and Allan 2012; Schaefer and Alber 2007b). In terms of magnitude, atmospheric deposition has since the 1950's been the most important NANI term (Figure 3a); however it has also seen the most dramatic declines since the 1990's. Indeed a 35% reduction has been observed and is a direct consequence of the amendment of the Air Quality Agreement, which resulted in the reduction of NOx emissions [*Air Quality Agreement*, 2012] thus showing the widespread impact of legislation for positive change.

In the case of P, one of the most important and stable NAPI terms overall was net feed import to the SLB. The most dramatic increase was in fertilizer use (Figure 3b). All other terms contributed a relatively small amount to total NAPI. Legislation passed in the 1970's and 2010 that banned the use of P in clothes and dishwasher detergent respectively, has led to a reduction in this term to rates similar to those observed at the beginning of the century (overall 8.54 Kg P km^{-2} in 1971 to only 1.08 Kg P km^{-2} in 2011). Albeit a minor component of NAPI, the reduction in detergents may nevertheless have significant consequences in terms of their impact on water quality at local scales [*Lee and Jones,* 1986].

Changes in agricultural practices in both the first and second half of the century played a significant role in the increase of both NANI and NAPI in the SLB. Both were a result of animal intensification, with increased dairy production in the first half, while the second was driven by increased hog and chicken production combined with greater fertilizer use for feed (Table S4). Similar patterns of overall increase over time were also observed in both the Lake Michigan and Erie basins for N and P respectively (Han and

Allan 2012; Han et al. 2012) but these increases were a function of different farming types. Those basins experienced a rise in crop and grass production relative to animal and human needs with trends towards higher feed export.

Another important driver of NANI and NAPI in several basins is human population growth combined with change in their diets, both in terms food choice and amount. In the SLB, the increase in protein consumption per capita between 1901 and 2011 went from 96 to 111 g day^{-1} [*Statistic Canada,* 2013a; *USDA-CNPP*, 2015] and has thus impacted net imports of N and P through food demand. However, this overall change is minor when compared to the nearly 2-fold increase in human N food consumption per capita over the last 30 years in Lake Dianchi basin, China due to a diet richer in animal protein (Gao et al. 2015). While the diet shift was the largest driver for changes in NANI in the afore mentioned study, changes in net food imports in the SLB over the century were more related to increased population densities in urban centers. For example, net food import in the Montreal Urban watershed increased by ~30-fold for N and ~15-fold for P over the study period. Increasing population densities have important implications for the management of point source pollution of both N and P. Zhang et al. (2015) refined the NANI model to distinguish between point and non-point sources of loading and showed that urban domestic N sewage discharge, although a small component of NANI, was a much more important explanatory variable of riverine loads than non-point sources. This can be explained by large and variable retention of diffuse N on the landscape (denitrified or stored in biomass and soils) relative to minimal N removal from sewage sludge (Zhang et al. 2015).

We've shown that NANI and NAPI correlate very well with riverine N and P exports, in multiple watersheds in the SLB. The coefficients for the slopes and intercepts of our regression analyses are in accordance with similar studies across the globe (Han et al. 2011; Hong et al. 2012; Schaefer and Alber 2007a; Zhou et al. 2014) and our median fractional N export of 22% is very close to the mean value of 25% generally observed across NANI studies (Swaney et al. 2012). Studies using global process-based models also report similar values of fractional N and P export for our region (Tysmans et al. 2013) and globally (Beusen et al. 2016). The variance in fractional N and P export across years and watersheds in our study (11 to 68% and 3 to 173% for N and P respectively) could be explained by climate (Han et al. 2009; Howarth et al. 2006), landscape features such as the number of water bodies and dams which favor N and P retention (Harrison et al. 2009; Schaefer and Alber 2007a; Zhang et al. 2015) as well as modes of delivery (point vs non-point sources) (Zhang et al. 2015). Warmer temperatures and flatter landscapes in more agricultural watersheds may favour enhanced denitrification losses to the atmosphere by microbes, which results in greater N "retention" and lower fractional exports (Howarth et al. 2006). Irrigation has also been suggested as an important factor of nutrient retention in intensive agricultural watersheds (Lassaletta et al. 2012). Human removal of water from rivers (and thus nutrient removal) for irrigation may explain the lower fractional export we observed in the most agriculturally intense watershed in this study, the Yamaska, for example. Another possibility however is that high fractional export may be explained by N and P stored in soils and aquifers due to historical activities, known as legacy effects, that are being flushed to rivers particularly during wet years (Chen et al. 2014; 2015; Sharpley et al. 2013).

Uncertainties

The cross-check validation of our budgets over 3 decadal years of riverine data has shown that our estimates were rather successful at capturing regional and temporal variability. However, uncertainties remain in the generated information due to data limitations and methodological challenges. For example, we have shown that estimates of biological N fixation can vary widely between area- versus yield-based approaches, particularly when non-alfalfa hay mixtures represent a large proportion of the fixing crops, which was the case in the early part of the century in the SLB (Figure S2). Moreover, we recognize biological N fixation may be an underestimate since we did not account for the belowground contribution (Anglade et al. 2015). Another source of uncertainty resides in our historical estimates of the net feed import term. Livestock consumption has likely increased over time due to agricultural practices. While we were able to track the changes in animal weights and production rates throughout the century, intake rates likely also changed but were kept constant due to data limitations. Accounting for variable coefficients over time would have likely reduced N and P inputs from feed imports in the early century and thus strengthened the total increases in NANI and NAPI over the whole period.

Several studies have observed a drop in the application of P fertilizers through the 1980's and 1990's (Hale et al. 2013; Han et al. 2012; MacDonald and Bennett 2009). While our estimates concur with this reduction, we also captured an increase between 2001 and 2011(Figure 3b). Indeed, purchase of P fertilizers clearly increased in the last decade in the provinces of Quebec and Ontario in Canada [*Statistic Canada,* 2014a]. Fertilizer application in 2011, may have been overestimated if amount purchased was not totally applied within the same year, as it was assumed in our calculations. One possible reason for this is that farmers may have stocked more P fertilizer given increasing costs (Mitchell 2008) or potential global P shortages (Cordell et al. 2009; Elser and Bennett 2011). Alternatively however, the high value of crops in global markets (Babcock and Fabiosa 2011) may have stimulated more fertilizer application. Indeed, between 2001 and 2013, prices of major crops nearly doubled in Quebec (129 to 267$CAN per tonne for corn) [*Financière Agricole du Quebec*, 2014]. Thus a recent increase in application is both plausible and non-negligible given its dominant role for NAPI to the SLB.

Conclusion

Although NANI and NAPI models have been used primarily to assess modern anthropogenic inputs to basins around the world [*Han et al.,* 2011; *Hong et al.,* 2012; *Swaney et al.,* 2012; among others], our analyses of N and P budgets to the 76 watersheds of the SLB throughout the last 110 years have increased our comprehension of the pronounced impacts of changing human activities on N and P inputs to lands and waters. By tracking changing yields of animal products, shifts in land use, population growth and fertilizer use over time, we refined the NANI and NAPI approach for historical reconstructions at smaller spatial scales for SLB. This lead to a better analysis of the link between human activities and the increased N and P fluxes to adjacent rivers over time.

In terms of successful reductions of inputs to land, our study has highlighted the importance of large-scale legislation (such as bans on P in detergents and the Clean Air Act that controlled atmospheric emissions of N) as a successful mechanism for reducing nutrients. This work provides insight for N and P management at the local scale by quantifying watershed-specific sources of concern while also broadening our understanding at the larger regional scale about the impacts of social transitions on the disruption of the N and P cycles. Research on how different watersheds respond to changes in climate and land use legacies in terms of N and P export to receiving waters represents an opportunity to broaden our comprehension of land-water linkages and provide more targeted solutions to aquatic eutrophication.

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Supplementary Information

Contents of this file

Introduction

The following texts and figures supplement the methods and results presented in the main text. Texts S1 and S2 give further details on methodologies to estimate historical inputs of N and P through fertilizer application and to adjust animal population accounting for slaughtered animals and life cycles. Text S3 and corresponding figures (Figures S2 and S3) compare the results derived from two different approaches to estimate biological N fixation through time. Figure S1 presents NAPI terms through time as complementary information to the NANI figure (Figure 4) in main text. Tables S2 and S3 presents coefficients that were used to calculate detergent P inputs. Finally, Table S4 presents human and livestock populations for the entire SLB throughout the century.

Text S1. Methods - Fertilizers

Canadian county expenditures of fertilizers were unavailable for years 1951 and 1961 (Canada Dominion Bureau of Statistics 1951, 1961), so tonnages of generic fertilizers purchased in each county were used instead. Fertilizer tonnage sales in Quebec and Ontario were reported for each province beginning in 1934 (Canada Dominion Bureau of Statistics 1935) while sales in Vermont and NY state were retrieved for year 1941 from Mehring (1945). However National sales were available for Canada since 1921 and from 1901 for the US (USDA-CRB 1966). Hence, provincial (or state) tonnage sales were estimated by applying the percentage of change in national sales from 1934 to 1921 and from 1941 to 1901 for Canada and the US, respectively.

Text S2. Methods - Net Food and Feed Imports

Adjusted livestock populations - Sources and disaggregation methods (when needed) to estimate slaughtered animals per province

Data for slaughtered pork and lamb were available at the provincial level for years 1920 to 1990, beef and veal for years 1940 to 1990 and chickens and turkeys for 1941 to 2011 (Statistics Canada 2013b, c, d). However, slaughtered pork, lamb, beef and veal were also available at the national level on a longer time span, from 1920 to 2011 (Statistics Canada 2013f). Slaughtered pork, lamb, beef and veal were disaggregated to the provincial level for years 1991, 2001 and 2011 using the province to nation ratio of slaughtered animal to inventory in 1990. Similarly, slaughtered beef and veal were disaggregated to the provincial level for years 1921 and 1931 using the province to nation ratios of slaughtered animals to inventory in 1941. For years 1901 and 1911 (as well as 1931 for chickens and turkeys), slaughtered animals were estimated using the province to nation ratios of slaughtered animals to inventory in the earliest year for which we had data. Table S1 presents final estimates of slaughtered animals for both provinces of Quebec and Ontario, Canada.

Text S3. Comparison of biological N fixation estimates: Yield- versus Area-based approach

The yield-based approach, when compared to the area-based approach, led to very different estimates of biological fixation, particularly in the early century (Figure S2). Yield-based estimate of total biological fixation is then nearly 25% of the area-based estimate. This difference is mainly driven by the assumption that only 25% of non-alfalfa hay mixtures is composed of fixing crops such as clovers as well as by the proportional importance of non-alfalfa hay mixtures in the early century. The difference between the two approaches is thus attenuated in the second half of the century with the increased cultivation of alfalfa and soya and the concomitant decreased areas of non-alfalfa hay mixtures (Figure S2). The yield-based approach also slightly increases the fit of NANI with riverine N export (Figure S3). This is consistent with results from Hong et al. (2013) and Han and Allan (2008) and suggests that the yield-based approach lead to more realistic estimates of biological N fixation.

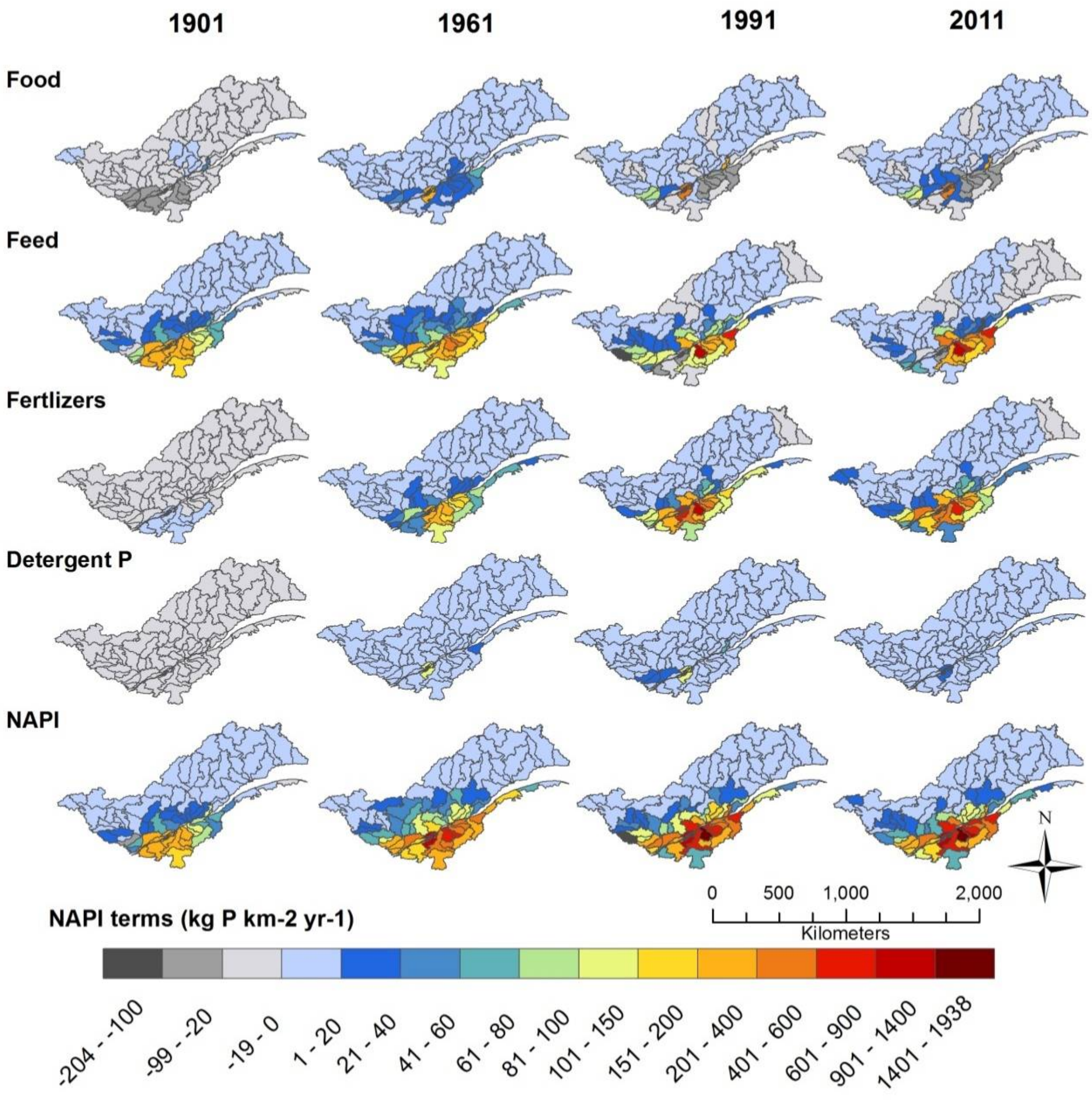

Figure S1. NAPI terms in 1901, 1961, 1991 and 2011. Negative values signify net exports of P through food and feed (or zero fertilizer application and detergent use). Ramp color in legend was constructed proportionally to the ramp color of the corresponding figure for NANI presented in main article (Figure 4), so that trends can be comparable.

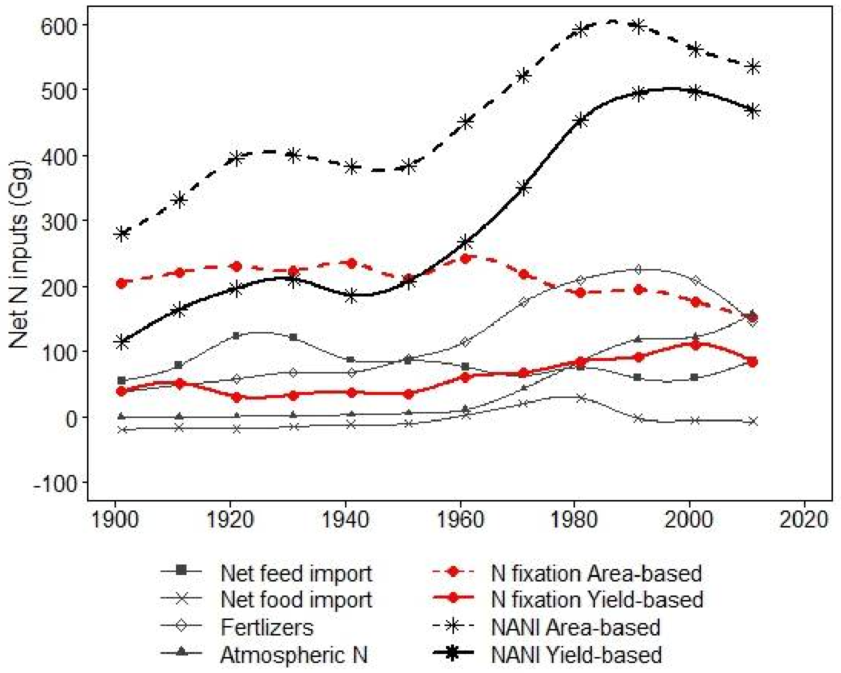

Figure S2. Comparison of NANI and biological N fixation derived from fixation estimates derived from the area-based approach [*Boyer et al.,* 2002] versus the yield-based approach [*Hong et al.,* 2013; *Han and Allan,* 2008].

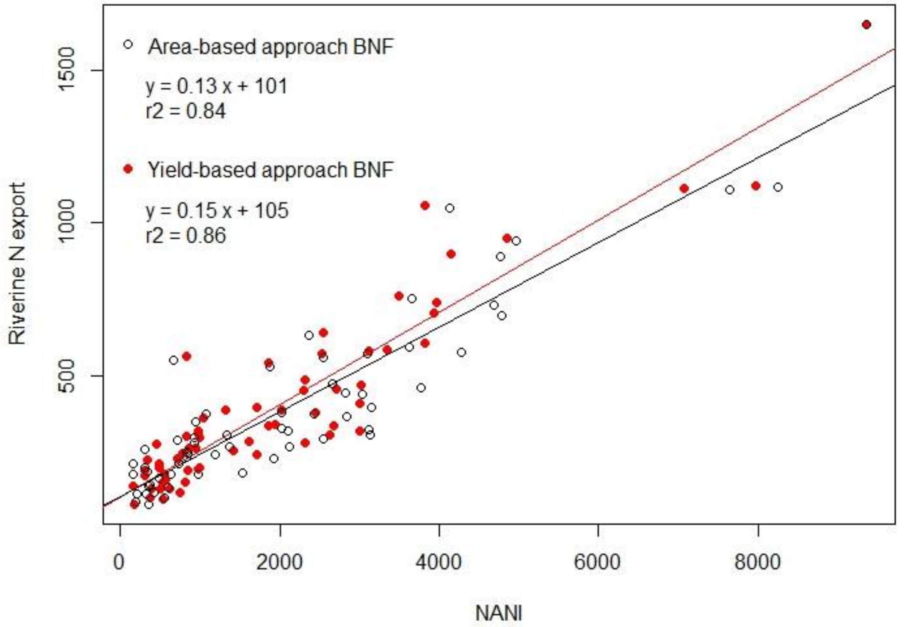

Figure S3. Comparison of fits between riverine N export and NANI with biological N fixation being derived from Area- and Yield-based approaches. Both axes are in Kg N km^{-2} yr^{-1}.

Tableau SI Estimated slaughtered animals per province.

years	Beef and veal	Beef	Veal	Hog	Sheep and lamb	Chicken	Turkey
				Québec			
2011	487596	288849	198747	8684710	124491	171016000	4339000
2006	562852	339660	223192	8896831	135937	164910000	4557000
2001	555865	322692	233173	8452908	119255	167393000	4542000
1996	539526	293045	246482	6197403	92276	141701000	4817000
1991	543757	254158	289599	5848373	92771	118036000	4746000
1986	780163	367753	412409	5913995	80447	102886000	4508000
1981	629720	295041	334680	5842346	63422	86914000	4393000
1971	803202	289426	513776	2254013	42809	73258000	5476000
1961	849278	303261	546017	1311564	152709	36520000	1771000
1941	831815	267737	564078	1455619	251917	5420000	169000
1931	563178	116576	446602	834588	359928	na	na
1921	397753	112129	285624	571979	374723	na	na
				Ontario			
2011	950601	880692	69910	6764443	86310	204957000	8584000
2006	1114121	1035613	78508	6929662	94245	202450000	8933000
2001	1065897	983878	82019	6583894	82679	200298000	8495000
1996	980184	893483	86701	4827102	63975	161795000	9274000
1991	876786	774919	101867	4555245	64318	140855000	8038000
1986	1165803	1014179	151624	4385807	33220	124238000	6876000
1981	1317395	1198498	118897	4537482	74050	106900000	7153000
1971	1289849	1100178	189671	3563083	186023	78748000	7330000
1961	1002363	817930	184433	2489873	207284	50287000	4456000
1941	837107	564374	272732	2713113	394842	15603000	628000
1931	465041	302583	162458	1466726	557435	na	na
1921	394941	291041	103900	1925674	593764	na	na

Tableau SII. P content of laundry detergent over time.

		1941	1951	1961	1971	1981	1991-2001	2011
Laundry detergent per capita (kg/per capita/yr) [1]		0.7945	1.816	2.27	5.94	6.67	6.67	6.67
% of P by weight	NY and VT	0.15	0.15	0.15	0.15	0.005	0.005	0.005
	Canada[2]	0.15	0.15	0.15	0.087	0.022	0.022	0.005

[1] Per capita consumption was interpolated to fit decadal canadian census

[2] From Chris Knud-Hansen 1994. http://www.colorado.edu/conflict/full_text_search/AllCRCDocs/94-54.html. Value for 2011 was retrieved from Canadian environmental protection act. http://laws-lois.justice.gc.ca/eng/regulations/SOR-89-501/page-1.html.

Tableau SIII. Changes of dishwasher detergent use. P content in detergent and proportion of households equipped with automatic dishwashers over time in Quebec. Ontario and the US.

Year	Dishwashing detergent use per capita (spoons/per capita/yr)[1]	P content (kg P/Spoon)[3]	Proportion of households equipped with automatic washers			P dishwashing detergent consumption per captia (kg-P/ per capita/ yr)		
			USA[1]	Qc[2]	On[2]	USA[1]	Qc[2]	On[2]
1941	364	0.0009687	0.024	0.014	0.013	0.008	0.005	0.005
1951	364	0.0009687	0.044	0.026	0.024	0.016	0.009	0.009
1959	364	0.0009687	0.150	0.089	0.083	0.053	0.031	0.029
1961	364	0.0009687	0.190	0.113	0.105	0.067	0.040	0.037
1969	356	0.0009687	0.375	0.222	0.208	0.129	0.077	0.072
1971	359	0.0009687	0.425	0.252	0.236	0.148	0.088	0.082
1981	327	0.0009687	0.788	0.467	0.437	0.249	0.148	0.138
1986	291	0.0009687	0.825	0.489	0.458	0.233	0.138	0.129
1991	291	0.0009687	0.825	0.489	0.458	0.233	0.138	0.129
1996	291	0.0009687	0.825	0.489	0.458	0.233	0.138	0.129
2001	291	0.0009687	0.825	0.517	0.480	0.233	0.146	0.135
2006	291	0.0009687	0.825	0.575	0.534	0.233	0.162	0.151
2011	291	5.56724E-05	0.825	0.574	0.574	0.013	0.009	0.009

[1] From Han et al.. 2012. Detergent use per capita and proportion of households equipped with dishwashers were interpolated to fit years of Canadian censuses.

[2] From Statistic Canada (2014d).for years 1996 to 2011.http://www5.statcan.gc.ca/cansim/a26. Previous years were estimated proportional to the changes in the US.

[3] From Canadian environmental protection act. http://laws-lois.justice.gc.ca/eng/regulations/SOR-89-501/page-1.html.

Tableau SIV. Human and livestock population in the SLB

Year	Human	Milk cow	Beef cow	Hogs and pigs	Chickens and turkeys	Sheep	Horse	Goats
1901	1648898	1306208	368452	761762	3083374	1073272	581633	178
1911	2002712	1655396	409832	886848	3328908	761212	543286	799
1921	2361199	1963019	522689	816140	4530932	1075574	521342	834
1931	2874255	1972594	540233	829924	5657471	912600	500458	1823
1941	3331882	2066781	370239	913154	6657703	602210	439387	1581
1951	4055681	2016831	351482	1172191	8865976	339113	296633	1979
1961	5422706	2029997	695676	1237865	14340812	216998	117064	4722
1971	6027764	1926853	505826	1355406	25111638	104811	64797	3215
1981	6438403	1706314	438389	3309390	22137136	133283	39122	21500
1991	6895963	1421953	454143	3086290	23742884	156028	42720	18795
2001	7237479	1230167	490222	4357260	29715743	274041	44423	30933
2011	7903001	1090584	384213	4203647	29357770	298686	50526	53632

Chapitre II. Influence des caractéristiques du paysage, des barrages, des lacs et du climat sur le transport de l'azote et du phosphore dans l'ensemble du bassin versant

The influence of landscape features, dams, lakes, and climate on uncoupling nitrogen and phosphorus transport throughout the watershed

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Abstract

Anthropogenic activities have led to increased transfers of nitrogen (N) and phosphorus (P) to surface waters where changes in the absolute amounts and in N: P ratios threaten water quality. However, predicting riverine nutrient loads from watersheds remains a challenge, particularly when trying to account for retention processes within the basin. In this study, we used an integrative empirical approach to quantify the relative transport of N and P through landscape compartments under a variety of climate regimes. Using a linear mixed model approach in a multiple regression, we identified where N and P cycles are decoupled within a watershed and by what relative extent. Precipitation patterns and water retention capacity within the landscape were the features that most strongly influenced nutrient export from land to water, where P was preferentially retained in the landscape over N when water retention capacity was highest. Lakes and reservoirs also emerged as features that differentially influenced nutrient fluxes, where lakes preferentially retain more P over N and reservoirs act as sources. Furthermore, our data suggested the presence of an important legacy effect for both N and P in terms of export to surface water. By empirically identifying the magnitude of the decoupling capacity of each driver, we provide valuable information for better understanding the potential N: P ratios in receiving waters.

Introduction

Anthropogenic activities such as urban development and the widespread use of fertilizers for industrial agriculture have led to increased transfers of nutrients to surface waters, often resulting in their eutrophication (Carpenter et al. 1998). Changes in the absolute amounts of nutrient influx influence the productivity of aquatic ecosystems while alterations in N: P export ratios modify community structure (Sterner and Elser 2002) potentially favoring toxic species of cyanobacteria (Scott et al. 2013; Van de Waal et al. 2014), with all of these effects impinging water quality (Dodds et al. 2009). Predicting the relative nutrient loads from multiple sources in a watershed to major rivers remains a challenge that is further compounded when trying to simultaneously account for the retention processes within the basin (Alexander et al. 2008). Understanding the relative roles of the different landscape and climatic features that influence nutrient transport is essential to provide management guidance to conserve water quality.

During their passage through soils, most anthropogenic N and P surpluses are differentially retained in various landscape compartments (Jarvie et al. 2013b; Sharpley et al. 2013; Van Meter and Basu 2015), potentially altering relative export. Firstly, N can be lost permanently to the atmosphere through denitrification (Knowles 1982), whereas gaseous P loss is minimal. Furthermore, nitrate moves more freely in water than phosphate given its higher solubility (Frank et al. 2000; Hill et al. 1999). Phosphate tends to be adsorbed to soil particles and often enters water in particulate form (Holtan et al. 1988; Ockenden et al. 2016), although transitions to fluvial loads dominated by dissolved forms were also recently observed in the Great Lakes region, likely as a result of buffer strip implementations (Joosse and Baker 2011). Such differential export of N and P and of chemical forms (particulate or dissolved) can be influenced by multiple regional and temporal drivers (Collins et al. 2017; Seitzinger et al. 2005). Yet, few studies have specifically aimed to identify how different climate and landscape features, either natural or human-made, uncouple transfers of N and P from the watershed to the receiving waters, and within aquatic networks.

Transport and retention of nutrients across watersheds and within aquatic networks are largely influenced by hydraulic velocity and soil/sediment contact rates

(Harrison et al. 2009; Nixon et al. 1996; Vought et al. 1994). Soil type, land use cover, catchment geomorphomology and climate influence water residence time as it travels from land to water. One metric that potentially captures the integrative influence of these features on the movement of water through the landscape is the annual water-balance of a catchment (Budyko 1974) that represents the proportion of precipitation that makes its way to the outlet as runoff (Runoff: Precipitation ratio). Given the widely applied framework of Budyko (Roderick and Farquhar 2011; Zhou et al. 2015), the catchment water balance varies as a function of precipitation, evapotranspiration and watershed characteristics (see equation in Zhou 2015), and thus integrates climate and catchment water retention capacities at the basin scale. In that sense, the Runoff:Precipitation ratio may act as a simple metric that help predict nutrient transport downstream. Changes in precipitation patterns will also influence delivery where wet years tend to favor downstream nutrient transfers (Howarth et al. 2006; Zhou et al. 2014), with extreme events potentially influencing the transfer of different nutrient forms (Ockenden et al. 2016).

Nutrients that reach the receiving waters continue to be actively transformed throughout the aquatic network (Newbold et al. 1981; Wollheim et al. 2006). Indeed surface waters, per unit area, are among the most important sites of nutrient retention (Seitzinger et al. 2010; Harrison et al 2009). This is heavily influenced by high water-sediment contact in small streams (Mulholland et al. 2008) as well as increased water residence times in larger lentic rivers (Saunders and Kalff 2001). Wetlands and lakes have even longer water residence times that promote efficient N removal through denitrification and P sedimentation (Hansen et al. 2018; Kirchner and Dillon 1975; Larsen and Mercier 1976). Human-made reservoirs also trap particles and nutrients (Alexander et al. 2008; Van Cappellen and Maavara 2016; Wollheim et al. 2008) and are increasingly recognized as distinctive from lakes in terms of ecological functioning (Hayes et al. 2017; Thornton et al. 1990). For example, reservoirs have larger drainage ratios than lakes, increasing their material influx which results in their retaining a disproportionate amounts of P (Maavara et al. 2015) as well as N per unit area as compared to lakes (Harrison et al. 2009). However, lakes and reservoirs can also become net sources of nutrient fluxes when stores are mobilized and exported, as shown at the seasonal time scale for N in lakes (Wurtsbaugh et al. 2005) as well as for both nutrients and ecosystems at time frames ≥ 1 year (Nowlin et al. 2005; Powers et al. 2015; Teodoru and Wehrli 2005). For example, on the Danube River, the iron Gate I Reservoir was shown to increase N and P loads by 18% and 13%, respectively, likely through internal loading (Teodoru and Wehrli 2005). In the mid-western US, lakes and reservoirs were shown to introduce time lags in nutrient transport through retention (both N and P) in high flow years and subsequent gradual release downstream (Powers et al. 2015; Powers et al. 2014).

Previous studies have explored how climate, geomorphology, or land use affect the delivery of N or P downstream (Harrison et al. 2009; Howarth et al. 2012; Seitzinger et al. 2010), yet few have identified the relative importance of these features on N versus P export. Here we aim to assess how different drivers, categorized as "land to water" and "within aquatic networks", influence downstream N and P transfers. More specifically, we asked how watershed slope, landscape water retention capacity, climate patterns, and lentic water bodies (lakes and reservoirs) alter the relative delivery of N versus P as well as their different chemical forms to rivers. To evaluate this, we reconstructed annual anthropogenic N and P surpluses for 18 moderately large watersheds of the St-Lawrence Basin across a gradient of land use and geomorphic characteristics and calculated annual loads of N and P at their outlet from 1985-2011. We tested the following hypotheses: 1) that wet years will result in the increased delivery of both nutrients, but that flashier precipitation patterns will favour relatively higher P inputs due to increased erosion; 2) that lakes and reservoirs will settle relatively more P than N due to the stronger impact of reduced velocity on particle settling; and 3) that catchment water retention capacity will better predict nutrient export over using annual runoff alone, since it would capture both the effects of climate and landscape features that regulate water flow.

Methods

Study area

The 18 watersheds used in this study drain part of the St. Lawrence River Basin and are entirely located in the province of Quebec, Canada. These watersheds range in size from 2567 to 21 065 km^2, have different land use and landscape features, and are subject to different climate conditions and geological properties [Figure 1; *Natural Resources Canada,* 2003]. Watersheds on the right bank of the St-Lawrence, situated on the Interior Plain (Figure 1), are largely agricultural with a number of small dams; whereas basins to the north, on the left bank are located mostly on the Canadian Shield, covered largely by boreal forest, with many lakes and some with large reservoirs for hydropower. Given the St. Lawrence Basin is located north of 40°N, it is subject to a strong seasonality that promotes snow pack accumulation in winter and an important spring freshet.

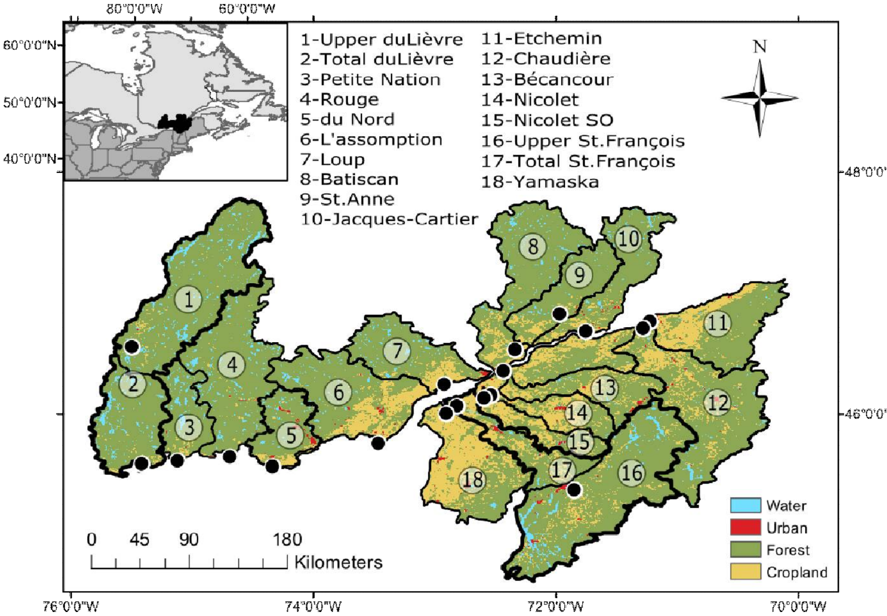


Figure 1. The 18 watersheds considered in this study. General land use categories and water quality monitoring stations are shown.

Riverine N and P exports

Annual riverine exports of total nitrogen (TN) and total phosphorus (TP) were estimated from 1985 to 2011 for all 18 rivers. Different chemical forms were considered: total N (TN), dissolved inorganic N (DIN; by summing NO_x+NH_3), Organic N (ON; by subtracting DIN from TN), total P (TP), total suspended P (TSP) and total dissolved P (TDP). Annual riverine N and P loads of all chemical forms (with the exception of ON) were calculated from daily discharge (*Centre d'Expertise Hydrique du Quebec*; *Environment Canada*, 2014) and monthly or bi-monthly nutrient concentrations [*MDDEFP-BQMA*; *Environment Canada*, 2014b], using LOADEST (Runkel et al. 2004). LOADEST is an approach that allows for flow-weighted interpolations of the discrete concentration measurements, thus reducing bias by accounting for exceptionally high or low daily discharge events. From 9 potential models tested, the best model was selected based on the corrected Akaike information criterion (AICc). For each river and each focal year, models were calibrated over a 5-year time interval (i.e., from 1994 to 1998 for the focal year 1996) before being used in combination with daily discharge to predict annual loads. The LOADEST procedure was conducted in R with package loadflex (Appling et al 2015). When gauging stations were not located where water chemistry was sampled, discharge was estimated by multiplying the specific discharge (m^3 km^{-2}) at the gauging station by the drainage area (Km^2) of the monitoring site. Specific riverine load (kg N or P km^{-2} yr^{-1}) was calculated by dividing annual load by drainage area.

N and P budget construction

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

Geospatial data

Mean watershed slope was calculated from digital elevation models at 30 m^2 resolution. Surface area of lentic water bodies (reservoirs and lakes) was retrieved from Natural Resources Canada (2016b). To estimate total lake area per watershed, reservoir surface area was subtracted from the lentic total. Specific information on reservoirs (location, volume, area, dam height) was retrieved from *Centre d'Expertise Hydrique du Quebec* (2017). Mean reservoir depth was calculated by dividing volume with area. Volume Development (Dv), calculated as three times the depth ratio (mean depth over maximum depth; Kalff 2002), was used to estimate reservoir morphometry (Table 1). *Dv* values around 1.3 reveal systems with shallow margins and an anomalous deep hole while impoundments with *Dv* >~2 have flat floors and steep sides (Kalff 2002). Dam height was used as a proxy for maximum depth. Reservoirs mean depths and *Dv* were then calculated as an integrative mean per watershed. The number of dams within a basin was normalized per unit area (km^{-2}) for cross comparison among watersheds.

Annual runoff was calculated as the sum of daily discharge at the outlet. The coefficient of variation (CV) of daily runoff within a year (*CVflow*) was used as an indicator of flow regime. Similarly, we used the CV of daily precipitation within each year (*CVprec*) as a proxy of flashiness of rainfall events, arguing that high CV values represent years with flashier precipitation patterns. Annual and daily precipitation were obtained for the period of the present study (1986 to 2011) at a spatial resolution of 10 km using thin plate smoothing splines (Natural Resources Canada 2016a; McKenney et al. 2011). The annual water balance of catchments (or catchment water retention capacity) was estimated as a single variable through the annual *Runoff* to *Precipitation* ratio (*R: P*; Table 1). Calculations of all geospatial variables were conducted using ArcGIS 10.0.

Tableau I Variables tested in multiple regression models (lower table), symbols, units and data sources.

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

[1] Natural resources Canada (2003)

[2] MDDEFP-BQMA (Environment Canada, 2014)

[3] Centre d'Expertise Hydrique du Quebec (CEHQ 2017)

Statistical analyses

Factors that influence spatial and temporal variability of fractional export

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

Prior to conducting the multiple linear regressions, we used variance inflation factor (VIF) analysis to identify which independent variables were collinear (Blanchet et al. 2008; Graham 2003). VIF values greater than 5 or 10 suggests autocorrelation (Mason et al. 2003), and a threshold of 5 was used in this study to remove collinear variables. For the multiple regression analyses, the random structures of LMMs were identified and selected first. This was followed by a backward selection of predictor variables, using the corrected Akaike information criterion (AICc) to assess model performance (Zuur et al. (2009). All variables were log-transformed to meet normality assumptions of linear regression and fully standardized to allow comparison of model coefficients as indicators of the relative strengths of predictors.

We used two different approaches (or metrics) for comparing the N and P models. First, we considered the selection order of each predictor during the backward selection process to compare the relative influence of each driver on the export of N and P independently. Second, we did a more focused effort at comparing the influence of targeted variables on relative transfers of N and P. This was done by comparing standardized regression coefficients of specific model terms. To assess significant differences, the comparison was done using the standard errors of each coefficient to calculate z scores and p-values (Cohen et al. 2013). Additionally, variables not selected in the backward selection approach were tested in alternative models to explore their potential influence on N and P export. All analyses were conducted in R and LMM were fitted following (Zuur et al. 2009) using restricted maximum likelihood in the lme4 package [*Bates et al.,* 2012; *R development Core Team*, 2012].

Prior to the multiple regression approach, we also evaluated the sensitivity of each watershed to inter-annual variability in fractional N and P export. To remove long term trends and focus the analysis on annual patterns of variability only, we conducted linear regressions between log-transformed fractional export and time (year) for each watershed and kept the residuals (Fig S2). We then calculated the standard deviation (SD) of those residuals (detrended data) within each watershed.

Dominant chemical forms

We explored how the different chemical forms contributed to total N and P annual loads and how they varied over space and time. First, linear mixed models (LMM) were used to relate loads of all N and P chemical forms (TN, DIN, ON, TP, TSP and TDP) to NANI and NAPI, respectively. Since LMM is fitted with maximum likelihood and does not provide a traditional R^2, *Pseudo-*R^2s were calculated following Nakagawa and

Schielzeth (2013). Secondly, we calculated the contribution of DIN to total N load (%DIN) and of TSP to total P load (%TSP) and explored how that changed with level of watershed enrichment (NANI and NAPI). Finally, we assessed how the export of the different chemical forms was influenced by key spatial and temporal drivers. We used the predictors previously identified in the afore mentioned models of fractional TN and TP export to run multiple regressions explaining fractional export of each chemical form (i.e., FrDIN = DIN/NANI). As presented in section 2.5.1, we explored the spatial and the temporal structure of the dataset independently by centering all explanatory variables within groups (watersheds or years; Enders and Tofighi 2007).

Results

Downstream transport of NANI and NAPI in riversRiverine loads of TN and TP were well predicted by NANI ($R^2 = 0.62$) and NAPI ($R^2=0.68$), respectively (Fig 2a and 2b). Fractional N and P export however varied both across watersheds and among years within a watershed (Fig 2c and d). Mean fractional export over the 26-year period ranged from 16% to 69% across all watersheds for N (overall mean of 30%) and from 5% to 49% for P (overall mean of 16%) (Table 2; Fig 2c and d), thus highlighting differences in nutrient retention capacity among basins. We also observed inter-annual variability in fractional export within watersheds. Standard deviation (SD) of detrended fractional export ranged from 0.15 to 0.52 for N (mean of 0.25) and from 0.19 to 0.51 for P (mean of 0.37; Fig S3). This suggested that some basins were more sensitive to inter-annual drivers of export, particularly for P. Indeed, exceptionally large transfers were observed in some years where export exceeded net annual inputs (163% and 187% for N and P, respectively). Export in excess of annual inputs may be a function of the mobilization of legacy sources (Fig 2c and d). Conversely, in some years, fractional export was as low as 2% and 8% for N and P, respectively, suggesting higher rates of retention upstream or in the case of N, increased loss to the atmosphere via denitrification.

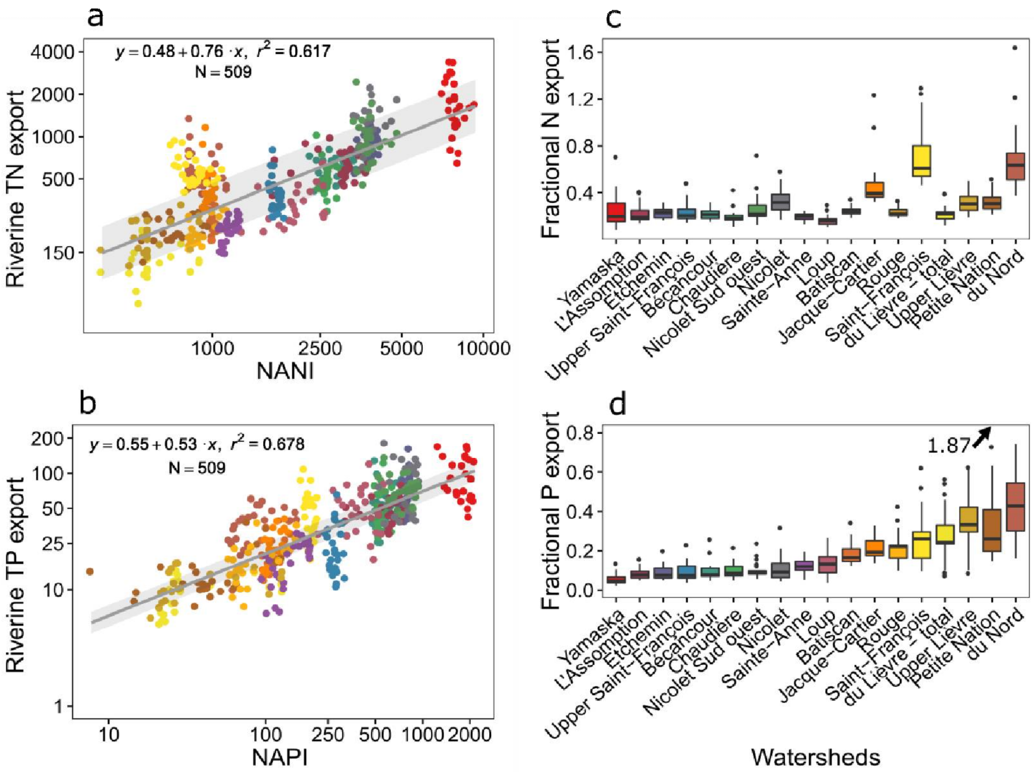


Figure 2. Log-Log Relationships between riverine N or P loads (Kg N or P km^{-2} yr^{-1}) and net anthropogenic N or P inputs to watersheds (NANI/NAPI; Kg N or P km^{-2} yr^{-1}), a) and b) respectively. Regressions were fitted using linear mixed models (LMM) with "Years" as a random factors varying between intercepts only. Variability in fractional N or P export across years and in different watersheds is explicitly shown on right panels, c) and d) respectively.

Range of independent variables

The 18 watersheds used in this study varied considerably in terms of climate, geomorphology, land-use, impoundment density as well as the differential morphometry of reservoirs (Table 2). This wide range allowed us to explore which features more strongly influence the relative retention or export of both nutrients. In terms of human made changes in hydrologic flow, dam density ranged from one dam every 4 km^2 of drainage area to approximately one dam per 100 km^2. Overall reservoir mean depth (ResZ) varied from 1.85 to 5 m across watersheds, whereas the Dv of reservoirs, from 1.43 to 4.68 suggesting not only a diversity in depth, but also in shape. While the long term mean of annual Precipitation did not vary much among watersheds (~1100 mm), annual Runoff varied considerably, from 607 to 1115 mm (Table 2) highlighting large differences in water retention capacity across basins likely due to the broad range in land use, reservoir density and geomorphometric characteristics. Indeed the range in the watershed Slope of 1.7 to 8°, likely influenced the observed R: P ratios, 0.53-0.83 (Table 2). The VIF analysis revealed strong autocorrelation of R: P with both annual Runoff and Precipitation (Table S1 and S2). R: P was therefore the only variable excluded in the backward selection to identify the best models of fractional export. In terms of response variables, fractional N and P exports varied much more over all years and watersheds (CV of 63% for N and 89% for P) than the molar N: P ratio did (CV of 47%). This low variability of N:P ratios is likely due to the high collinearity of N and P loads (Fig S4) where for high riverine loads of N, P was also highest.

Tableau II Average of different watershed characteristics over the study period (1985-2011). Bolded variables were tested as predictors of either spatial or temporal variability (or both) in fractional N and P export

		Spatial					*Spatial &Temporal*				*Temporal*							
Watershed name	Area (km^2)	**#dams**	**Reservoir Mean depth (m)**	Dv	**Lake area (km2)**	**Slope (°)**	**Runoff (mm)**	**Prec (mm)**	**R:P**	**Temp (°C)**	**CVPrec**	**CVflow**	NANI	NAPI	TN export	TP export	Fractional export (%)	
											(CV)		(Kg km^{-2} yr^{-1})				N	P
Batiscan	5023	131	2.00	1.83	553	5.5	816	1178	0.69	6.57	162	95	1009	115	250	22	24.7	19.1
Bécancour	2567	54	3.70	2.89	26	3.2	769	1175	0.65	7.84	156	132	2911	573	626	54	21.5	9.4
Chaudière	6600	220	2.15	2.09	462	3.5	713	1160	0.61	7.9	179	153	2682	561	517	55	19.3	9.9
du Lièvre - total	7099	218	5.00	2.18	426	5.1	866	1023	0.85	7.67	189	69	609	44	125	9	20.5	20.4
du Nord	2224	543	2.49	2.37	133	6.4	763	1110	0.68	8.36	184	118	930	92	611	38	65.8	41.0
Etchemin	3936	183	4.21	4.68	394	3.4	837	1196	0.70	7.83	196	132	3847	795	883	70	22.9	8.8
Jacque-Cartier	3191	124	2.66	2.28	447	7.6	1115	1347	0.83	6.65	198	101	973	118	460	25	47.2	21.4
L'Assomption	5204	746	2.64	2.31	1197	4.9	654	1082	0.60	8	183	127	2948	622	627	49	21.3	7.9
Loup	3289	248	2.42	2.19	789	5.3	596	1077	0.55	6.9	186	124	2050	409	327	52	15.9	12.7
Nicolet	1692	36	1.95	1.43	344	2.3	778	1137	0.68	7.98	176	151	3837	790	1260	81	32.8	10.2
Nicolet Sud ouest	1688	32	1.82	1.66	332	2.1	750	1123	0.66	7.85	179	148	3688	723	989	76	25.8	9.6
Petite Nation	2189	47	1.85	1.57	153	5.6	607	1079	0.56	7.57	181	89	728	54	233	15	32.0	27.3
Rouge	5549	219	2.14	2.11	333	6.4	705	1108	0.63	8.21	183	91	926	91	217	19	23.5	21.1
Saint-François	10666	460	2.61	1.84	320	2.1	877	1131	0.77	8.15	184	88	863	195	592	49	68.5	25.1
Sainte-Anne	2758	113	2.17	2.18	55	8.0	911	1301	0.70	6.88	170	115	1169	151	226	19	19.4	12.4
Upper Lièvre	7099	111	4.55	1.80	462	5.1	659	1023	0.65	7.67	189	69	609	44	194	11	31.8	24.8
Upper Saint-Françoi	8255	369	2.68	1.82	248	3.9	877	1194	0.73	7.97	176	88	1735	283	409	26	23.6	9.0
Yamaska	4626	287	2.70	2.09	1203	1.7	599	1116	0.53	8.09	176	151	7885	1838	1890	97	24.0	5.3

Factors influencing fractional nutrient export across space

We characterized which variables (Table 2) best described the different fractional N or P export across space. The best models of N and P fractional export included the exact same set of seven independent variables (Table 3), however the order in which these drivers entered the models was different. Annual runoff was the single best predictor of spatial variability for N while for P it was watershed slope (Table 3). This is likely due to the more labile properties of N as compared to the lithophilic behavior of P. Interestingly, annual precipitation as well as annual runoff entered both models, suggesting that together they provide additional information beyond climate. Counterintuitively, precipitation showed negative coefficients (Table 3; Fig 3). This is likely due to the differential water retention capacities across the watersheds where for the same amount of annual runoff, relatively more precipitation remains in the basin. Lakes entered the fractional P export model before reservoirs, whereas for N, it was the inverse (Table 3).

Tableau III Regression models of spatial variability of fractional N (A) and P (B) export using a backwards-stepwise selection based on AIC. All variables were log-transformed and clustered by year. Model coefficients, the random term (τ), residuals (σ), AIC and BIC are presented.

A ***Nitrogen***

Models	Intercept	τ	Runoff	Prec	ResZ	#Dam	Watershed Slope	Lake	Dv	σ	AIC	BIC
FrN0	-1.323	0.118	x	x	x	x	x	x	x	0.464	719	732
FrN1	-1.323	0.125	0.161	x	x	x	x	x	x	0.436	663	680
FrN2	-1.322	0.127	0.254	-0.143	x	x	x	x	x	0.423	639	660
FrN3	-1.323	0.121	0.309	-0.191	-0.125	x	x	x	x	0.406	606	632
FrN4	-1.322	0.126	0.323	-0.186	-0.121	0.118	x	x	x	0.390	572	602
FrN5	-1.322	0.128	0.327	-0.177	-0.119	0.138	-0.067	x	x	0.385	567	601
FrN6	**-1.322**	**0.128**	**0.293**	**-0.134**	**-0.200**	**0.195**	**-0.104**	**-0.144**	**x**	**0.375**	**548**	**586**
FrN7	-1.322	0.132	0.195	-0.169	-0.123	-0.098	0.291	-0.127	-0.029	0.375	554	597

B ***Phosphorus***

Models	Intercept	τ	Watershed Slope	Runoff	Prec	Lake	ResZ	#Dam	Dv	σ	AIC	BIC
FrP0	-2.013	0.161	x	x	x	x	x	x	x	0.699	1146	1159
FrP1	-2.014	0.175	0.296	x	x	x	x	x	x	0.633	1054	1071
FrP2	-2.014	0.176	0.283	0.105	x	x	x	x	x	0.625	1048	1069
FrP3	-2.014	0.184	0.306	0.306	-0.313	x	x	x	x	0.580	978	1004
FrP4	-2.015	0.185	0.290	0.252	-0.263	-0.101	x	x	x	0.573	973	1003
FrP5	**-2.015**	**0.188**	**0.274**	**0.272**	**-0.279**	**-0.210**	**-0.235**	**x**	**x**	**0.552**	**941**	**975**
FrP6	**-2.015**	**0.189**	**0.239**	**0.266**	**-0.256**	**-0.242**	**-0.296**	**0.088**	**x**	**0.548**	**940**	**979**
FrP7	-2.015	0.189	0.090	-0.171	-0.247	0.254	0.261	-0.240	-0.068	0.547	944	987

Since the same drivers entered both models, comparing their slope coefficients allowed us to consider the relative influence of each on the fractional export of both nutrients. In terms of climate related variables, the annual runoff entered both models with similar slope coefficients (0.29 and 0.27 for N and P, respectively), highlighting more nutrient leaching in wetter regions (Table 3 and Fig 3). Annual precipitation entered both models in addition to annual runoff and was negatively correlated with fractional export. Our results thus showed that watersheds with a higher water retention capacity retain more nutrients, especially P (Table 3 and Fig 3). Indeed, given a fixed amount of runoff, the precipitation term was significantly stronger for P (-0.26) than for N (-0.13) ($p=0.005$; Fig 3). Mean watershed slope had a strong positive effect on the fractional export of P (coefficient of 0.24), highlighting increased transfers in steeper watersheds. Conversely, a negative correlation was observed in the case of N (coefficient of -0.10), highlighting accentuated downstream transfers of N in flatter watersheds.

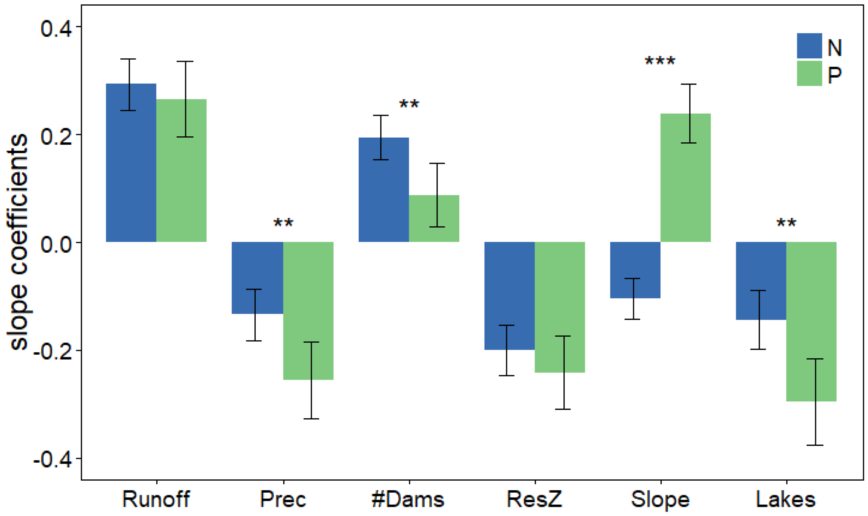


Figure 3. Differential effects of regional variables on N versus P fractional export. Slope coefficients of the multiple regression predictors are presented with their 95% confidence intervals as error bars. Stars (*) indicate if the slope coefficient of a given predictor was significantly different for N and P ($p<0.001$***, $p<0.01$**, $p<0.05$*). It is worth noting that multiple regression coefficients control for the effect of other predictors. In that sense, Precipitation showed a negative coefficient likely due to the differential water retention capacities across the watersheds where for the same amount of annual Runoff, relatively more precipitation remains in the basin.

In terms of processing within aquatic networks, our results showed that, after controlling for the number of dams, deeper reservoirs increased the retention of both nutrients more or less in a similar fashion (slope coefficient of ResZ = -0.20 and -0.24 for N and P, respectively; Table 3 and Fig 3). Counterintuitively, the specific number of dams (per km^{-2}) showed positive correlations with fractional N and P export. This result suggests that reservoirs in these basins are primarily nutrient sources likely remobilizing legacy stores that have accumulated in sediments over time. Finally, lakes on the landscape retain significantly more P (p=0.002) given that slope coefficient for P (-0.30) was twice that of N (-0.14).

Alternative models exploring the potential influence of other variables on fractional N and P export were also tested (Table S3). The annual water retention capacity of catchments (or "water balance") was estimated as a single predictor using the annual runoff to precipitation ratio (R:P; see models FrN2 and FrP2 in Table S3) and tested as an alternative predictor to Runoff and Precipitation used as two separate terms. In both models, R:P was positively correlated (p<0.001) with fractional nutrient export, highlighting increased downstream nutrient transfers in watersheds having a lower water retention capacity (high R:P). However, the P model that included Runoff and Precipitation as separate terms (Table S3) explained more variance (lower AIC), likely since it captured both the effect of climate, and water retention capacity. For N, R:P was considered a slightly better model (ΔAIC =4) than the one with the separate terms (Table 3 and S3).

Beyond the impact of reservoir depth on N and P retention, we also considered the role of a reservoir's shape by replacing ResZ with Volume Development (Dv) in alternative models (Table S3). Dv entered both N and P models as a significant predictor (at α=0.05) of fractional export and showed that more nutrients were retained when reservoirs were more convex (shape of a cauldron with limiting areas of riparian shallow waters). This effect was significantly (p=0.044) stronger for P (coefficient of -0.19) than for N (-0.13). These results reinforced that deeper systems better retain P than N, but also highlighted broad shallow systems with an anomalously deep hole (low Dv) disproportionately favor N retention relative to P (Table S3).

Factors influencing inter-annual variability in downstream transfers of nutrients

We characterized which variables (Table 2) best described the different fractional N or P export over time. The best models of N and P fractional export included Runoff and CVflow only, but for N, the latter variable was only significant at p=0.09 level (Table 4 and Fig 4). The slope coefficient for annual Runoff was significantly higher (p=0.002) for P (0.20) than for N (0.13) highlighting a greater influence of climate on P transport (Fig 4). The positive slope coefficients of flow regime (CVflow; 0.02 and 0.07 for N and P, respectively; Table 4 and Fig 4) suggested that, for a same amount of annual runoff, flashier discharge patterns promoted the export of both nutrients, but this effect was more pronounced for P (p=0.050; Fig 4).

Tableau IV Regression models of temporal variability in downstream export of anthropogenic N and P identified using a backwards-stepwise selection based on AIC. All variables were log-transformed and clustered by watershed. Model coefficients, the random term (τ), residuals (σ), AIC and BIC are presented.

Models	Intercept	τ	Runoff	CVflow	temp	σ	AIC	BIC
			Nitrogen					
FrN0	-1.305	0.386	x	x	x	0.289	270	283
FrN1	**-1.305**	**0.387**	**0.121**	**x**	**x**	**0.262**	**181**	**198**
FrN2	-1.305	0.387	0.129	0.023	x	0.262	186	208
FrN3	-1.305	0.387	0.129	0.024	0.007	0.262	195	221
			Phosphorus					
FrP0	-1.926	0.619	x	x	x	0.419	667	680
FrP1	-1.925	0.620	0.175	x	x	0.381	578	595
FrP2	**-1.925**	**0.621**	**0.198**	**0.066**	**x**	**0.377**	**573**	**594**
FrP3	-1.925	0.621	0.198	0.065	-0.009	0.377	581	606

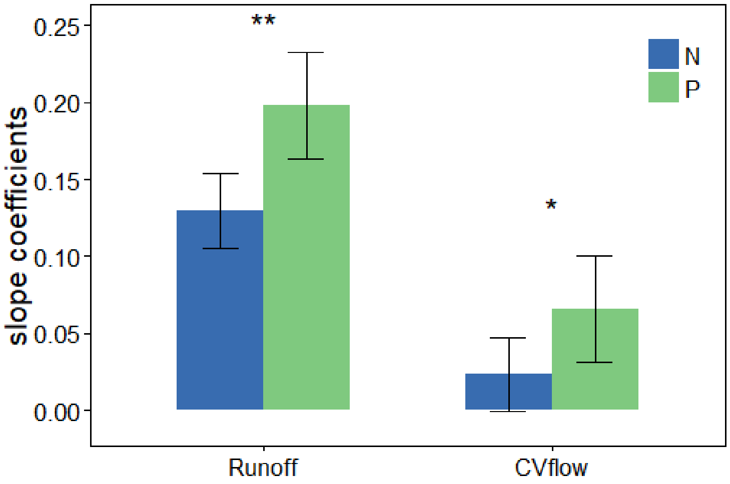


Figure 4. Differential effects of inter-annual variables on downstream export of N and P. Slope coefficients of the multiple regression models are presented with their 95% confidence intervals as error bars. Stars (*) indicate if the slope coefficient of a given predictor was significantly different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

Riverine export of the different N and P forms

Loads of the different N and P forms were also well predicted by NANI and NAPI (Fig S5). TSP and TDP showed a good fit with NAPI (R^2=0.55 and 0.48, respectively) yet TP had the strongest relationship (R^2=0.68). In the case of N, NANI was much better at predicting DIN (R^2 = 0.64) and TN (R^2=0.62) rather than Org. N (R^2 = 0.20; Fig S5). The relative proportion of the different chemical forms to total loads appeared to vary both over space and time (Fig S6). As an overall mean, 65% of total P was exported as TSP with low variability across watersheds (CV= 12%) while DIN dominated N exports with an overall mean of 60% and higher variability (CV= 27%; Fig S7).

Spatial variability in the dominant chemical forms

The contribution of DIN to total N riverine load increased with the level of anthropogenic N surpluses however no such pattern emerged for P (Fig 5).

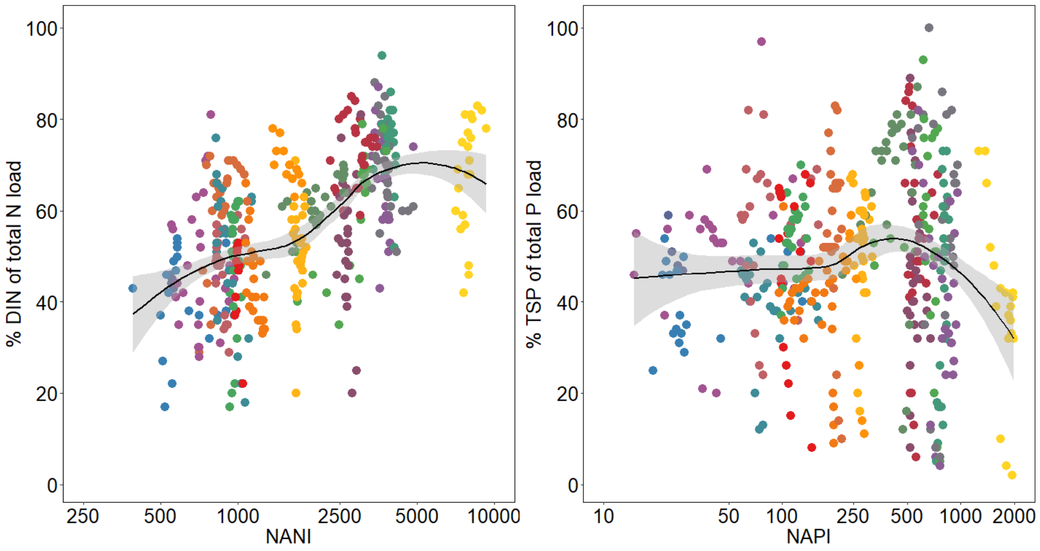


Figure 5. Contribution of DIN to total annual N riverine loads relative to NANI (Kg N km^{-2} yr^{-1}, and B) contribution of TSP to total annual P riverine loads relative to NAPI (Kg P km^{-2} yr^{-1}).

We then tested how annual *Runoff* and *Precipitation* (previously identified as dominant drivers of spatial variability in both fractional TN and TP export; see section 3.3), influenced the delivery of the different chemical forms. Both variables entered the multiple regression models as significant predictors in all cases (Table 4). Comparison of coefficients showed that water retention capacity (*Precipitation* given a fixed *Runoff*) more strongly influenced the retention of particulate forms, particularly for P (coefficient of -0.28 for TSP relative to -0.23 for TDP).

Tableau V Coefficients of multiple regression models explaining fractional riverine export of the different N and P chemical forms across space. All coefficients were significant at $p<0.001$.

Model	Intercept	Runoff	Prec
TN	-1.32	0.25	-0.14
DIN	-1.62	0.21	-0.10
ON	-1.74	0.30	-0.13
TP	-2.01	0.32	-0.28
TSP	-2.63	0.32	-0.28
TDP	-3.43	0.31	-0.23

Temporal variability in the dominant forms

In terms of temporal variability, wet years appeared to favor the export of the dominant N and P forms, DIN and TSP. This inter-annual variability in the relative contribution of the chemical forms was also apparent in Fig 5, with data from a single watershed, represented by a single colour, being spread along the y axis. We therefore tested how annual *Runoff* and *CVflow* (previously identified as the main drivers of temporal variability in riverine TN and TP loads; see section 3.4), influenced the export of the distinct chemical forms. Both variables entered the multiple regression models as significant predictors of all forms (Table 5). Comparing coefficients, flashy discharges (high *CVflow*) favored downstream transfers of particulate (TSP and Organic N) over dissolved forms (DIN and TDP; Table 5), and this pattern was particularly pronounced for P (coefficient of 0.14 for TSP versus 0.06 for TDP).

Tableau VI Coefficients of *inter-annual* multiple regression models (p-value) of fractional riverine export of the different N and P chemical forms.

Model	Intercept	Runoff	CVflow
frTN	-1.30	0.13 ***	0.02 (0.07)
frDIN	-1.62	0.15 ***	0.03 (0.05)
frON	-1.75	0.10 ***	0.07 (0.01)
frTP	-1.93	0.20 ***	0.07 ***
frTSP	-2.54	0.14 ***	0.14 ***
frTDP	-3.32	0.05 (0.08)	0.06 (0.03)

Discussion

We used an integrative empirical approach to quantify the relative transport of N and P through different landscape compartments as well as under different climate regimes, to evaluate the differential impact of these drivers on riverine fluxes. By considering how these two macro-elements move together, we enabled the identification of where and how N and P cycles are decoupled within a watershed and in certain compartments within the aquatic network. Moreover, since our study focused on explaining the proportion of anthropogenic N and P surpluses that reach the outlet (fractional export), the influence of human activities on changes in riverine loads was truly accounted for. Precipitation patterns and water retention capacity within the landscape were the features that most strongly influenced nutrient export from land to water, whereas lakes and reservoirs emerged as features within the aquatic network that differentially influenced retention. More importantly, landscape and climate features as well as the presence lakes decoupled N and P fluxes downstream. By empirically identifying the magnitude of the decoupling capacity of each driver, we provide valuable information for a better understanding of the potential N: P ratios in receiving waters.

Nutrient transport and the role of precipitation patterns/flow regimes

Annual runoff was the main driver of fractional export for both N and P (Fig 3 and 4). Yet, overall, fractional export of N was greater than that of P (Fig 1), highlighting the more labile and lithophilic properties of N and P, respectively (Green and Finlay 2010). This finding supports previous studies that considered fractional N and P export more generally (Goyette et al. 2016; Hong et al. 2012; Howarth et al. 2012) as well as those that demonstrate that a greater proportion of agricultural activity in the watershed tends to increase N concentrations relative to P in lakes (Arbuckle and Downing 2001; Collins et al. 2017). At the basin scale, wet years resulted in higher loads of both nutrients. These entered predominantly as dissolved inorganic N (DIN), which is highly mobile within the soil matrix, and as total suspended P (TSP), which is typically bound to particles. Overall, wet years favored P over N delivery (Fig 4), likely because of erosion of P accumulated in different landscape compartments. Indeed, beyond the annual timescale, more flashy daily discharge (*CVflow*) within a year also favored P export relative to N through the transport of particulate forms. These finding support previous work showing that P transport from watersheds are generally much more episodic than that of N (Green and Finlay 2010), particularly increasing during storm events (Carpenter et al. 2017; Ockenden et al. 2016) and spring freshets (Cooke and Prepas 1998). Our work also provides empirical evidence that erosion also influences N delivery, albeit to a lesser extent than P, through mobilization of particulate organic N.

Nutrient retention within watershed compartments

Our study highlights three main features that can promote a greater retention of P relative to N in watersheds: 1) the overall water retention capacity of the landscape, 2) the presence of lakes and dams, and 3) the morphometry of reservoirs. While precipitation promotes downstream transport of nutrients, the water retention capacity of the landscape plays a critical role at buffering this export. The catchment annual water balance, which serves as an integrative metric of different landscape characteristics that influence water residence time, emerged as a strong predictor of nutrient export. As it depends on climate and landscape characteristics that influence water movement (precipitation and evapo-transpiration; Budyko 1974), both annual runoff and precipitation entered as complementary predictors of nutrient export in our models. The landscape compartments that retain water favour particle settling (N and P), the sorption of different nutrient forms and microbial processes that can eliminate N from the systems. Interestingly, there has been a marked change in landuse in this region, particularly with a dramatic loss in wetland cover in exchange for agricultural and urban development (Pellerin and Poulin 2013). In that sense, we observed a reduction in the water retention capacity within nearly half of our 18 watersheds throughout the study period (mean increased in *R: P* of 0.14, suggesting that 14% more water from precipitation makes its way to the outlet). These observations supports a previous study showing that catchment water balances in the St. Lawrence region would be mainly controlled by land use change (>60%) rather than by climate (Zhou et al. 2015). In terms of relative effect on N and P, we showed that this loss of water retention capacity through land use change would disproportionately favour P over N exports, thus lowering N: P ratios in downstream waters (Table 3).

In terms of decoupling the movement of nutrients within the aquatic network, natural lakes and human made reservoirs tended to favour the relative retention of P over N. This pattern has also been observed in other systems (Alexander et al. 2008; Grantz et al. 2014). While lakes significantly retained more P than N, due to the effect of reduced hydraulic velocity on particle settling (Vollenweider 1976), that relative influence was not significant in the case of reservoir mean depth (*ResZ*). However, when overall reservoir morphometry was considered, deeper systems, more convex in shape, favored P retention relative to N whereas, broad shallow reservoirs with an anomalously deep hole had an increased capacity to retain N relative to P. Indeed, deeper systems are known to increase P settling and burial through increased water residence time (Kõiv et al. 2011; Powers et al. 2015; Saunders and Kalff 2001) while shallow systems tend to favor denitrification losses by increasing sediment-water contact (Stanley and Doyle 2002). It has been suggested that reservoirs, with more complex perimeters, more extensive littoral zones and shorter water residence times are more efficient at eliminating N than natural lakes (Harisson et al 2009; Hayes et al. 2017). Indeed our study suggests that lake and reservoir morphometry will differently influence the stoichiometric delivery of N and P to downstream waters and should be considered in future studies.

Even though reservoirs can dampen nutrient enrichment of downstream waters on the short term, nutrient accumulation in the sediments of these human made systems over time will eventually result in the delivery of legacy sources (Nowlin et al. 2005; Powers et al. 2015; Teodoru and Wehrli 2005). Indeed the presence of dams in our study basins favored nutrient export. This is likely a function of the size of these dams and their ages. Small dam reservoirs may act as sinks in their early years, but as nutrients accumulate over time, may potentially switch to net sources when nutrients are remobilized in the water column (Power et al 2015). Most dams within our study watersheds are small and were constructed over 60 years ago with some prior to the 1900's (CEHQ 2017), thus supporting the notion that these reservoirs might have already surpassed an optimal threshold in their capacity to retain nutrients (Power et al 2015). Furthermore, dam reservoirs in our study tended to export more N relative to P, supporting the notion that a reduction in hydraulic velocity favours particle settling and that the main P forms in our systems was particulate. In terms of functional role on the landscape, reservoirs could initially be considered as nutrient export control measures, such as buffer strips but only up until a certain point. The buildup of legacy nutrient stores resulting in their ultimate export, can only counter water quality issues in the short term (Jarvie et al. 2013a). It would be interesting to evaluate quantitatively at what stage different reservoir types tip from net sinks to net sources of nutrients and determine whether some level of flow regulated measures can optimize retention in the longer term.

Evidence of legacies

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

Results regarding the influence of watershed slope on nutrient export also suggest a strong relative contribution of legacy nutrients to riverine loads. In the case of P, while controlling for annual runoff and other land use characteristics, accentuated downstream transport in steeper watersheds likely results from erosion of P-enriched soils and sediments with past anthropogenic inputs under strong discharge pulses (Ockenden et al. 2016; Sharpley et al. 2013). In the case of N, legacies may operate in a more leaky and continuous manner through transient storage in groundwater (Hamilton 2012; Tesoriero et al. 2013; Van Meter and Basu 2015). The negative correlation between fractional export and watershed slope may reflect N legacies contributing to riverine loads in flat watersheds where water infiltration is favored (Price 2011; Soulsby et al. 2006) particularly through aquifers more prone to nitrate contamination due to intensive agriculture (Van Meter and Basu 2017). The legacy effect appeared stronger for P than for N since CVflow, Runoff and Slope all influence P delivery more strongly than N. This suggests the contribution of P legacies to be more sensitive to climate and potentially more pervasive through time relative to N legacies. Indeed it has been suggested that N legacies may last a few decades (Tesoriero et al. 2013; Van Meter et al. 2016) whereas in the case of P, they may last for centuries (Sharpley et al. 2013; Carpenter

2005; Goyette et al. submitted). Thus managing for legacy stores remains a challenge for long term sustainability of water quality in several of these basins.

Conclusion

Climate regimes and landscape features interact with human activities (agriculture, urban development and dams infrastructures) in complex ways that alter both the absolute magnitude of nutrient loads to rivers as well as their stoichiometric ratios. Understanding how both change along the aquatic continuum is essential to effectively tackle eutrophication at multiple spatial scales (Howarth et al. 2011; Paerl 2009). This requires a better understanding of what features decouple N and P fluxes through the watershed and by how much. Our study offers an integrative approach that not only identifies which key climate and landscape features decouple N and P fluxes at the annual timescale, but also the relative magnitude of each effect.

While lakes and reservoirs can play a significant role in retaining nutrients upstream, drivers that promote transport from land to water, such as anthropogenic nutrient surpluses, climate, and water retention capacity within the landscape, emerged as the dominant drivers of N and P transfers downstream. Water retention capacity of the watershed and lakes in the aquatic network are critical features that retain both elements, P more so than N. Factors that favor erosion processes, such as flashiness, geomorphology and land-use will also decouple the elements as well, largely mobilizing legacy sources of P. In light of these results, and given projections of increased precipitation and storm events due to climate change (IPCC 2014) combined with the expansion of urban development and agriculture that will reduce the landscape water retention capacity, P delivery downstream may be favoured over N. Despite regulations that aim to reduce P, downstream transfers will continue together with increasing N inputs. Efforts should be made to reduce the use of both in the landscape, while increasing their use efficiency through practices that minimize loss, and creating condition that favour overall water retention capacity.

Supplementary information

Statistical analyses

A major benefit of using linear mixed models (LMM) in regression and multiple regression is that, while correcting for potential errors related to pseudo-replication, it also allows for the use of all of the available information by "pooling" them together within a single analysis. This increases the statistical power and probability of finding significant relationships. LMM captures information at different levels of organization simultaneously (i.e. space and time) where the slope coefficient of a predictor represents a mix of its relationship at both temporal and spatial levels (Fig S1). Since we aimed at comparing the precise effect of different features on nutrient transfers, we focused our analyses on the slope coefficients of the different models rather than on maximizing the coefficient of determination (R^2). In order to assess the spatial and temporal structures of the dataset separately, we centered all of the explanatory variables within groups (years or watersheds) following Enders and Tofighi (2007; Fig 1).

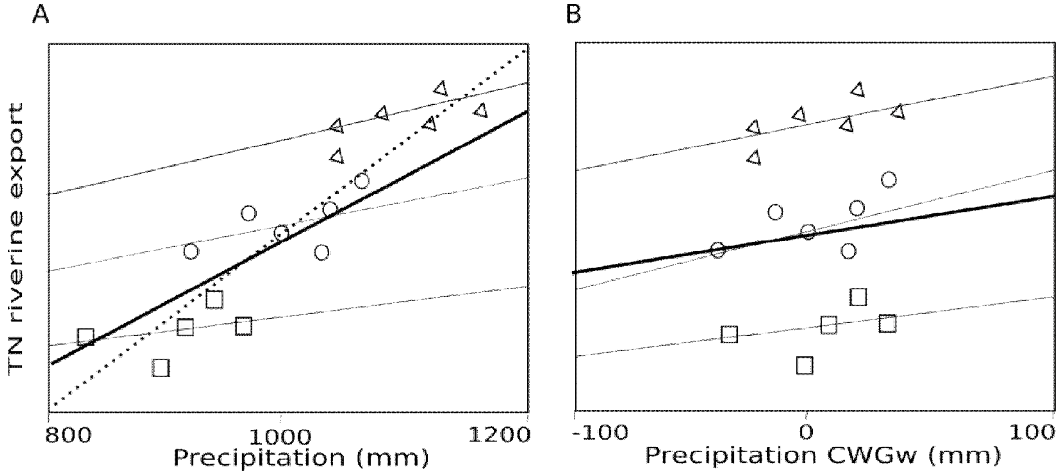


Figure S1. Schematic of a relationship between Riverine TN export and precipitation for 6 years in 3 different watersheds. Panel A shows models fitted with OLS (dashed line) and LMM (thin lines for specific relationships to each watershed and bold line for the general LMM relationship). Panel B shows the same dataset fitted by LMM for which precipitation values were centered within groups (here watersheds) to test for the effect of time.

Figure S1a shows that applying LMM directly leads to a mix in the final model slope coefficient (bold line) between the effect of precipitation across watersheds (dashed line) and its effect over time within watersheds (thin lines). In order to identify the slope coefficient (effect) of a predictor on temporal variability only, the spatial component of the regression needs to be cancelled. This can be done by centering within groups (CWG) each independent variable (Enders and Tofighi 2007). As shown in figure S1b, by centering data within watersheds, the spatial variability can no longer be captured by the regression (no more trend across watersheds) and so, only temporal variability in each watershed (thin lines) is detected and averaged (bold line) in LMM. The slope coefficient then effectively represents the mean effect, across all watersheds, of precipitation on inter-annual variability of nutrient loads. The latter approach was applied on data centered within watersheds (CWG_W) to analyze the temporal variability alone (as exemplified here above), as well as on data centered within years to analyze the spatial variability across watersheds. As usually done in multiple regressions, all predictors were not only centered but fully standardized to allow coefficient comparison within and across models.

Testing collinearity between potential drivers

Tableau SI. Variance inflation factors (VIF) of all variables considered in this study to explain fractional N or P export **a)** before removal of highly collinear variables, and **b)** after removal of highly collinear variables.

a)

Variables	VIF
Dv	1.48
spDamCount	1.61
ResMNdepth_MN	1.66
Lake density	2.03
Temp	1.35
CVPrec	1.39
CVflow	2.17
slope	1.46
Runoff	72.57
Prec	11.73
R:P	48.05

b)

Variables	VIF
Dv	1.46
spDamCount	1.61
ResMNdepth_MN	1.61
Lake density	2.01
Temp	1.35
CVPrec	1.39
CVflow	2.16
slope	1.46
Runoff	2.24
Prec	2.26

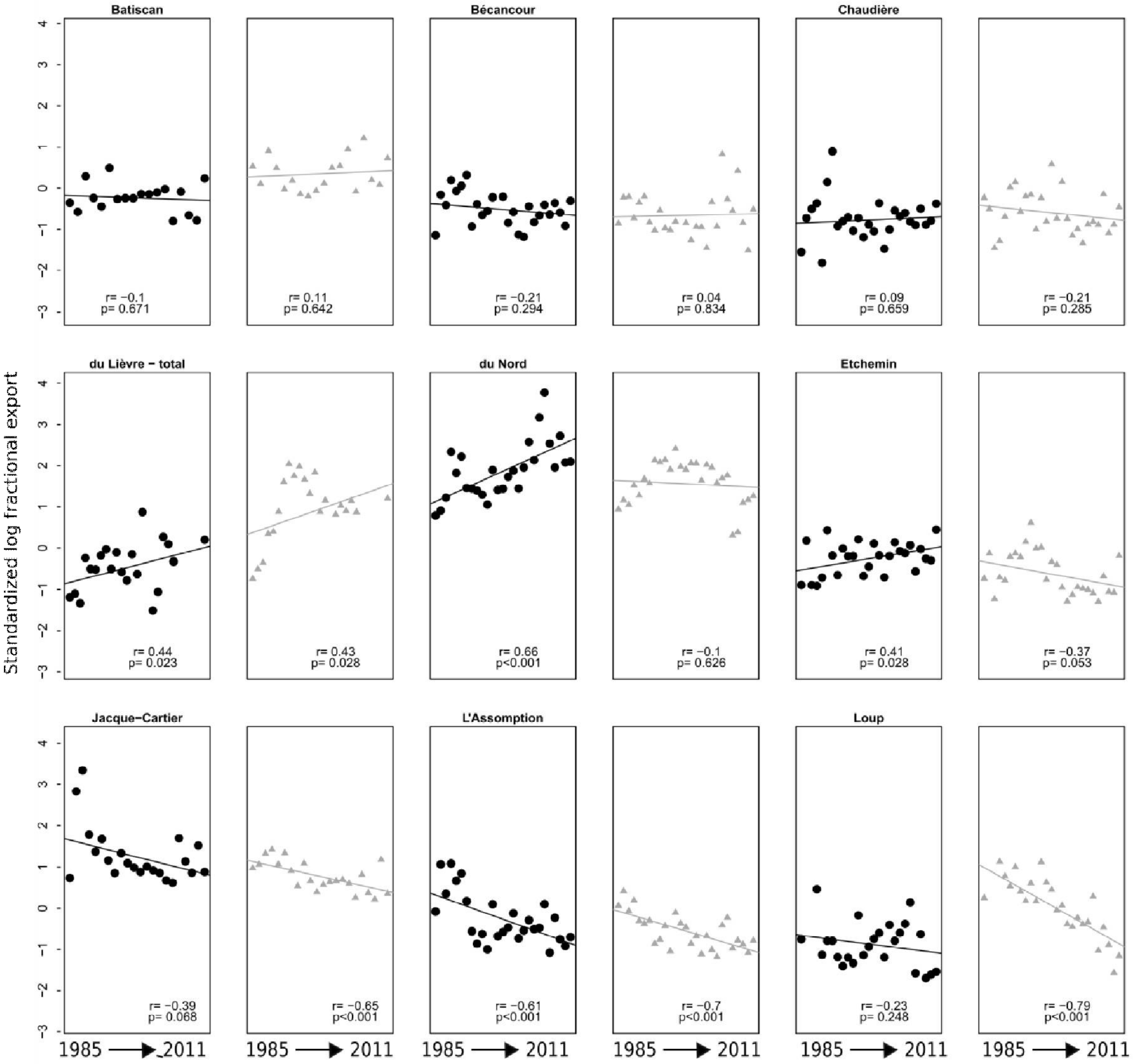


Figure S2 (continued on next page)

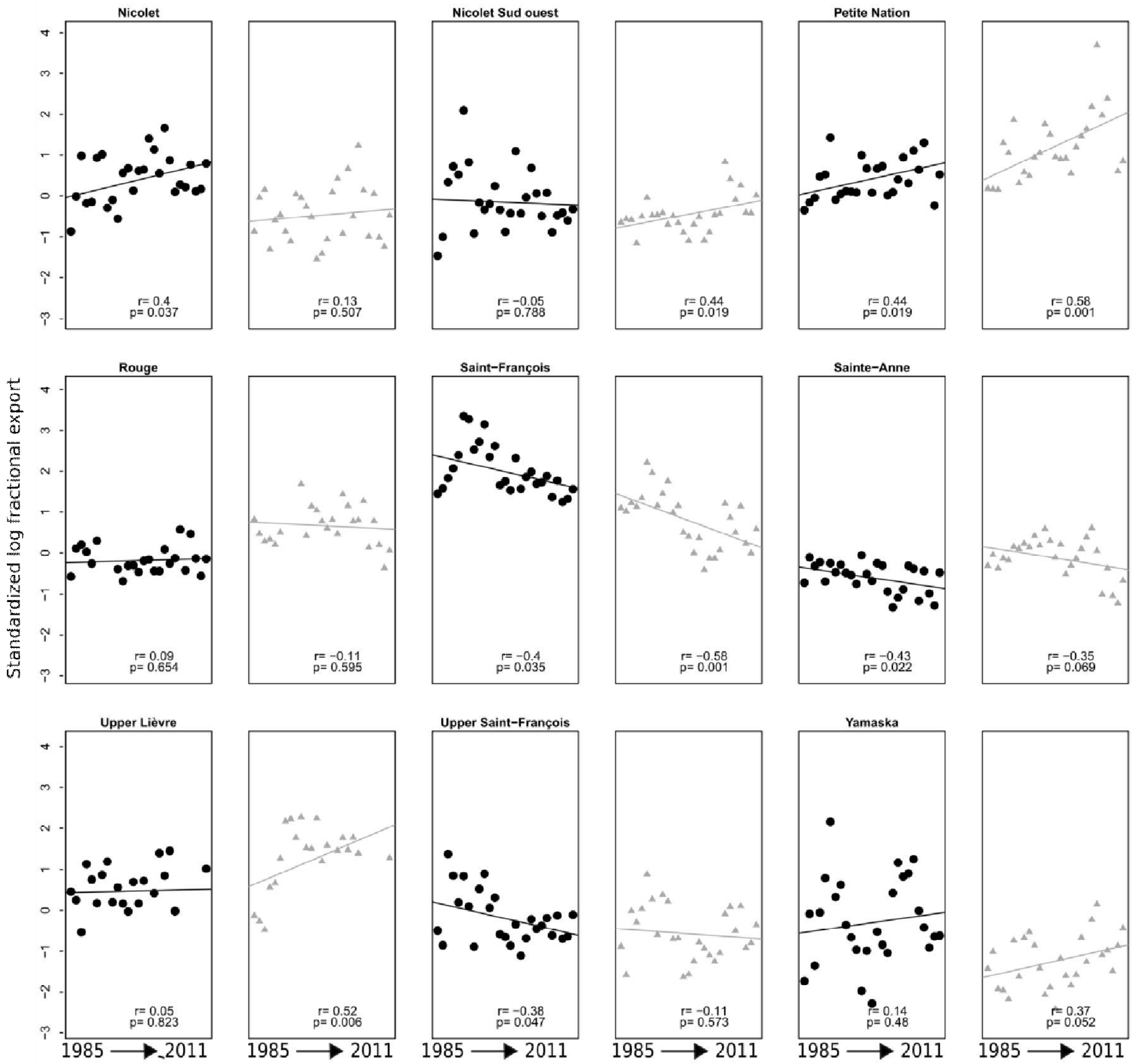


Figure S2. Changes in fractional export of N (black circles) and P (gray triangles) between 1985 and 2011 and the 18 watersheds. Linear regressions between log transformed fractional export and years were used to detrend data and analyse inter-annual variability by excluding long term trends and emphasizing inter-annual changes. Pearson correlation coefficients and p-value of each linear regression are shown. All data were standardized for visualization and comparison across watersheds

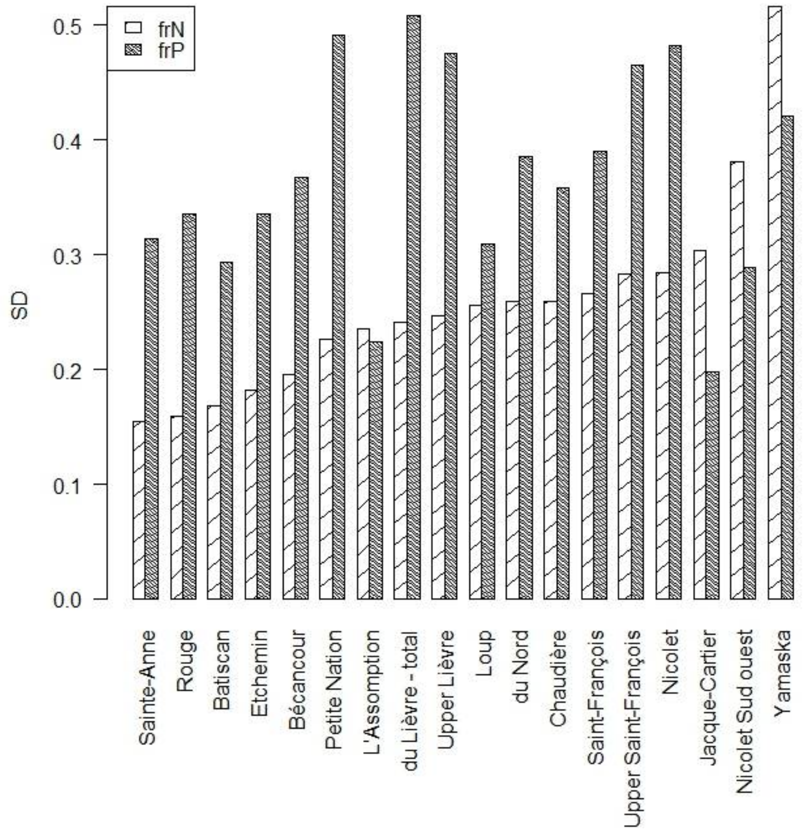


Figure S3. Inter-annual variability of fractional export within each watershed, as shown through standard deviation (SD) of detrended data (residuals from linear regressions between riverine fractional N and P export and time; (see Figure S2) over the 26-years period of the study.

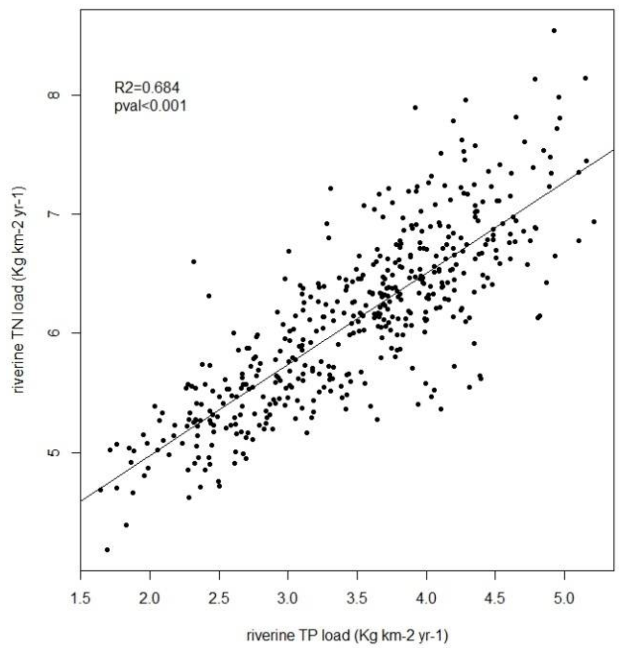


Figure S4. Log-Log relationship between riverine TN and TP loads across all watersheds and years.

Alternative models

Tableau SII. Alternative models of spatial variability in transfers of anthropogenic N and P downstream. Models FrN1 and FrP1 were previously identified as the best models of spatial variability (see main text; Table 3) and are presented here for comparison with alternative models. All variables were log-transformed and clustered by year. Model coefficients, the random term (τ), residuals (σ), AIC and BIC are presented.

Models	Intercept	τ	Runoff	Prec	R:P	ResZ	Dv	spDam Count	Slope	Lakes	σ	AIC	BIC
FrN1	**-1.322**	**0.132**	**0.293**	**-0.134**	**x**	**-0.200**	**x**	**0.195**	**-0.104**	**-0.144**	**0.375**	**548**	**586**
FrN2	**-1.322**	**0.132**	**x**	**x**	**0.226**	**-0.203**	**x**	**0.202**	**-0.110**	**-0.155**	**0.376**	**544**	**578**
FrN3	-1.322	0.131	0.280	-0.105	x	x	-0.132	0.180	-0.063	x	0.381	558	592
FrP1	**-2.015**	**0.189**	**0.266**	**-0.256**	**x**	**-0.242**	**x**	**0.088**	**0.239**	**-0.296**	**0.548**	**940**	**979**
FrP2	-2.015	0.186	x	x	0.146	-0.250	x	0.131	0.200	-0.364	0.564	964	998
FrP3	-2.015	0.189	0.249	-0.217	x	x	-0.189	0.075	0.289	-0.125	0.551	947	985

Riverine loads of the different chemical forms of N and P

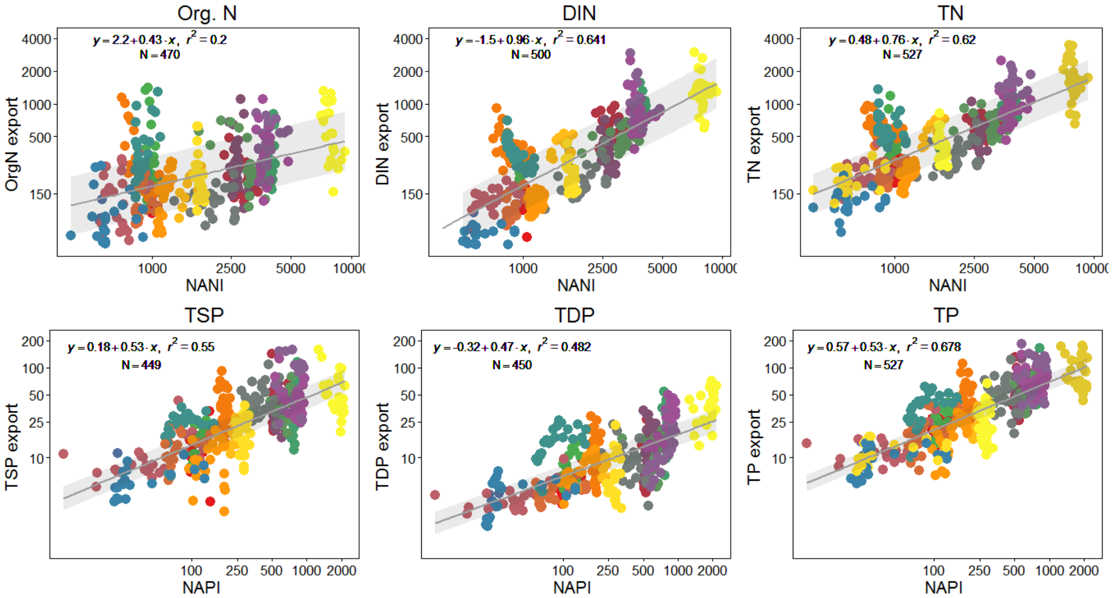


Figure S5. Log-Log relationships between riverine loads of the different chemical N and P forms and net anthropogenic inputs of N and P (NANI/NAPI) to watersheds. Regressions were fitted using linear mixed models (LMM) with "Watershed" as a random factor that was allowed to vary between intercepts only. *Marginal R^2s* account for the predictive power of NANI and NAPI alone. All units are in Kg N or P km^{-2} yr^{-1}.

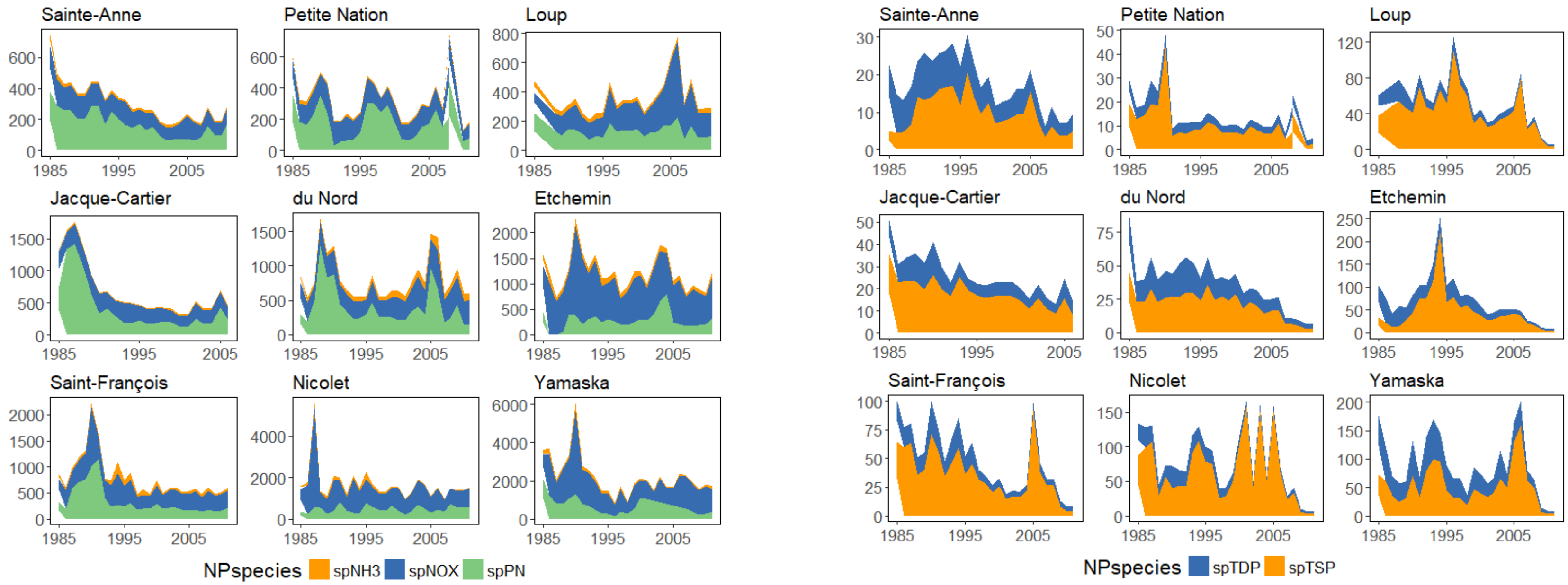


Figure S6. Annual riverine loads (kg km^{-2} yr^{-1}) of the different N and P chemical forms from 1985-2011

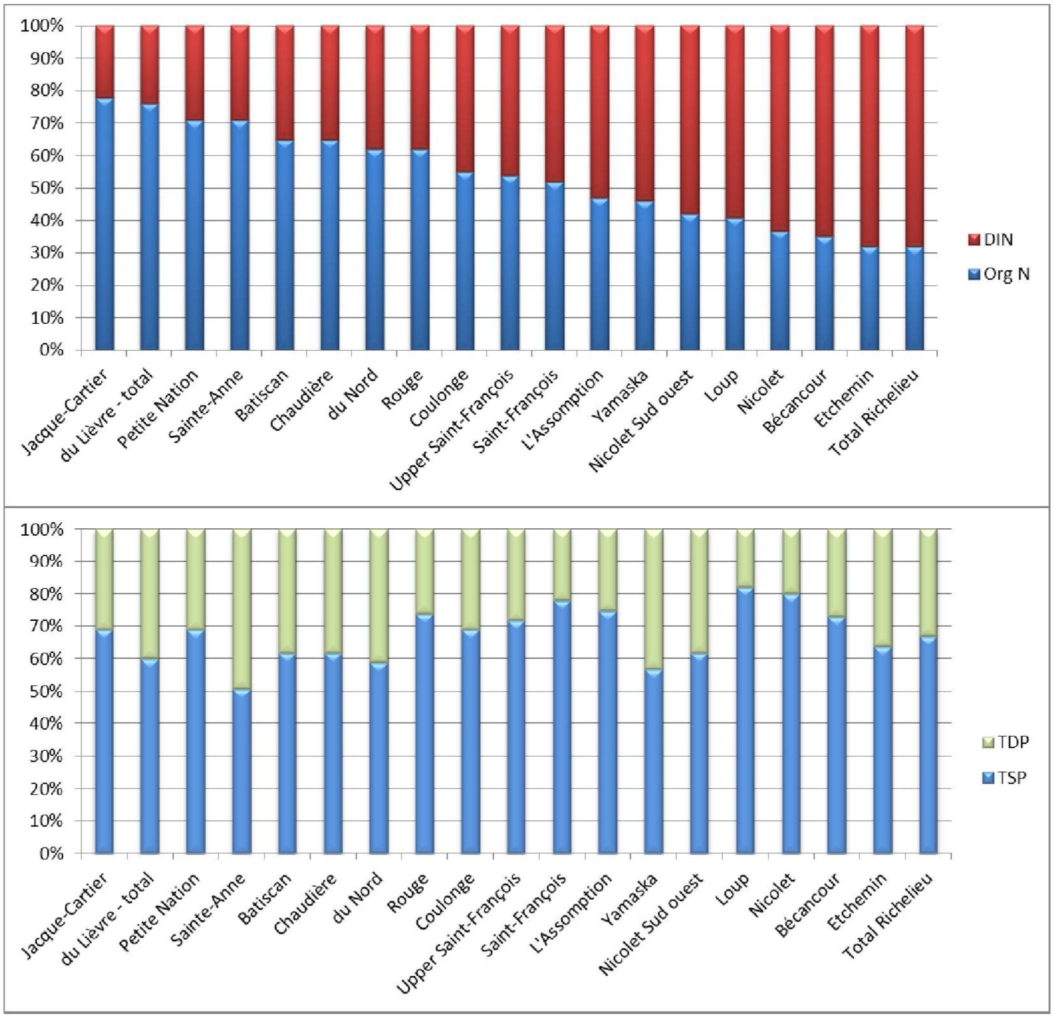
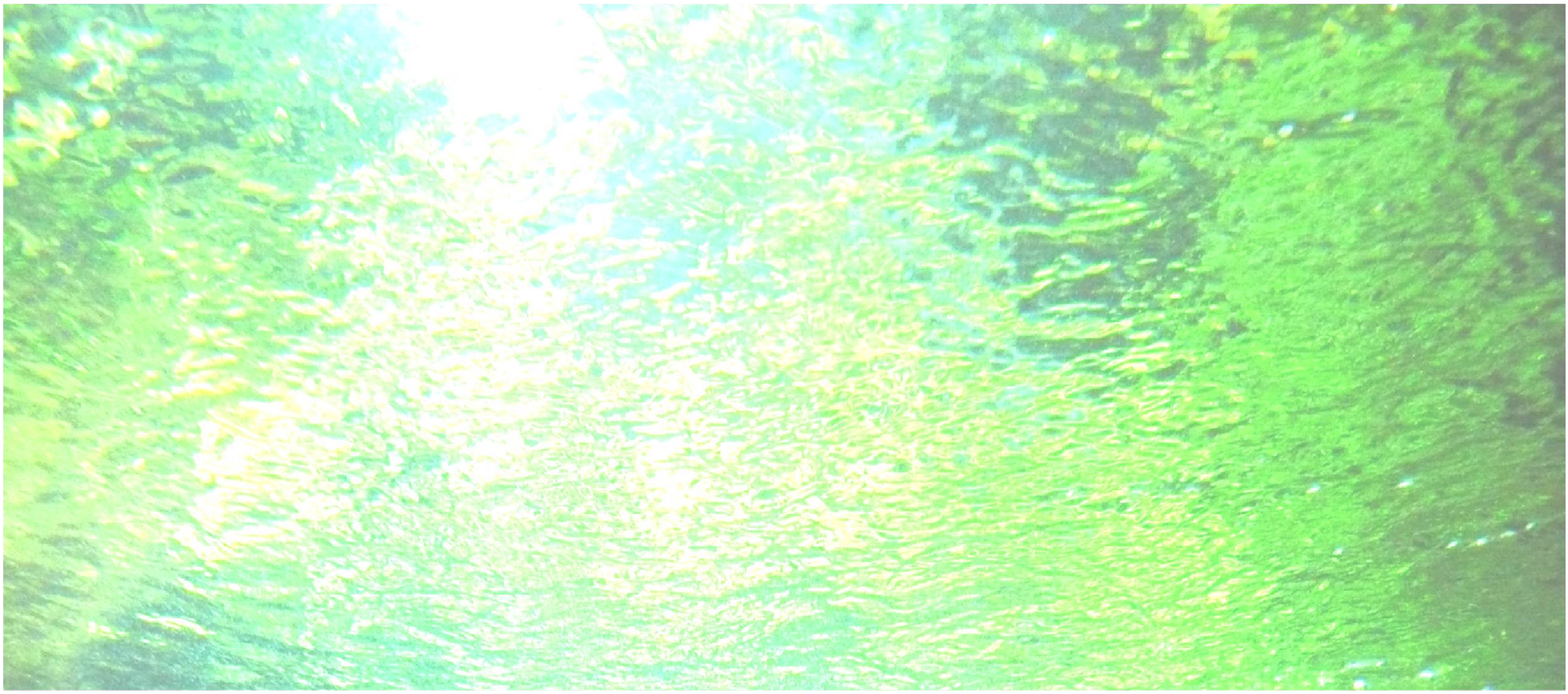


Figure S7. Mean proportion of A) DIN and Org N to TN, and B) TSP and TDP to TP, for the 18 watersheds.



Chapitre III. Seuil de capacité tampon du phosphore par les bassins hydrographiques et délais temporels pour un retour aux conditions initiales des charges fluviales

Low phosphorus buffering capacity and long legacies in watersheds threaten water quality

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Abstract

Excess anthropogenic phosphorus (P) in watersheds, lost through runoff, can result in aquatic eutrophication. Watersheds retain a certain amount of P, which can buffer the effect of excessive use of P on downstream transfers. However, whether a P buffering capacity threshold exists, where riverine loads would drastically increase beyond a certain level of P accumulation on land remains unknown at the watershed scale. Here, we quantify watershed P buffering capacity threshold, which is surprisingly low. Beyond an accumulation of 2,606 kg P km^{-2}, further human inputs to watersheds severely accelerate P loss in runoff. Using a simple exponential decay model, we estimate that the time required to eliminate legacy P (that accumulated in past years) via run-off in our watersheds ranges from 50 to over 2000 years. The rapid rate at which watershed buffering can be surpassed, particularly with current rates of anthropogenic inputs, versus the long return to baseline suggests that new strategies to reconcile watershed activities and water quality around P, including legacy P, are urgently needed.

Introduction

Human activities have fundamentally altered the phosphorus (P) cycle (Elser and Bennett 2011). Fertilizer applications to crops, animal manures, and human sewage all result in high inputs to watersheds, which increases P transfers to surface waters (Bennett et al. 2001), often causing their eutrophication (Carpenter et al. 1998), a major economic and public health concern (Dodds et al. 2008). The ability to predict P inputs to aquatic ecosystems is made more complex by the lithophilic properties of P in soils and sediments, which create time lags between anthropogenic P inputs to watersheds and resulting eutrophication (Meals et al. 2010; Sharpley et al. 2013), and increase the stochasticity (Green and Finlay 2010; Ockenden et al. 2016) of P transfers along the land-freshwater continuum. Understanding the long-term dynamics of P fluxes at the watershed scale, where both biophysical and technological retention mechanisms operate (such as in natural wetlands or sewage treatment plants), is essential to better manage human activities and maintain water quality (Foley et al. 2011; Powers et al. 2016). To do so effectively requires quantification of the P buffering capacity, defined here as the ability of a watershed to modulate P export to downstream waters by retaining excess P in different landscape compartments. .

The buffering capacity of a watershed would influence the rate of P loss to surface waters both during the accumulation and depletion phases of P flux to and from watersheds (Haygarth et al. 2014). Whereas anthropogenic P that accumulates in the watershed over time, known as legacy P is a form of storage, this stock can act as a chronic, diffuse P source to downstream waters, even when new inputs are arrested, as it is gradually depleted for ensuing decades or centuries (Carpenter 2005; Carpenter et al. 1998; Jarvie et al. 2013a). Yet these time-lags are highly uncertain and most likely watershed specific due to different landscape features, socio-ecological characteristics and histories (Sharpley et al. 2013). Indeed, as P accumulates in the watershed, there should be a tipping-point or threshold level after which P delivery to surface water increases substantially. There is evidence, at the plot scale, of a potential P buffering capacity tipping point, where the threshold of soil P sorption saturation (Maguire and Sims 2002; Nair 2014; Vadas et al. 2005) was determined as the point where P mobility increased within the soil matrix (Maguire and Sims 2002; Nair 2014). However, we do not know whether excess P released in the soil solution enters surface water downstream, or is intercepted in other landscape compartments along its flow path, such as in riparian wetlands and aquatic sediments (Jarvie et al. 2012; McDowell et al. 2015). A more comprehensive metric which considers all P inputs and determines the P buffering capacity threshold at the watershed scale is needed.

In order to identify a threshold at which P retention capacity starts to decline, and to quantify the time lags involved during a return to baseline conditions that might occur if anthropogenic P surplus cease, we reconstructed 110 years of P fluxes in 23 watersheds in the St Lawrence Basin (Quebec, Canada; Fig. S1) (Goyette et al. 2016) that spanned a large gradient of P enrichment. We consider all anthropogenic sources of P inputs to watersheds. To determine the threshold for P buffering capacity, we compared P riverine export with the P accumulated in the 23 watersheds across our different basins. To estimate time lags in recovery for each individual watershed, we modeled P stock depletion through runoff only as an exponential decay process considering a range of climatic scenarios.

Methods

Riverine Total Phosphorus (TP) loads

Annual Riverine TP loads at 23 watershed outlets were calculated for the 26 years between 1985 and 2011 from monthly TP concentrations [*MDDEFP-BQMA*; *Environment Canada*, 2014b] and daily discharges [*Centre d'Expertise Hydrique du Quebec*; *Environment Canada*, 2014a] using LOADEST (Runkel et al. 2004). LOADEST is an approach that allows for flow-weighted interpolations of the discrete concentration measurements, thus reducing bias by accounting for exceptionally high or low daily discharge events. From nine potential models tested, the best model was selected based on the corrected Akaike criterion (AICc). For each river and each focal year, models were calibrated over 5 years (i.e., from 1994 to 1998 for the focal year 1996) before being used in combination with daily discharge to predict annual loads. LOADEST procedure was conducted in R (Team 2013) with package loadflex (Appling et al. 2015). Discharge gauging stations were not necessarily located where water chemistry was monitored. In such cases, discharge at the monitoring site was estimated by multiplying the specific discharge (m^3 km^{-2}) at gauging station by the drainage area (km^2) at the monitoring site. Specific riverine loads (kg P km^{-2} yr^{-1}) were calculated by dividing annual loads by the drained area.

Annual P Budget and P accumulation reconstructions

We calculated annual P budgets for each of the 23 watersheds in our study area (Supplementary information Fig S1) using 10-year time steps from 1901 to 1981 and 5-year time steps from 1986 to 2011. These budgets were linearly interpolated to estimate annual P surpluses throughout the century (1901 to 2011) following Goyette et al (2016). Briefly, annual P surpluses were calculated using the Net Anthropogenic P Inputs approach (NAPI) (Russell et al. 2008) which quantifies all known anthropogenic P inputs (mined P fertilizers, P in detergents and imports of P in food and feed), and outputs (exports of P in food and feed). The NAPI methodology accounts for "new" P input into a watershed and mainly uses agricultural censuses as a source of data. Other governmental historical data were used for the reconstruction of inputs through detergents or human food consumption. All details on methodologies and data sources used to calculate NAPI are presented in Goyette et al., 2016.

While NAPI values represent annual P surpluses due to human activity, they do not account for P outputs through riverine exports at the watershed outlet and so cannot be used directly as an estimate of annual P accumulation in the watershed. Annual riverine TP loads (see previous section) were thus subtracted from surpluses on the landscape (NAPI) to obtain estimates of annual P accumulation in watersheds. For years prior to available water quality data (1901 to 1984), riverine loads were estimated based on NAPI reconstructions and the relationship between riverine TP loads and NAPI in years 1985 to 2011 ($R^2=0.90$, $p<0.001$; Supplementary Information Fig. S3). However, that relationship was not linear as we identified a break point at the NAPI value of 42 kg P km^{-2} yr^{-1} ($p<0.001$; see next section on statistical analyses). Both segments of the relationship (left and right of the inflection point) were tested as simple linear regressions to assess the statistical significance of their slope coefficients. The slope of the first segment was not significant at $\alpha=0.05$, suggesting no impact of annual NAPI on riverine TP exports below NAPI values of 42 kg P km^{-2} yr^{-1}. However, the slope of the 2nd segment was positive ($p<0.001$), indicating increased riverine TP exports with increased values of NAPI. To estimate riverine loads in years 1901 to 1984, we used the regression model of the 2nd segment along with NAPI reconstructions in those years. When NAPI was lower than 42 kg P km^{-2} yr^{-1}, we kept riverine loads constant at the intercept value of the 1st segment (13 kg P km^{-2} yr^{-1}; Supplementary Information Fig. S3). Annual P accumulation was then estimated in years 1901 to 1984 by subtracting these modeled riverine TP loads from NAPI values in those years. P accumulations throughout the century were then estimated for each watershed by summing their annual P accumulation since 1901. Since riverine TP load estimates were used to calculate P accumulation, we tested for the possibility of introducing a circularity effect that would have artificially inflated the statistical strength of the threshold relationship (Kriegeskorte et al. 2009) in Fig 1. Two different approaches were used to test for this possibility and we found no significant influence of this effect on the reported relationship (see SI, Table S2 and Fig. 4, for details).

Statistical analyses

The relationships between riverine TP loads and NAPI (Supplementary Information; Fig. S3), and between riverine TP loads and Accumulated P since 1901 (Fig. 1), were fitted with a split line model using the Segmented package in R (Muggeo 2008; Team 2013). This model approach allowed us to statistically identify inflection points in the relationships. The approach uses maximum likelihood fitting in an iterative procedure and provides estimates of slopes and breakpoints along with standard errors. From that standard error, we calculated the 95% confidence intervals around our breakpoint value. Data were log transformed to meet statistical prerequisites of linear regressions. Since some watersheds did not accumulate P but rather mobilized P throughout the century (Fig. 1), resulting in negative values of P accumulation (net cumulative P export from the watershed), we conducted a translation on the "accumulation" variable to get only positive values prior to log transformation. The minimum value of P accumulation (-945 kg P km^{-2}) was added to all values (all years and watersheds). However, all values of P accumulation (x axis of Fig. 1) were corrected for that translation and appropriately reported (subtracting 945 kg P km^{-2} from the results of the analysis). Regressions were performed on per-watershed mean values of NAPI, riverine TP loads and Accumulated P to avoid pseudo-replication. As stated in the previous section, once an inflection point was detected, both segments of the relationship (left and right of the inflection point) were tested as simple linear regressions to assess the statistical significance of their slope coefficients.

P depletion time

We used an assumption of balanced anthropogenic inputs and outputs to estimate the time needed to deplete the accumulated P pools over the century back to baseline conditions through runoff only. We modeled P depletion times of each watershed as an exponential decay process expressed by the equation:

$$P_{(t)} = P_0 e^{-pt},$$

where P_0 is the P stock in 2011, p is the P runoff coefficient (constant over time) and t is the number of years over which P is depleted. P runoff coefficients (p) were identified from the relationship between riverine TP loads at the outlet and the P stock of that watershed for a given year (Fig. 1). These coefficients are watershed-specific but vary among years (Supplementary information Table S1) likely as a function of changes in precipitation patterns. For each watershed, we used the minimum, mean and maximum value of p (Supplementary information Table S1) to simulate watershed P depletion through riverine export under a range of precipitation scenarios.

Results

Indeed we identified a breakpoint ($p<0.001$) in the relationship ($R^2=0.80$) between watershed P accumulation and riverine total P (TP) export at 2606 kg P km^{-2} (CI=33-11 955 kg P km^{-2}; Fig. 1), which we call the P buffering capacity threshold. Up to this threshold, watershed P accumulation had no significant influence on P transferred to surface waters, but the significant positive slope ($p<0.001$) of the second segment of the breakpoint regression showed a dramatic increase in riverine TP exports with P accumulation. Compared to the level of accumulated P observed in our most enriched watershed (50 000-100 000 kg P km^{-2}; Fig. 1), the threshold is surprisingly low, indicating that these watersheds have limited capacity to cope with additional P without impacting downstream waters. Furthermore, this threshold value was reached very rapidly.

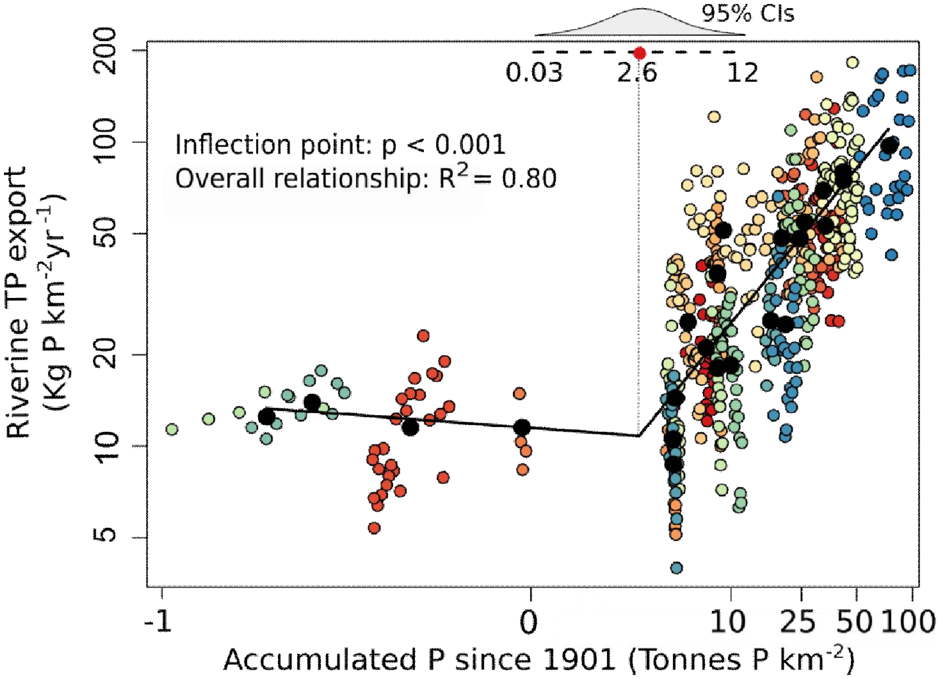

Figure 1. Threshold of watershed P buffering capacity. Relationship between riverine TP export from 1985 to 2011 and watershed P stocks accumulated since 1901. Different colors represent the 23 watersheds with each circle a different year for a single watershed. Black dots show per-watershed mean values that were used to perform the segmented regression analysis.

When we examined our historical reconstructions of accumulated P, we found that more than half of the watersheds in this study had crossed the P buffering capacity threshold by the 1950s or 60s (Fig. 2) with some surpassing this point already in the 1920s, well before the so-called Great Acceleration (Steffen et al. 2004). Examples of earlier-than-anticipated lake eutrophication exist. Paleolimnological studies have shown eutrophication as early as the beginning of the 20th century across Europe (Jenny et al. 2016), during the middle-ages in the Arctic (Douglas et al. 2004), and even during the Roman Empire (Hutchinson et al. 1970). However, these studies concluded that the phenomenon of enrichment was due to increased point source nutrient inputs associated with population growth. Our results suggest that human activities may have overwhelmed the capacity of entire watersheds to cope with excess P from both point and diffuse sources, even prior to modern intensive agricultural practices.

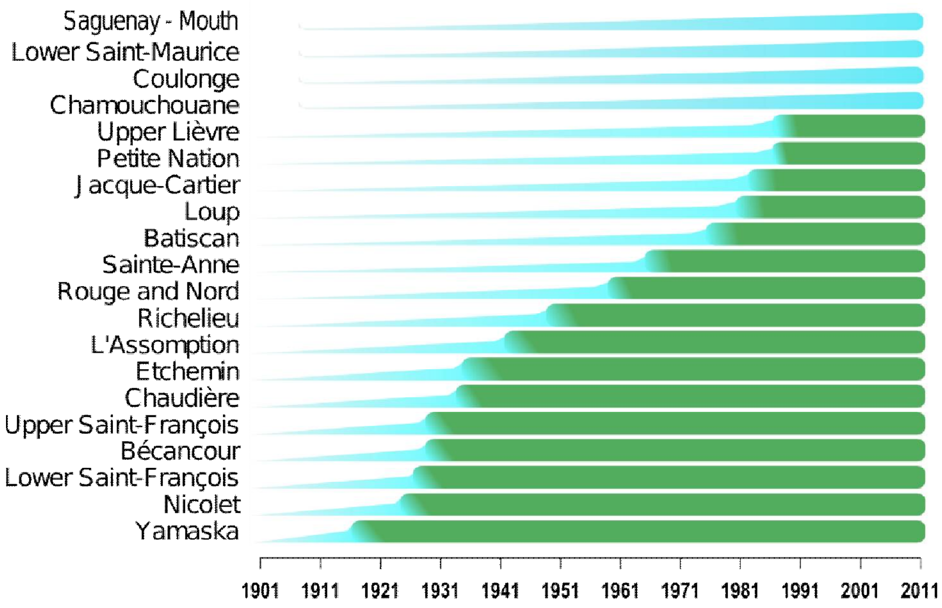

Figure 2. Time to cross the watershed P buffering capacity threshold. Year, using 1901 as the start point, when P accumulation in specific watersheds were found to exceed the threshold of P buffering capacity of 2606 kg P km^{-2}.

Almost all of our study watersheds that accumulated P during the last century reached a peak in annual excess P around the 1980s, after which declines in total inputs were observed (Supplementary Information; Fig. S2). Despite these reductions in inputs, none of our watersheds have entered a depletion phase in which P stocks would have been reduced by outputs exceeding inputs. We thus modeled P depletion times of each watershed as an exponential decay process based on P runoff coefficients (*p)* identified for each year and each watershed. We used an assumption of balanced anthropogenic inputs and outputs to estimate the time needed to deplete the accumulated P pools over the century back to the critical level of 2606 kg P km^{-2} through runoff only under a range of precipitation scenarios.

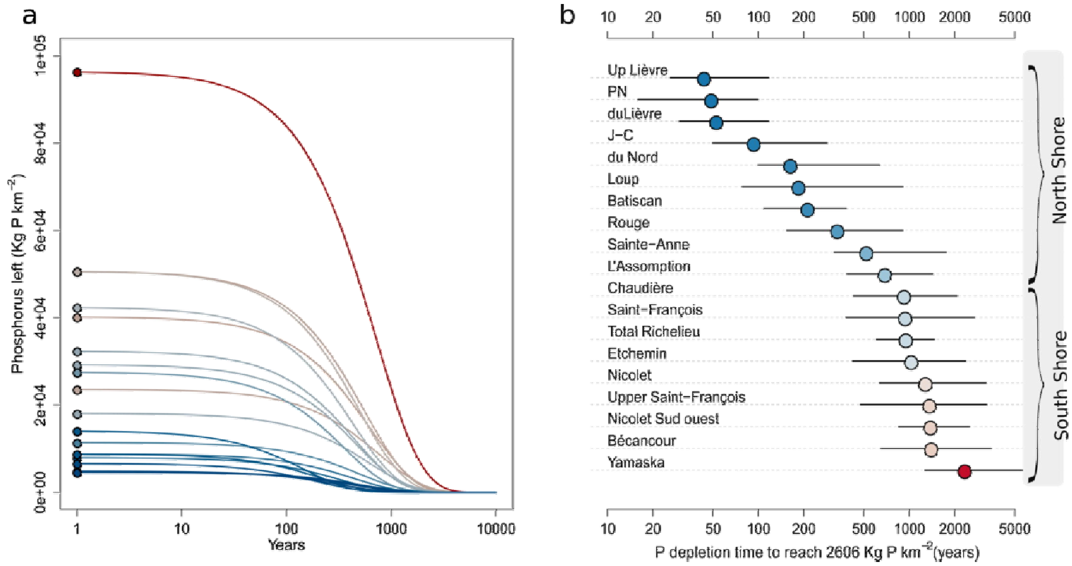

Figure 3. Time required to return to baseline conditions. Projections of the time needed for riverine exports to deplete the anthropogenic P pools that accumulated between 1901 and 2011. **a**, Decay curves using watershed-specific, mean P runoff coefficients (Supplementary Information Table S1). **b**, Depletion time to reach the critical level of 2606 kg P per km^2. Coloured circles show the depletion times estimated with mean P runoff coefficients while bars show the potential range under extreme climate scenarios. Colors were assigned based on the distribution of mean P depletion times across watersheds using a blue-to-red palette.

Our modeled results showed that average decay curves varied across watersheds due to their specific *p* and P stock at time 0 (in 2011; Fig. 3a). In contrast to the short time needed to increase P stocks to the critical threshold of 2606 kg P km^{-2}, the time required to return to this level ranged from a few decades in relatively pristine systems to several millennia in agricultural ones (Fig. 3b). Depletion times for watersheds located on the more forested north shore of the St. Lawrence River (Goyette et al. 2016) ranged from between ~50 and ~500 years, whereas those of the intensive agricultural watersheds of the south shore were on the order of ~1,000 -1,500 years. Under extremely wet and dry conditions, most of the watersheds of the south shore required ~500 to ~2000 years to deplete their P pools back to the critical level, respectively (Fig. 3b). Exceptionally, the watershed with the highest P store in 2011 (Yamaska), had a probable depletion time estimate of ~2000 years but these ranged from 1000 to ~5000 years under different climate scenarios (Fig. 3b and Supplementary Information Table S1).

Discussion

This study provides the first conclusive evidence of a threshold in P buffering capacity at the watershed scale. While the concept of P buffering capacity implies the notion of a "safe operating space" in which agriculture does not impinge on water quality at the food water-nexus, our study suggests that at typical P application rates this grace period is very short (Fig. 1 and Fig. 2). Large P accumulations in relatively short time frames have been observed for the Thames and Maumee Rivers, with ~ 20 000 and 15 000 kg P km^{-2} accumulated in 75 and 35 years, respectively (Powers et al. 2016). Current P surplus rates typically range from 700 to 1200 kg P km^{-2} yr^{-1} across a variety of agricultural systems (Bennett et al. 1999; Goyette et al. 2016; Han et al. 2011; Hong et al. 2012). Using these rates and assuming 10% export through runoff (Goyette et al. 2016; Han et al. 2011; Hong et al. 2012), crossing our most probable threshold of 2606 kg P km^{-2} would take between 2.5 to 5 years in a typical agricultural watershed, and just 12 to 18 years to reach the upper limit of 12 000 kg P km^{-2} of our estimated threshold (Fig. 1). Watershed buffering capacities may vary among different regions however this variability remains to be assessed. Nevertheless, the range of "time to threshold" we report here is strikingly low, suggesting that most systems have tipped in terms of accelerated P export to surface waters that threatens water quality.

We also found that P accumulated in our study watersheds within just a few decades, could take centuries to millennia to return to this baseline threshold. Although surprisingly long, this time frame is in accordance with P residence times estimated for riparian zones (Jarvie et al. 2013b) and also supports the projected time period that legacy P could continue to maintain the eutrophic state of lake Mendota (Carpenter 2005). However, the estimated times to return to a level of low risk for P transfers to surface waters may be overestimated by these depletion curves as they do not account for older P that is strongly occluded by soil particles that may potentially never be released (Schnug and De Kok 2016). Regardless of the potential caveats, the relatively short time scales to attain a threshold that increases P delivery risk to surface waters, compared to the long time scales required to deplete it, suggests that we must look at alternative ways to manage P at the food-water nexus.

Efforts toward reducing P loads in sewage effluents, balancing fertilization with crop requirements and reconnecting animal farming with crop agriculture (MacDonald and Bennett 2009), and developing new ways to exploit existing soil (and sediment) stocks (Rowe et al. 2016) will be essential components to a better P management plan. These approaches may be inevitable in the face of increasing population growth and imminent shortages of P mineable deposits (Cordell et al. 2009). While multiple approaches to reduce the amount of P that enters aquatic systems exist and should be promoted, the over enrichment of watersheds with P will make reduction of runoff or downstream flux ever more difficult (Carpenter et al. 1998; Jarvie et al. 2013a; Motew et al. 2017). Transport control measures can only reduce transfers on the short-term, as they become watershed legacy stores over the long-term. Feeding an ever-growing human population while protecting water quality is an immense challenge that requires solutions. Our study clearly demonstrates how rapidly diffuse and point source P pollution becomes and remains an issue in terms of watershed accumulation and release. Nutrient management strategies developed using novel creative approaches at multiple scales are urgently required for long-term sustainability of water resources.

Acknowledgements

We thank T. Poisot, J.F. Lapierre, D. Morse and members of the Maranger lab for helpful suggestions. This research was supported by Fonds de Recherche Nature et Technologie du Québec (FQRNT) and Groupe de Recherche Interuniversitaire en Limnologie et environnement aquatique (GRIL) student scholarship grants to J.O.G. and a National Science and Engineering Research Council of Canada (NSERC) Discovery grant to R.M.

Author Contributions

All authors participated at developing the idea and the conceptual framework of the study; J.O.G. and R.M. designed the analysis and J.O.G. analyzed the data and performed the simulations; All authors wrote the manuscript.

Author Information

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Data availability

The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Supplementary information

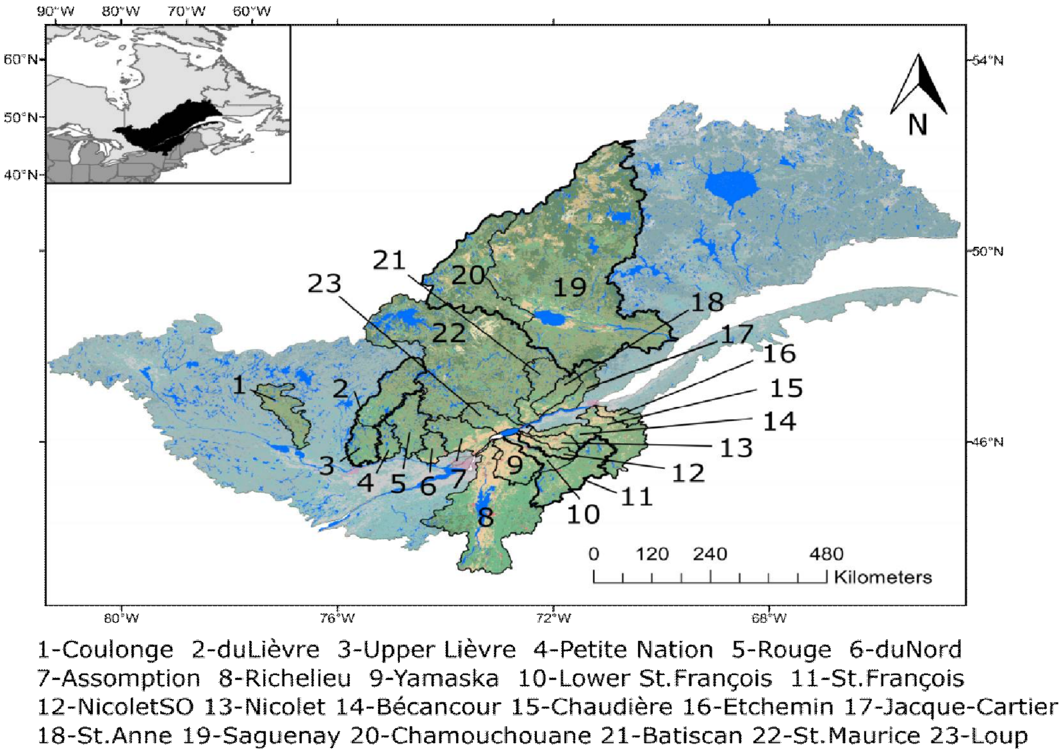

Figure S1. The 23 watersheds considered in this study.

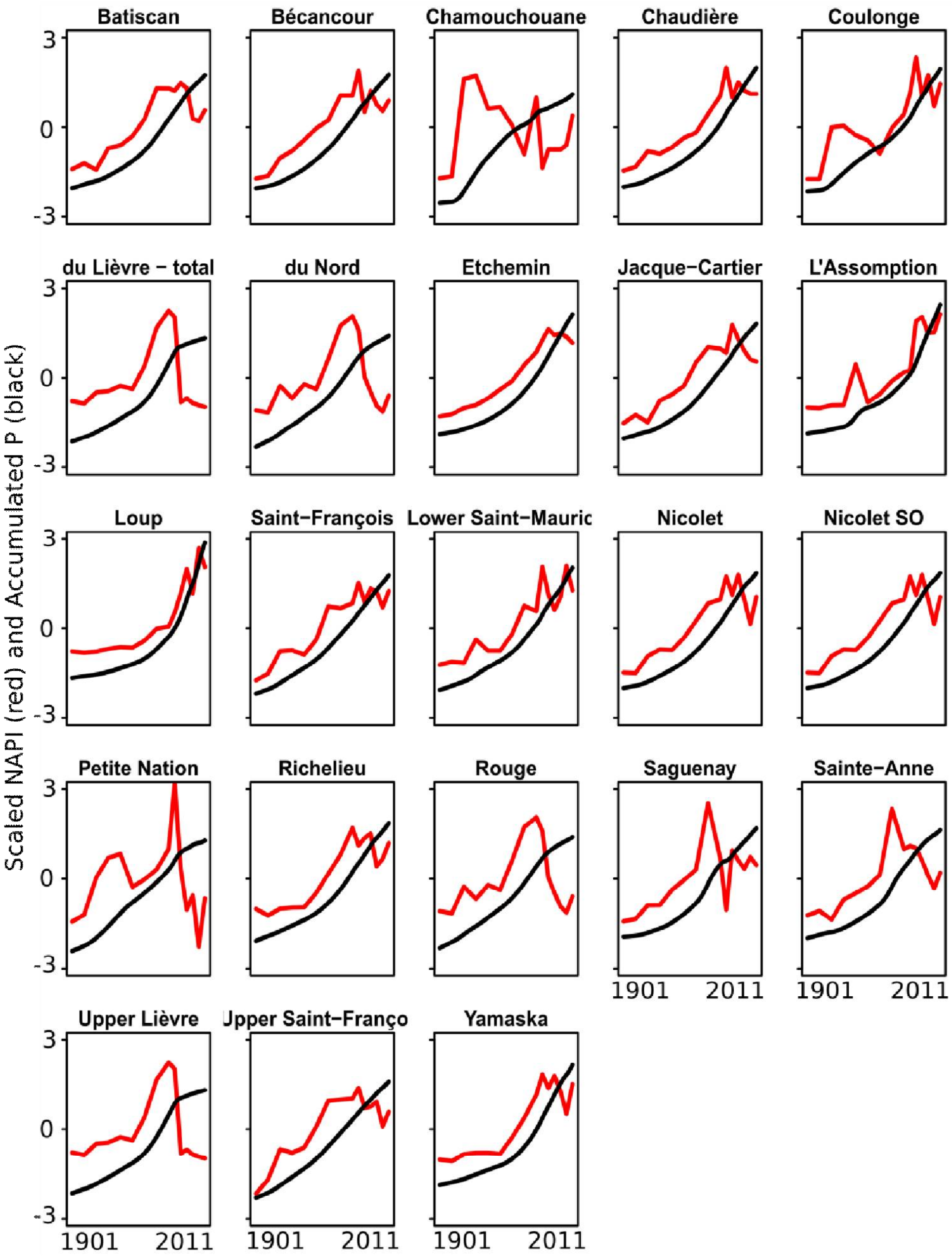

Figure S2. Annual P surpluses (NAPI) and P accumulation throughout the century. P accumulation (black line) and NAPI (red line) between 1901 and 2011 for each watershed. All values were standardized per watershed (mean=0, SD=1) for ease of comparison.

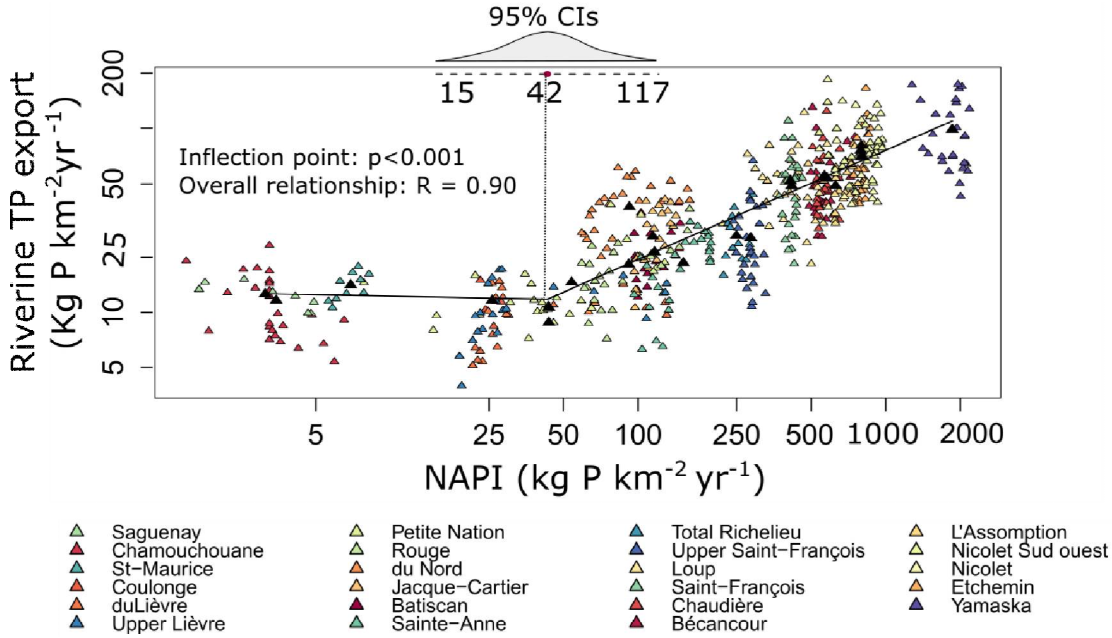

Figure S3. Relationship between annual riverine TP export and annual P surpluses on the landscape (NAPI) in years 1985 to 2011. This relationship served to back calculate riverine TP export in years 1901 to 1984 using NAPI reconstructions in those years. Each color represents one of the 23 watersheds, and each coloured triangle is a different year for a single watershed. Legend is presented in order of appearance of watersheds in plot, from low to high mean values of NAPI.

Tableau I P runoff coefficients and P depletion times.

Rivername	P stock in 2011 (kg km-2)	P runoff coefficient*			depletion time** (years)		
		min	mean	max	shortest	mean	longest
Yamaska	96433	0.0006	0.0014	0.0025	1273	2303	5603
Bécancour	40201	0.0007	0.0016	0.0035	648	1382	3457
Nicolet Sud ouest	50662	0.001	0.0018	0.0029	849	1363	2488
Upper Saint-François	23639	0.0005	0.0013	0.0036	476	1343	3224
Nicolet	50662	0.0008	0.002	0.0039	632	1264	3207
Etchemin	42428	0.001	0.0023	0.0055	421	1017	2353
Total Richelieu	18102	0.001	0.0016	0.0024	606	936	1453
Saint-François	29273	0.0007	0.0021	0.0051	381	927	2694
Chaudière	32409	0.001	0.0022	0.0048	428	912	2073
L'Assomption	27561	0.0013	0.0028	0.0049	385	680	1422
Sainte-Anne	11449	0.0006	0.002	0.0032	317	513	1743
Rouge	8823	0.0008	0.0023	0.0048	154	329	900
Batiscan	7978	0.0017	0.0031	0.0059	109	209	379
Loup	14126	0.0013	0.0067	0.0155	78	182	901
du Nord	8823	0.0012	0.0046	0.0074	100	161	634
J-C	6649	0.0016	0.005	0.0091	50	92	284
duLièvre	4635	0.0009	0.0019	0.0034	30	52	116
PN	4865	0.0015	0.0031	0.0089	16	48	99
Up Lièvre	4635	0.0009	0.0023	0.0039	26	43	116

*P runoff coefficient is calculated as Riverine TP/Watershed P stock (kg km^{-2})

**depletion time to reach threshold value of 2606 kg km^{-2} (years)

Anthropogenic P stocks in 2011 due to accumulation since 1901 in 19 watersheds, the P runoff coefficients (minimum, mean and maximum) over the period 1985-2011 and the modeled P depletion times to reach back the threshold of watershed P buffering capacity of 2606 kg P km^{-2}.

Testing for a circularity effect in the relationship of Fig 1

Since riverine TP load estimates were used to calculate P accumulation, we tested for the possibility of introducing a circularity effect that would have artificially inflated the statistical strength of the threshold relationship in Fig 1. In order to test for that potential effect, we used two different approaches. Firstly, we repeated the same analysis as in Fig 1 but we omitted the correction of riverine TP loads from our P accumulation calculations. This resulted in a very similar relationship as the original Fig 1, thus highlighting the relatively minor contribution of fluvial P exports to watershed P accumulation over our 110-year time frame (Table S2).

Tableau II Comparison of threshold results from two different approaches in the calculations of watershed P accumulation. Similarity between results highlights the relatively minor contribution of riverine P exports to watershed P accumulation over our 110-year time frame. This analysis validates our approach in Fig 1 by demonstrating that the small amount of circularity (or endogeneity) introduced had no substantial impact on the relationship observed

Approaches	mean	CI 95%
	(Tonnes P km^{-2})	
Watershed P accumulation (including riverine TP export)	2606	32-11,955
Proxy of Watershed P accumulation (ignoring riverine TP export)	3540	773-16203

In a second test, we used a randomly generated data set emulating the variables of Fig 1, and verified whether a relationship emerged due to this potential circularity. Following the same sequence of methods as described in the methods for real data, we created random NAPI data for 100 watersheds over 100 years (without temporal patterns) and used NAPI to model riverine TP loads in each watershed for all years based on the relationship observed in Fig S3. We then calculated P accumulation in each watershed by subtracting riverine loads from NAPI throughout the century. No pattern emerged in plots of randomized riverine loads against randomized accumulated P (Fig S4), highlighting that the small amount of circularity introduced had no effect on the relationship observed in Fig 1 or on the threshold detected therein. Therefore, we decided to stay with our original mass-balance approach of subtracting riverine exports from watershed P accumulation over time, as it is conceptually more accurate as a representation of legacy P.

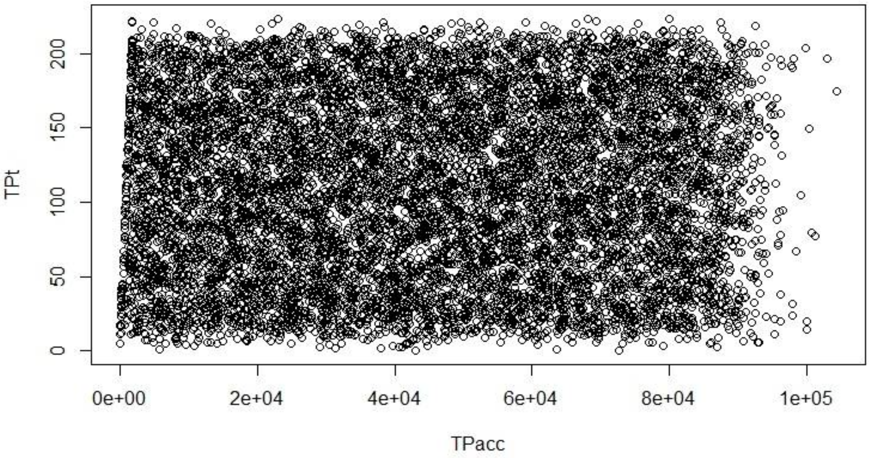

Figure S4. Test of the circularity effect in the relationship of Fig 1. The absence of an emerging pattern due to circularity within the relationship between riverine TP loads (TPt; Kg km-2 yr-1) and watershed P accumulation (TPacc; T km-2 yr-1) based on simulated random data mathematically validates the methods used to create Fig 1 and to detect a watershed buffering P capacity threshold.

Chapitre IV. Évolution de l'efficacité d'utilisation des nutriments dans le système agroalimentaire du bassin du Saint-Laurent au cours du dernier siècle

Changes in the nutrient-use efficiency in the agro-food system of the St. Lawrence Basin over the last century

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Target journal: Chemosphere; Environmental Research Letters; Ecosystems

Abstract

Improvement in nutrient use efficiency is necessary to meeting the dual challenge of food security and environmental sustainability. By reconstructing fluxes of N and P within the agro-food system of the St. Lawrence Basin (SLB) between 1901 and 2011 using the GRAFS approach, we assessed how important transitions of the XX^{e} century have shaped system's performance from both environmental and agricultural perspectives allowing to evaluate trade-offs and identify areas for optimization at the food-water nexus. We show that cropping practices were unsustainable in the first half of the century, depleting soils of nutrients (particularly P). With the advent of manufactured fertilizers and the intensification of animal farming, the agro-food system of the SLB rapidly tipped to a highly inefficient system in which ~70% of N and ~90% of P resources are now potentially lost to the environment. Also, we showed that accounting for the complete life cycle of nutrients in food products is essential to provide a true picture of the performance in each compartment of the system. Finally, we show that losses to the environment can continue to increase even under greater nutrient use efficiency if the absolute throughput of nutrient is allowed to increase. While nutrient use efficiency can substantially help to further reduce losses, we argue that targets of maximum nutrient loads to the environment should be identified and set in priority.

Introduction

The efficient use of nutrients is often presented as the key strategy to meeting the twin challenges of food security and environmental sustainability (Godfray et al. 2010; SDSN 2012; UNEP 2016). In recent decades, increased nitrogen (N) and phosphorus (P) application to agricultural lands has permitted feeding an ever growing population, but also favoured huge environmental costs, threatening soil, air, and water quality (Foley et al. 2011). Through the first half of the 20th century, the advancement of technologies, including development of the Haber-Bosch process (Hager 2009) as well as mechanization and increases in energy supply to mining (Smil 2000), allowed a massive scaling up of access to nitrogen and phosphorus, respectively (Sutton et al. 2013). The industrial and agricultural revolutions built on these successes led to massive intensification of agriculture and increased use of N and P (Smil 2000a). The mid-century shift from predominant reliance on recycled and renewable nutrient pools (manures and sewage; Ashley et al. 2011) to these new nutrient sources, fundamentally altered the N and P cycles globally (Cordell et al. 2009; Vitousek et al. 1997a). Increases in nutrient inputs to agricultural lands, coupled with the breeding of new crop varieties, led to increases in grain and grass production that outgrew needs of these crops for human consumption (Sutton et al. 2013). Production surpluses were thus available for animal feeding, triggering a rapid growth in the livestock sector in the second half of the 20th century (Oenema et al. 2005; Sutton et al. 2013). At the same time, animal and crop agriculture have become more geographically separate (Billen et al. 2013a; Billen et al. 2014; MacDonald and Bennett 2009; Metson et al. 2016) leading to the nutrient saturation of those croplands nearby animal inputs.

In order to feed a growing human population while reducing environmental degradation (Godfray et al. 2010), improvement in the use of N and P resources are urgently needed. The main solution to achieve this twin challenge is two-fold: 1) reducing the overall nutrient throughput, that can be defined as the flow of matter and energy within a system that transforms low-entropy raw materials into high-entropy wastes (Daly 1992), and 2) increasing nutrient use efficiency (NUE), particularly in agro-food systems (Gerber et al. 2014; Sutton et al. 2013). NUE is defined as the ratio of nutrients in intended food products to the total nutrients used in the production process. Thus, the greater NUE, the less excess nutrients susceptible to be lost to the environment, and the closer application rates are to what is needed for compensating export through harvest. Improving NUE requires site-specific knowledge, tools, technologies and adapted cultivars (Foley et al. 2011; Godfray et al. 2010; Roberts 2008). In that sense, the precise accounting of nutrient fluxes in regional agro-food systems under different agricultural practices and human needs can help identify trade-offs and optimal management options to reconcile food security and environmental sustainability. Several approaches have been developed for that purpose at different scales, from local to global, with different accounting procedures and various objectives (Anglade et al. 2015; Billen et al. 2014; Goyette et al. 2016; Lassaletta et al. 2014a). Yet, the majority generally focused on one single nutrient or on one single compartment of the agro-food production chain (i.e., the cereal sector). Few studies have considered N and P simultaneously (e.g., Le Noë et al., 2017), and so throughout the different compartments of the agro-food system, and few have taken an historical perspective that span the important transitions of agricultural practices over time (Le Noë et al., submitted).

Here, we characterize the changes in N and P use efficiency throughout the last century in agriculture for the St. Lawrence Basin, a region of the world that witnessed dramatic shifts in both agricultural practices and production rates (Goyette et al. 2016). We used a mass balance approach that allows a generalized representation of N and P fluxes in the agro-food system (GRAFS; Billen et al. 2014; Le Noë et al, 2017). By considering the nutrient exchanges between cropland, grassland, livestock biomass, the local human population, and potential losses to the environment, the GRAFS approach provides information on the performance from both environmental and agricultural perspectives that help to evaluate trade-offs and identify areas for optimization. Accounting for the full life cycle of N and P within the agricultural system, we identified trends of NUE in crop, animal and total food production. We hypothesized that 1) NUE in crop production (NUE_{crop}) substantially declined throughout the 20th century with the increased use of industrially produced fertilizers and manures originating from growing herds of domesticated animals; 2) that accounting for the complete life cycle of nutrients in animal food products (losses during feed production) would significantly alter the signal of NUE in animal production (NUE_{animal}); 3) and that transitions in breeding types of crops and animals throughout the century played a significant role in altering the relative trends of N and P use efficiencies.

Methods

To quantify trends of NUE in the agro-food system of the St. Lawrence Basin (SLB), we examined N and P fluxes between the different compartments through time. N and P budgets were thus constructed for agro-food systems of 76 watersheds of the SLB (Goyette et al. 2016) at a 10-year time interval from 1901 to 2011 using the GRAFS approach. While most previous analyses of this type consider agricultural surfaces overall, GRAFS separates agricultural surfaces between permanent grassland and cropland, (the latter including temporary grasslands which are part of crop rotations). GRAFS has been successfully applied in study cases of individual farms (Anglade et al. 2015; Bonaudo et al. 2014), small (Garnier et al. 2016) and large basins (Lassaletta et al. 2014b) as well as at national (Le Noë et al. 2017) and global scales (Billen et al. 2014). Data on input and output terms, modelled using net anthropogenic N and P inputs approach for the St-Lawrence basin (Goyette et al. 2016), were adapted to the GRAFS framework following Le Noë et al. (2017). The 14 major crops grown in the St. Lawrence Basin as well as 18 animal categories, considering type and age, were considered to represent the agro-food systems of the region (Goyette et al. 2016).

Soil nutrient budgets in cropland and grassland

Soil nutrient budgets were calculated as the difference between soil inputs through intended and non-intended fertilizers and outputs through harvest. Inputs include synthetic and mined fertilizers, manure (after all NH_3 volatilization has occurred in the case of N), biological N fixation (BNF) by legumes, and atmospheric N and P deposition. Due to lack of available data, urban sludge application was not considered in this study. However, we hypothesized that this nutrient source to agricultural lands is likely very minor in the St. Lawrence Basin since the majority is stored in landfills or incinerated (Metson and Bennett 2015). Positive nutrient budgets indicate potential accumulation in soils and/or losses through erosion, particularly for P. For N, soil surpluses predominantly represent potential losses to the atmosphere (mostly by denitrification as N_2 or N_2O, a greenhouse gas by-product) or to aquatic ecosystems through leaching, although a fraction may be stored in the soil organic matter pool (Anglade et al. 2015). Negative budgets indicate active nutrient mining by plants, and removal from the soil (Bouwman et al. 2013; Garnier et al. 2015).

N and P synthetic fertilizer application rates were taken from (Goyette et al. 2016). No data was available on recommendation of fertilizer application to permanent grasslands, so the total amount of fertilizer within a watershed was attributed to croplands. A fraction of N embedded in synthetic fertilizers was considered as lost by ammonia volatilization, which coefficients were taken from Le Noë et al. (2017). For atmospheric N deposition, we considered all chemical N forms using the CMAQ model (www.cmaq-model.org/) and tracked the changes in deposition rates throughout the century (Goyette et al. 2016). Atmospheric P deposition was estimated as 0.25 kg ha^{-1} yr^{-1} (Bouwman et al. 2013; Liu et al. 2008) and kept constant over time. We assumed atmospheric N and P deposition rates to be evenly distributed across landscapes. Symbiotic N_2 fixation was estimated based on Anglade et al. (2015). Finally, crop yields and grassland production, and the respective N and P uptake coefficients of all 14 crop types were retrieved from Goyette et al (2016).

Total manure production was calculated from livestock numbers using N and P excretion factors specific to each animal type and age (Goyette et al. 2016) and corrected for manure management practices and volatilization rates (Le Noë et al. 2017). Volatilization rates accounted for manure management practices and for the fraction of time spent indoors for each of the four animal categories (ovine, bovine, porcine, poultry). Excreted manure while grazing was allocated between temporary and permanent grasslands based on relative surface area, and managed manure (emitted indoors) was assumed to be evenly distributed on cropland (thus including temporary grassland). Regarding P, no loss was assumed between excretion and manure application to soils. Total N and P ingestion was defined as the sum of total production and total excretion.

Animal food products

Animal weights at slaughter and yields of animal products (milk and eggs) were retrieved from Goyette et al. (2016) while coefficients of N and P content in the different animal parts were gathered from Le Noë et al. (2017). Animal production was broken down into edible and non-edible products (Le Noë et al. 2017). Although the recovery of P in animal bones through industrial processing for pet food, animal feed additives or fertilizers is possible (Suh and Yee 2011), these practices are currently unaccounted for on the SLB. N and P ending in those non-edible products were thus all considered a loss to the environment. Finally, following (Billen et al. 2014), we defined a livestock unit (LU) as the number of animals of any species annually excreting 85 kg N yr^{-1}.

Import/export of food and feed

For each watershed, the import and export estimates of animal feed or human food were obtained through mass balance calculations. Data on commodity trade at the scale of our study (county scale) was not available. We assumed plant and animal food products to be consumed locally first, with the excess being exported. When local plant or animal food production was not sufficient to feed the local population, the gap was assumed to be filled through food imports from external regions. Similarly, livestock was assumed to be fed locally first. If livestock N and P requirements were not entirely met by local sources, feed imports (N and P content) were assumed to fill the gap. Excess local crop or human food production was considered to be exported outside the region. The human N and P demand in food was estimated through changes in population and protein consumption over time (Goyette et al. 2016). The human compartment of the system was considered to be steady-state, so that human excretion was assumed to be equal to consumption (inputs=outputs).

N and P imprints of agricultural production and NUE

Transfers of nutrients within the animal sector consider only the proportion of ingested nutrients that make their way to animal products. NUE within that compartment thus ignores losses encountered upstream in the production process through feed production. To quantify the true imprint of animal food production, we thus internalized losses associated with feed, whether it was grown locally or imported from external regions. Losses through feed production were estimated by calculating the NUE within the local crop and grass sector. For imported feed, losses were estimated being equal to those encountered locally depending on region and year. Note that the manure fraction derived from local crop and grass ingestion by livestock was excluded from NUE calculations, given that it represents internally recycled nutrients. Fluxes and environmental imprints were expressed *pro rata* to the surface of total agricultural land (i. e., kg N or P ha^{-1} yr^{-1}).

Results

Landuse and farming practices

Throughout the last century, agriculture in the SLB has intensified with a constant reduction in cropland and grassland area, despite a steady increase in crop yields and animal production (Fig 1). Between 1901 and 2011, cropland area decreased by 60%, going from ~6 to 2.4 M hectares while permanent grassland decreased by 86%, going from ~1.7 to 0.2 M hectares. Crop and grass production sharply decreased at the beginning following reductions in agricultural land area, but then gradually increased through further intensification. Meanwhile, increased intensification of animal food production was also observed (Fig 1).

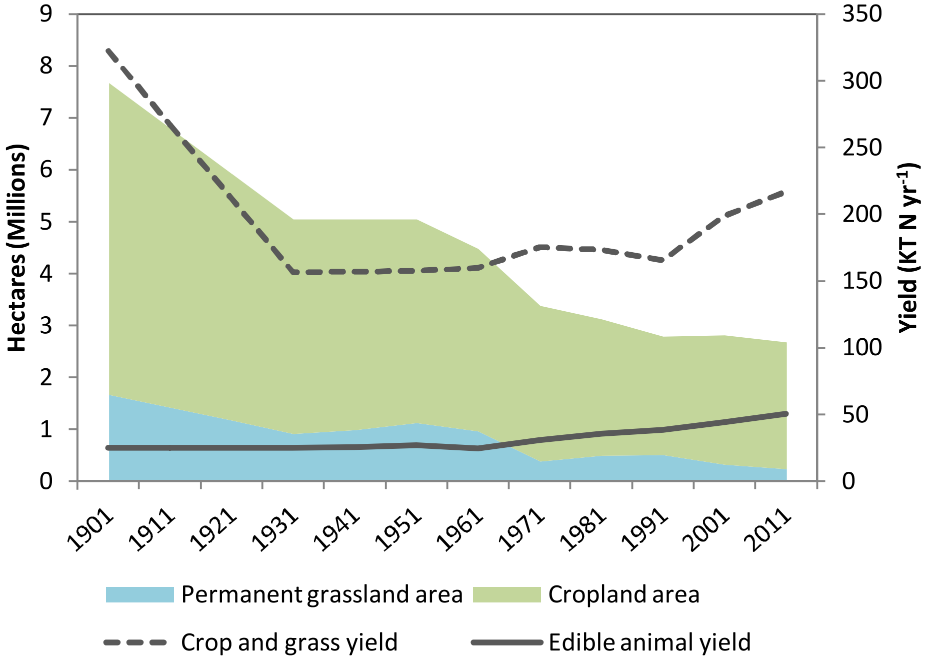

Figure 1. Cropland and permanent grassland area over time in the St. Lawrence Basin, and changes in relative farming productivity (crop and animal sectors).

Indeed, the intensification of crop production appeared to be partly driven by the growing livestock herds and by the shift from grazing to grain fed animals. From 1901 to 1961, there was a transition toward agricultural systems where crop and grass production was increasingly insufficient relative to animal and human demand (Fig 2). Data points under the 1:1 line suggest more "heterotrophic" systems (in the sense of Anthropogenic N-auto/heterotrophy of regional systems; Billen et al. 2010) where imports of N and P through animal feed were required to meet growing demand. Nearly half of our 76 watersheds experienced that transition (Fig 2). Between 1961 and 2011, yields of crop and grass nearly doubled in some highly agricultural regions (going from ~45 to ~100 kgN haUAA^{-1} yr^{-1}), which specialized meanwhile in the production of either crops or animals (Fig 2). By 2011, many agro-food systems produced more crop and grass than locally needed (above 1:1 line), while others further specialized in animal farming increasing their needs for feed imports from other regions.

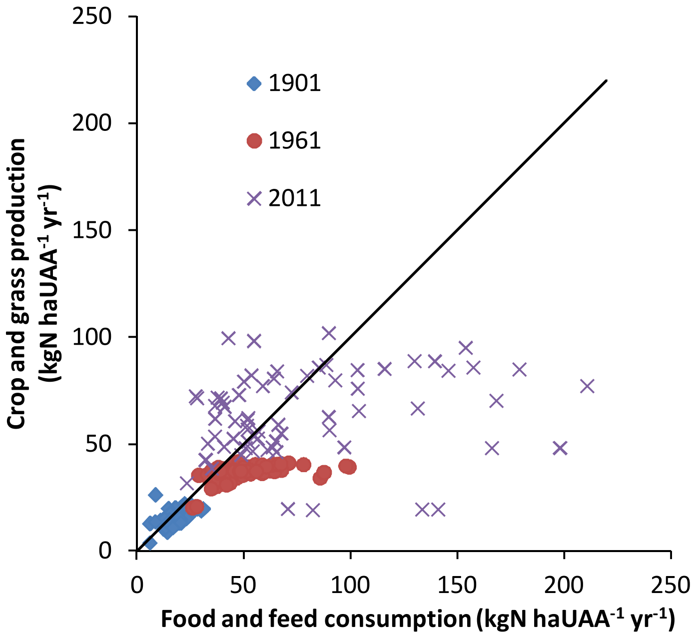

Figure 2. Crop and grass production versus human food and animal feed consumption in 1901, 1961 and 2011 in the 76 watersheds of the SLB showing the transition from a crop and grass-fed animal oriented-agriculture towards intensive and specialized crop or animal farming. Points under the 1:1 line (gray line) are interpreted as “heterotroph” watersheds in which significant imports of N and P through animal feed (or human food) are needed while those above the 1:1 line are "autotroph" watersheds producing more vegetal protein (on a kgN basis) than locally needed.

During that transition, pastures were replaced with grain crops, particularly corn and wheat (Fig 3). These new crops served to support the breeding of monogastric animals such as pigs and chickens that replaced ruminant herds of dairy cows, horses and sheep (Fig 4) that used to feed on pastures and tame hay (Fig 3). Milk was the main human source of protein throughout the 1st half of the century, but was slowly replaced by pork and poultry (Fig 4). It is worth noting that milk was primarily consumed locally while pork and poultry (especially pork) are now largely grown for exports on global markets (Verret 2010). While horses were included in the portrait of Figure 4, these animals were not used as food but rather as commercial commodities or power supply in agriculture and transportation during the early century (Perron 1954).

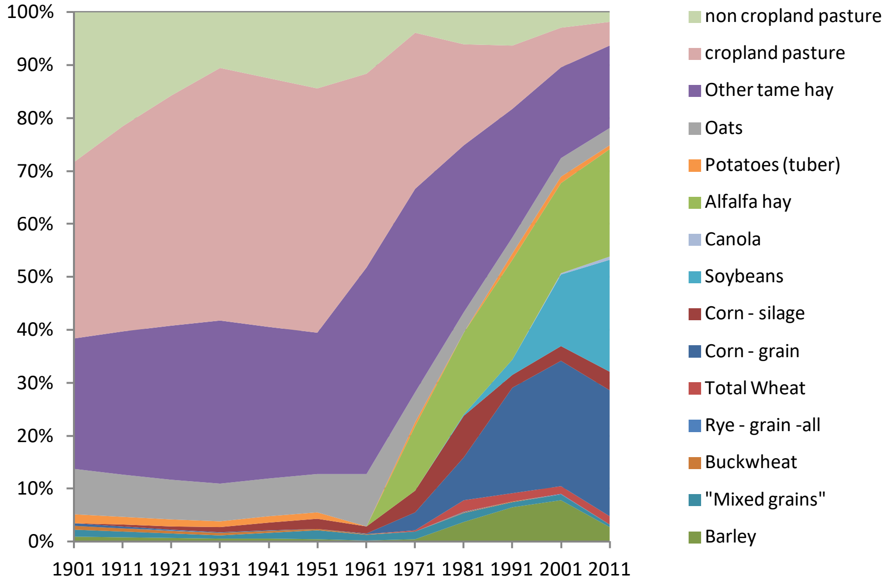

Figure 3. Proportion of major source of animal feed (and human food) over time on a kg basis.

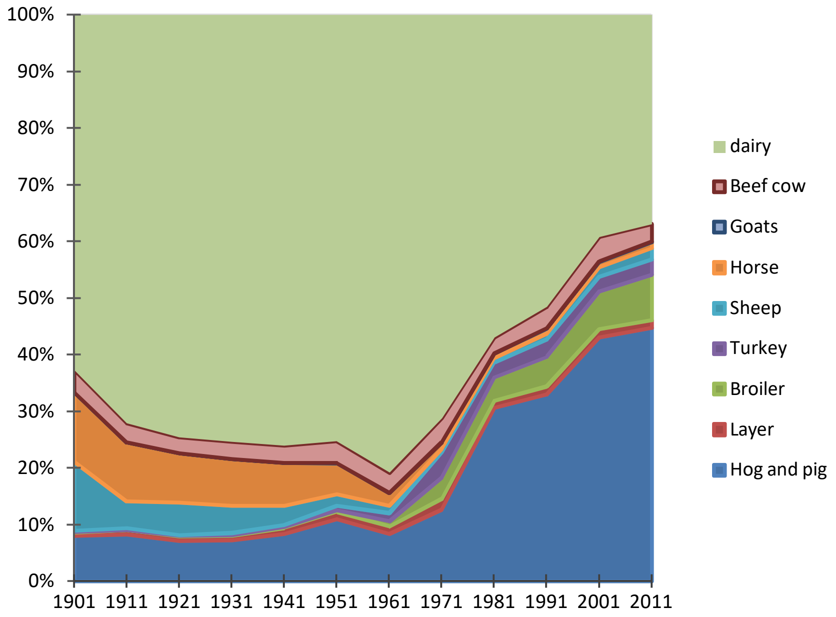

Figure 4. Proportion of animal herds over time in the St. Lawrence Basin represented as sources of protein (on a N basis) from animal products. Horses are included to represent variation over time although these animals were not used as food but rather as a commercial commodity or source of power.

Transitions toward intensive farming (crop and animal) increased the absolute magnitude of nutrient fluxes across the different compartments of the agro-food system, creating major surpluses in grasslands and croplands (Fig 5). This effect was particularly important in more intensive agricultural regions such as the central St. Lawrence sub-drainage region (Fig S1; Fig S2). While lack of fertilization lead to soil nutrient depletion in the early century in many regions (Fig S3), increased anthropogenic inputs of N and P to soils since have favoured potential losses to the environment (Fig 5). In 1901, grazing actively mined 0.3 kg N and ~0.5 kg P per hectare of permanent grassland per year (Fig 5) in the St. Lawrence basin as a whole. In croplands, crop harvests mined 0.6 kg N per hectare while conversely, P surpluses of 0.4 kg P per hectare were observed. In regions with large areas of temporary grasslands (that are part of crop rotations) soil depletion rates were even higher, reaching ~6 kg N and 1.5 kg P per hectare of UAA per year (Fig S3). In 2011, that pattern was reversed with surpluses in the St. Lawrence basin of 56 and 22 kg ha^{-1} yr^{-1} in croplands for N and P, respectively and of 6 and 5 kg ha^{-1} yr^{-1} in grasslands (Fig 5). IN the most intensive agricultural region, these surpluses reached 83 and 35 kg ha^{-1} yr^{-1} in croplands for N and P, respectively and of 5 and 8 kg ha^{-1} yr^{-1} in grasslands (Fig S2). Manufactured fertilizers, BNF and livestock were the main drivers of these surpluses. Fertilizer application went from none in 1901, to 56 and 25 kg ha^{-1} yr^{-1} in 2011 for N and P, respectively in the St. Lawrence basin as a whole. The cultivation of leguminous crops such as soybeans largely contributed to soil N surpluses in 2011 with a ~50-fold increase since 1901. Manure application to cropland went from 10.8 to 29 kg ha^{-1} yr^{-1} for N and 1.3 to 8.2 kg ha^{-1} yr^{-1} for P throughout the century (Fig 5). The proportion of manure returning to grassland relative to the total amount of manure produced by animals decreased substantially because of the transition from ruminant animals, passing more time in pastures, to monogastric confined animals, which manures are handled and preferentially applied to croplands. The huge amount of manures generated by the expansion of animal herds lead to important N losses to the atmosphere through volatilization during storage and application, going from 3 to 10 kg N ha^{-1} yr^{-1} over the study period (Fig 5). Moreover, increased animal production also lead to major N and P losses through non-edible products such as bones, blood and viscera, that reached 33 and 72% of total animal yields in 2011, for N and P respectively (Fig 5). This was particularly pronounced for P since it is a major constituent of bones.

While human population consistently grew throughout the century, the human compartment was considered in steady state in terms of nutrient flows, meaning no retention of N and P within that compartment. Thus, all N and P that reached humans as food were assumed to be excreted, creating a potential loss to the environment. Finally, feed imports appeared necessary to meet livestock demand throughout the century (1.2 and 3.2 kg ha^{-1} for N and P, respectively in 2011; Fig 5), and so particularly in the most intensive central region (18 and 8 kg haUAA^{-1} for N and P respectively in 2011; Fig S3). This shift towards intensive animal farming was also apparent in Figure 2 showing agro-food systems that evolved from autotrophic to more heterotrophic systems.

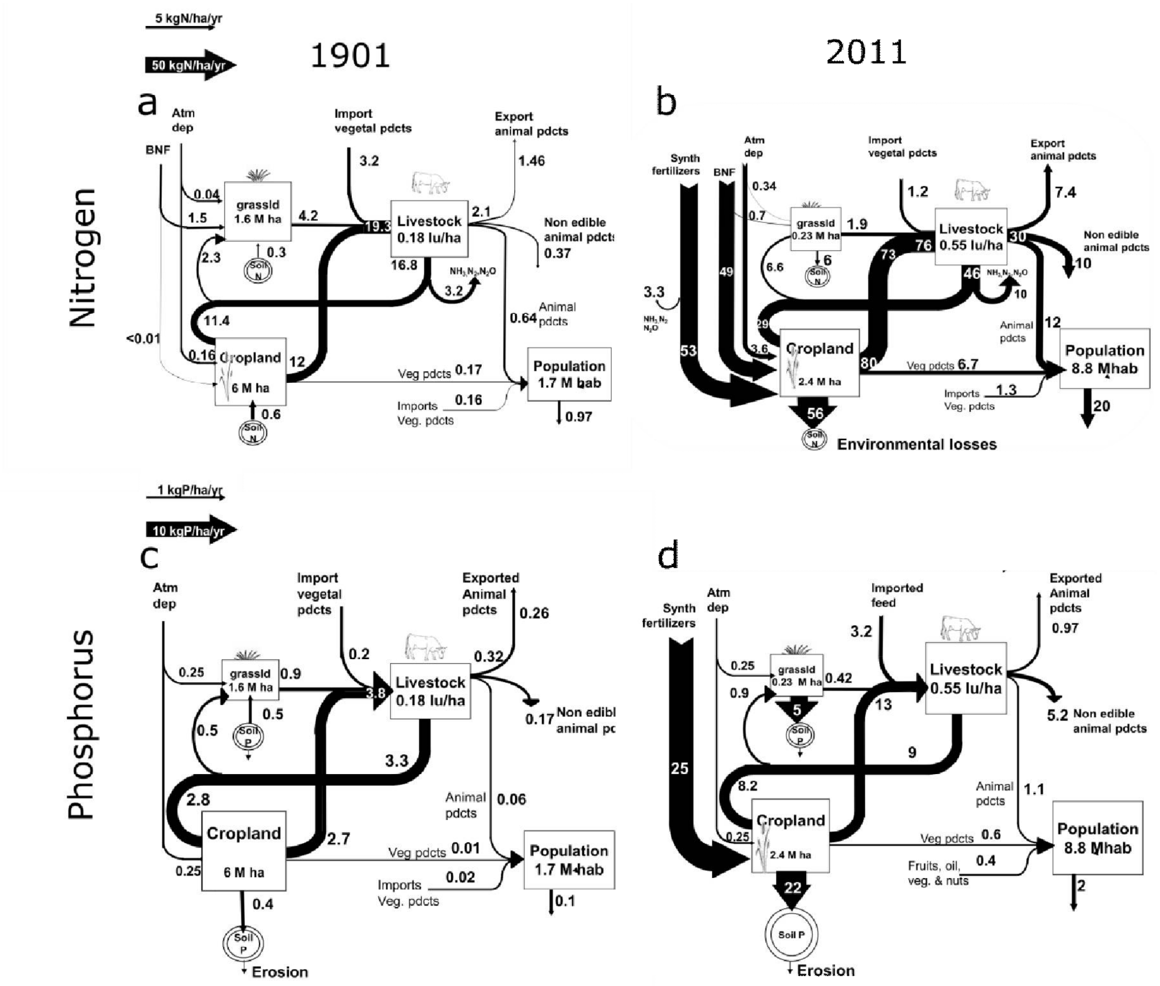

Figure 5. Changes in nutrient fluxes in the agro-food system of the SLB between 1901 and 2011. Fluxes are presented in 1901 (a for N, c for P) and in 2011 (b for N and d for P).

The other transition discussed above where soils went from depletion to over-enrichment was also apparent with decreasing trends of NUE throughout the century (Fig 6). Decline in NUE was particularly pronounced for crop production. As mentioned, in 1901, crop uptake and animal grazing exceeded rates of soils replenishment, which translated in NUE greater than 100% in some regions (Fig 6; Fig S3). These results suggested unsustainable agricultural practices in specific regions of the SLB for the maintenance of soil fertility on the long term (Fig 6). While harvests nearly balanced soil inputs at the scale of the SLB, harvests were nearly twice soil inputs in some regions, depleting nutrients from soils (NUE_{crop} of

~200%; Fig 6). With the utilization of P fertilizer in early years as well as with the large returns of P through manure application on agricultural land, NUE_{crop} of P rapidly decreased in the first half of the century (Fig 6). For N, soil depletion rates slightly increased until the 1950's while sustainable practices appeared to be met only in the mid 1960's, where NUE_{crop} crossed the 100% line (Fig 6). However, NUE_{crop} continued to decrease until the 1980's to levels of 67% for N, and by then, reached 32% for P. Then, NUE_{crop} stabilized, and subsequently even slightly increased for P, likely due to reductions in fertilizer use (Goyette et al. 2016) and sustained levels of crop yields.

NUE in animal transfers (vegetal to animal efficiency) increased for N (going from 11 to 26% at the scale of the SLB), and in a much lesser extent for P (9 to 13%). However, this estimate of NUE in animal transfer doesn't account for the complete life cycle of nutrients in animal food products. Losses that occurred during feed production need to be internalized, including the associated losses to feed that was imported from outside systems' boundaries. Taking all these into account, NUE of food production (vegetal and animal products) decreased for both N and P throughout the 20th century mainly due to declines of NUE in crop production (Fig 6). NUE of food production in the total production chain went from ~58 to 29% for N, and from ~25 to 11% for P between 1901 and 2011. Highest levels of NUE in food production were observed in the 1930's and 1950's (nearly 70% and 50% for N and P, respectively in the SLB as a whole) where grazing animal herds were at their peak and the use of human-made fertilizers was still limited.

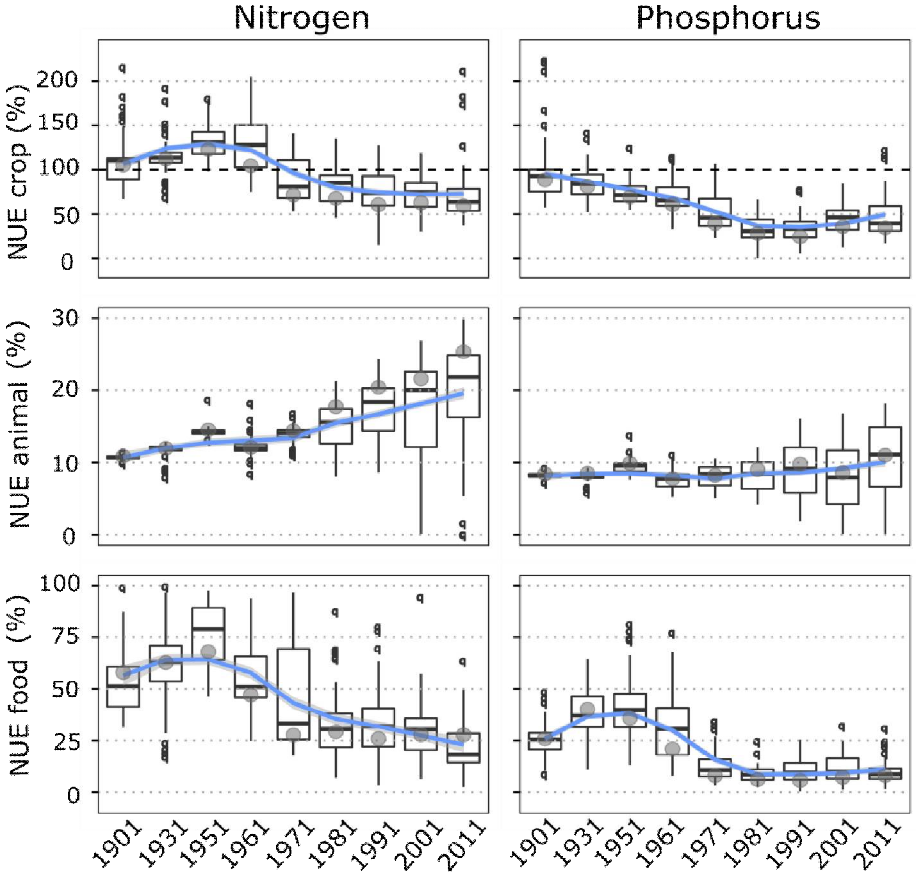

Figure 6. Changes in NUE in crop and grass production, transfers in the animal compartment only (production over ingestion) and in total human food production (animal and vegetal products) considering losses associated to feed production between 1901 and 2011 in the St. Lawrence basin. Boxplots represent the variability across the 76 sub-watersheds while large gray dots represent the St. Lawrence basin as a whole.

Discussion

In this study, we showed that accounting for complete nutrient life cycles in food production is necessary to realistically portrait the performance of the agro-food system and identify areas of optimization, and that focusing on NUE alone without considering the total throughput of nutrients cannot help mitigate nutrient losses to the environment. Furthermore, we showed that agricultural intensification and increased commercial trade of animal feed commodities has resulted in N and P imprints that now extend beyond systems' boundaries, creating highly tele-coupled agro-food systems at the regional and/or global scale (Nepstad et al. 2006) in terms of environmental costs. Finally, our long term reconstructions revealed that cropping practices were unsustainable in the first half of the century in many regions of the SLB, depleting soils of nutrients, and that with the advent of manufactured fertilizers and the intensification of animal farming (releasing large amounts of nutrients through manures), the agro-food system rapidly tipped around the 1960's to a highly inefficient system (Fig 6) in which, in 2011, ~70% of N and ~90% of P resources were lost to the environment.

Drivers of NUE on the long term

While improvement in NUE can significantly contribute at minimizing nutrient losses to the environment, reducing the total throughput of nutrients (and so the absolute amount of food being produced) is absolutely essential in meeting that goal. Indeed, we showed that, while the efficiency in growing animals increased in the second half of the century (represented by the trend of NUE_{animal} for N; Fig 6), this gain was counterbalanced by increased nutrient losses in feed production and the increased absolute amount of animals to be fed on farms (Fig 5). Moreover, disconnection of crop and animal farming through specialization as well as regional and global economic incentives apparently exacerbate these agricultural nutrient imbalances that promote losses to the environment. For example, highly subsidized pork production in the SLB (MAPAQ 2016) for export on global markets (Verret 2010) highlights the remote consequences of human demand as well as the important role of economic objectives in dictating nutrient throughput within a system and influencing losses to the environment.

Here, it is worth noting that the faith of these lost nutrients may differ substantially, with potential rapid transfers to surface waters in the case of N, mainly through lixiviation, and with more chronic transfers on the longer term for P depending on agricultural practices and soils characteristics that could induce erosion and losses (Green 2008; Goyette et al. submitted).

Specific N and P transition

Our study support previous research about both the trends in NUE over time (Bouwman et al. 2013; Lassaletta et al. 2014a) and the magnitude of soil nutrient depletion (Bouwman et al. 2013; Garnier et al. 2015; Le Noë et al. 2017) and surplus rates (Han et al. 2011; Hong et al. 2012; MacDonald and Bennett 2009). For some regions of the SLB, our P mining estimates for the 1900's were larger than those previously estimated for North America (NUE of 200% in our case compared to 125%; Bouwman et al. 2013), potentially reflecting different soils characteristics (MacDonald et al. 2012; Schoumans and Chardon 2015) as well as the particularly poor agricultural practices in Québec by that time in terms of soil nutrient replenishment (Perron 1954). In the 1981-2011 period, the stabilization of NUE in crop and grass production, despite increasing yields, highlights the better agricultural practices that favored plant nutrient uptake. For P, NUE in crop production even slightly increased in this period highlighting the reductions in P fertilizer application with no negative effects on crop productivity, likely due to plant uptake of soil residual P that had accumulated from past inputs (Goyette et al. submitted; Le Noë et al. 2018; Rowe et al. 2016). This pattern of legacy P recovery by crops was also observed in Europe where reductions of P inputs have been even more pronounced (Sattari et al. 2012).

The transition from extensive to intensive agriculture dependent on manufactured fertilizer inputs triggered a rapid shift toward a system with excess nutrients threatening soil, air, water quality and biodiversity (Leip et al. 2015). However, N and P fluxes within the system did not respond equally to evolving practices. Transitions in crop and animal types over time likely participated at creating diverging trends of N and P use efficiencies (Fig 6). Indeed, each crop or animal has a different capability to convert N and P into feed or edible food (Table 1). For example, milk is a P-rich animal product that favors P use efficiency in the animal compartment of the agro-food system. In the SLB, milk was the main source of animal protein throughout the first half of the century, but the shift toward pig and chicken production substantially contributed to reduced rates of P use efficiency in that sector by decreasing milk production at the benefit of meat production that mainly accumulated P in bones. While data on P recovery from non-edible products such as bones was unavailable for our study, we recognize that its inclusion would have likely increased our NUE estimates for P. Indeed, bones and blood can be used in the industrial processing of livestock feed P supplements, which was identified as an efficient tactic to optimize the use of P resources (Suh and Yee 2011).

Tableau I N and P content (%) and relative ratios in animal products. High ratios represent products with more N relative to P, while low ratios represent P-rich products.

animal products	%N	%P	ratio
boneless bovine meat	3.13	0.20	15.7
boneless ovine meat	2.70	0.19	14.2
boneless porcine meat	3.50	0.23	15.2
boneless poultry meat	3.00	0.19	15.8
eggs	1.79	0.19	9.4
cow milk	0.53	0.09	5.8
sheep and goat milk	0.94	0.14	7.0

Limiting agricultural losses

Many other options exist to optimize nutrient recovery in agro-food systems, from ones relating to timing and parsimony (applying nutrients at right rates, right time and right place) to more technological ones including GMO's and N stabilizers in soils (Cassman et al. 2002; Roberts 2008) as well as social ones, addressing diet shifts (e.g. demitarian diet; Westhoek et al., 2014) and schemes of payments for ecosystem services within watersheds (Godfray et al. 2010). However, efforts should focus where it matters most. For example, reduction of N volatilization through better manure management can only slightly improve the situation since it displaces N losses to the atmosphere to potential losses from soils to water (Bouwman et al. 2013). By addressing the problem upstream in the production process, efforts may have much more positive impacts. For example, a shift from beef to poultry farming or changes in diets that have lighter ecological imprints have both good potential for mitigating nutrient pollution (Table 1; Bouwman et al. 2013). In any case, strategies will need to be region specific and remain technology-neutral, embracing the multiple potential pathways (Foley et al. 2011).

While improvement in NUE can significantly contribute to meeting the dual challenge of food security and agriculture and environmental sustainability, we argue that it should come second after more structural changes in the agro-food system. Firstly, there is a need and an opportunity to reduce the overall agricultural throughput, by revisiting the economic objectives for agriculture and the human demand standards in developed countries especially. As shown in our results, nutrient surpluses and pollution may continue to increase even under better NUE if total volume of the throughput continues to increase. In that sense, targets of agricultural production that would consider the capacity of ecosystems to cope with nutrient losses while maintaining food security, possibly through an increased frugality in the demand for food, should be identified and set in priority.

Supplementary information

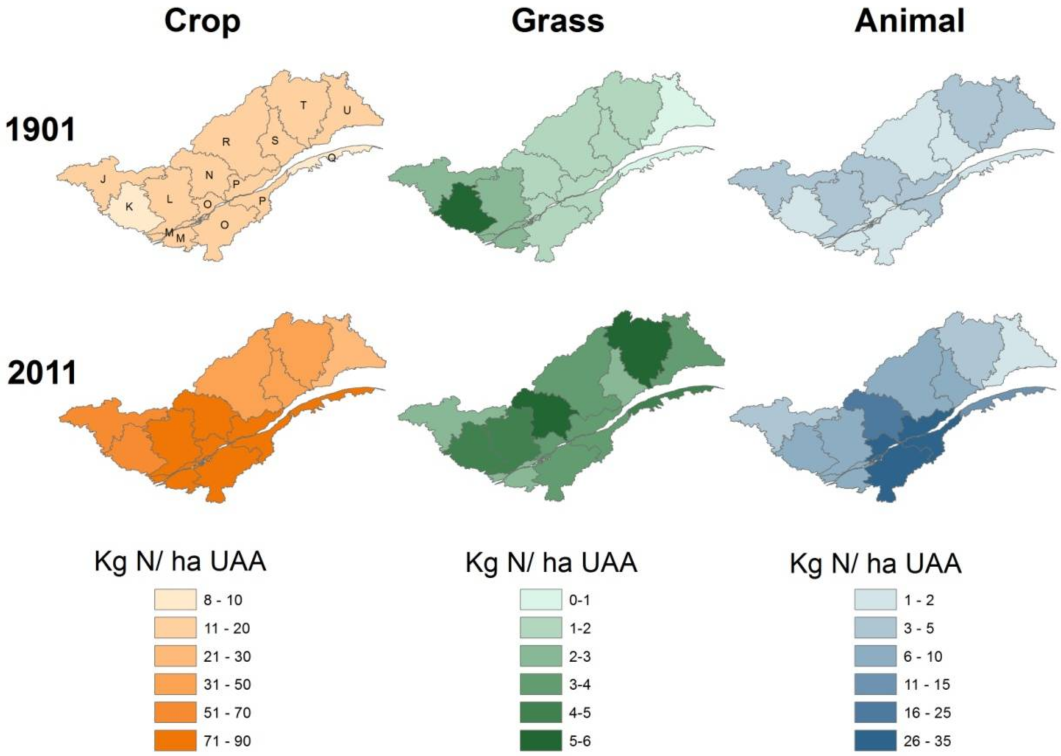

Figure S1. Annual crop (left), grass (middle) and animal (right) yields per hectare of utilized agricultural area on a kg N basis (kg N/ha UAA/yr) for 12 sub-drainage regions of the St. Lawrence basin in 1901 (top) and 2011 (bottom). Drainage regions were labelled in top left panel for better understanding of Fig S3.

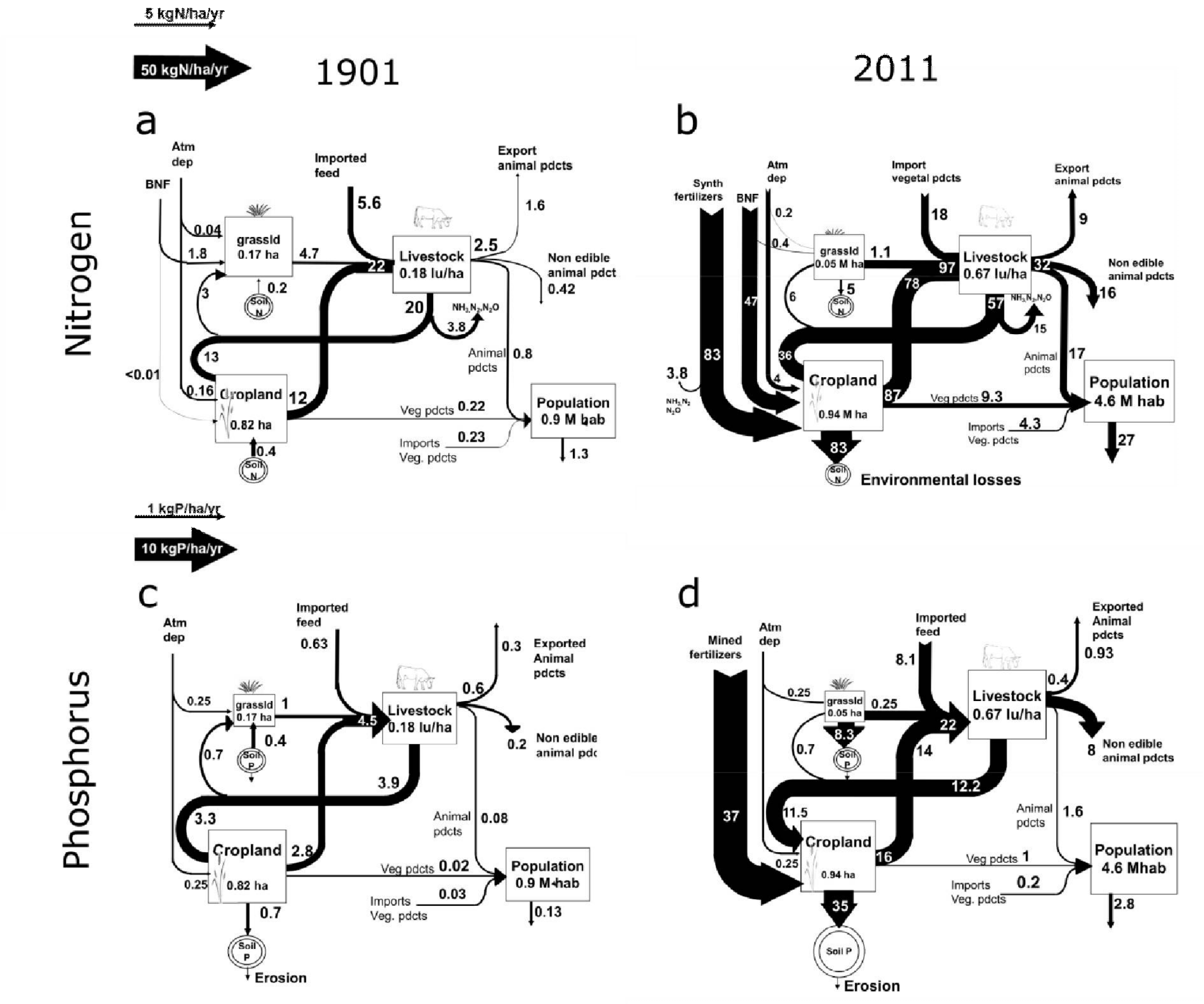

Figure S2. Changes in nutrient fluxes in the agro-food system of the Central St. Lawrence drainage region (the most intensive in terms of crop and animal farming; see Fig S1), for 1901 and 2011 (respectively a, b for N and c, d for P). The arrows from soils represent N and P mining (1901), whereas the ones to soils express mostly a loss to the environment and/or an accumulation.

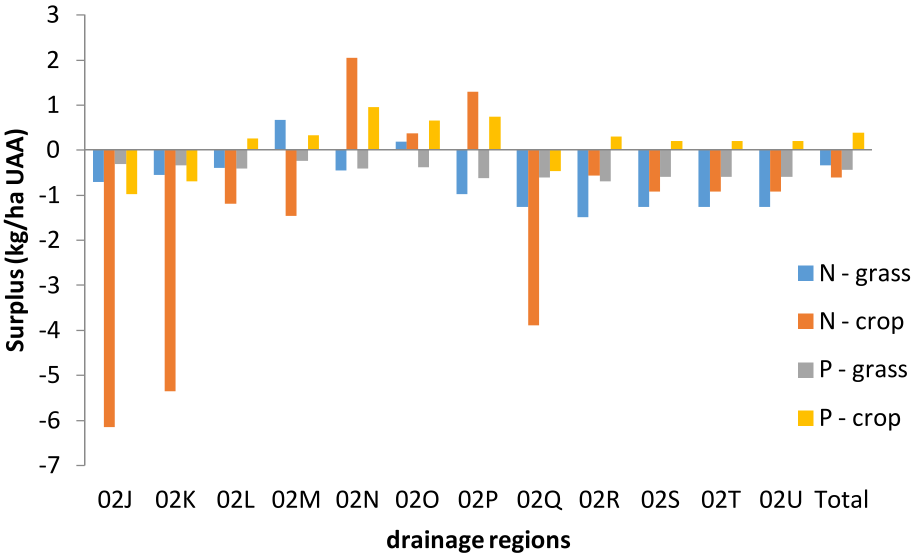

Figure S3. Anthropogenic N and P surpluses to grass and croplands in 1901 for the 12 drainage regions of the St. Lawrence basin shown in Figure S1. Negative values represent N and P mining from soils whereas positive values express potential losses to the environment and/or accumulation.

Conclusion

Tout au long de cette thèse, nous avons cherché à identifier comment les activités humaines modifient les cycles biogéochimiques de N et P et comment des caractéristiques climatiques et du territoire participent au contrôle des transferts de ces nutriments vers les eaux de surface. L'intérêt de cette question résidait dans l'importance de N et P au nexus de la sécurité alimentaire et de la qualité de l'eau et dans l'incertitude de la dynamique des flux de nutriments dans un contexte de changements globaux.

La comptabilisation des flux de nutriments dans les systèmes agricoles et dans le reste du territoire constitue une étape essentielle en voie d'une meilleure gestion des nutriments au nexus eau-alimentation. Un défi majeur dans la prédiction des charges en nutriments à la sortie de bassins hydrographiques est de tenir compte des nombreuses sources et processus de rétention (ou d'élimination dans le cas de N) par le système. Plusieurs approches ont été développées à cet effet à différentes échelles, avec différentes procédures et objectifs (Anglade et al. 2015; Billen et al. 2014; Howarth et al. 1996; MacDonald and Bennett 2009). Cependant, la majorité des études se sont concentrées sur un seul compartiment du territoire (Cook et al. 2010) ou de la chaîne de production agroalimentaire (Lassaletta et al. 2014a). Aussi, les flux de N et P sont influencés de façon différentielle par les processus écologiques et les activités humaines. Si, la stœchiométrie de N et P peut avoir un impact considérable sur l'intégrité des écosystèmes aquatiques (Sterner and Elser 2002), peu de ces études ont considéré N et P simultanément, et ce de façon holistique à l'échelle du bassin versant considérant les sources diffuses et ponctuelles dans l'ensemble les compartiments du territoire. Finalement, peu ont pris une perspective historique qui couvre d'importantes transitions sociales au fil du temps, incluant les pratiques agricoles.

En utilisant une approche historique sur 110 ans à grande échelle spatiale, nous avons créé un jeu de données unique, un des rares permettant l'analyse simultanée des flux de N et P pour un même système, de leurs dynamiques temporelles en réponse aux facteurs écologiques et sociaux, et des différences reliées aux caractéristiques régionales. En quantifiant les différents effets des activités humaines, du climat et de certaines caractéristiques clés du territoire sur le transport et la rétention de N et P à l'échelle du bassin versant, cette thèse dégage de l'information pertinente à une meilleure compréhension des dynamiques de N et P au sein de systèmes socio-écologiques.

D'abord, nos portraits historiques mettent en lumière d'importantes transitions ayant fortement affecté les flux de N et P dans le BSL au cours du dernier siècle, tant au sein du système agroalimentaire qu'à l'échelle des sous-bassins versants. En considérant ensemble ces deux macroéléments, nous montrons la divergence des tendances en réponse à la demande humaine, aux pratiques agricoles et aux différentes législations ayant été adoptées. Le système agroalimentaire du BSL serait passé d'un système aux pratiques culturales insoutenables, épuisant les sols en nutriments (en particulier P), à un système largement inefficient créant des pertes importantes vers l'environnement avec l'intensification de l'élevage et l'utilisation de fertilisants manufacturés.

Nous montrons ensuite que nos modèles de surplus de N et P anthropiques au territoire expliquent de manière robuste les exports fluviaux à l'exutoire des bassins versants. Le transport de N et P le long du réseau aquatique semblent être fortement régis par le temps de résidence de l'eau dans le territoire, où un ralentissement de la vitesse hydraulique favorisera la sédimentation des formes particulaires et l'élimination de N vers l'atmosphère par dénitrification. En quantifiant la capacité de découplage de différents facteurs clés (rétention d'eau du territoire, lac), nous fournissons des informations pertinentes à une meilleure compréhension de la dynamique des ratios N: P dans les eaux de surface (Maranger et al. 2018) tout en considérant l'effet potentiel des changements anticipés dans l'utilisation du territoire et des patrons climatiques en changement (Altieri and Gedan 2014). En considérant comment ces deux macroéléments se déplacent ensemble, nous avons identifié d'une manière intégrative où et comment les cycles N et P sont découplés dans un bassin versant et dans certains compartiments du réseau aquatique. Aussi, notre étude appuie l'idée que les réservoirs ont un fonctionnement écologique distinct de celui des lacs (Hayes et al., 2017) et suggère qu'au-delà de la profondeur moyenne, la morphométrie globale des lacs et des réservoirs influencera les charges fluviales de N et P ainsi que leur ratio stœchiométrique dans les eaux de surface, soulignant donc ainsi la pertinence de considérer ces facteurs dans de futures études.

Nos études mettent en lumière la rétention temporaire de N et P dans les différents compartiments du territoire créant des décalages entre leurs apports et leur transfert vers les eaux de surface, complexifiant ainsi substantiellement les scénarios de prédiction de charges fluviales en nutriment. Nous estimons que cet effet de legs historique en P pourrait contribuer aux charges fluviales contemporaines pendant près de 1500 ans (±500 ans selon nos différents scénarios climatiques) dans les bassins à forte vocation agricole. Certains de nos résultats appuient aussi l'idée récente d'un effet de legs historique de N pouvant occasionner des décalages temporels de l'ordre de quelques décennies (Tesoriero et al. 2013; Van Meter et al. 2016). Il sera intéressant d'étudier ce phénomène de manière détaillée pour les bassins hydrographiques considérés dans cette thèse. Aussi, conjointement à l'étude de legs historiques, nous avons abordé pour la 1re fois dans cette thèse le concept de capacité tampon du P à l'échelle du bassin versant. Notre étude suggère que la capacité de rétention optimale (capacité tampon) des bassins versants serait relativement peu élevée, et que rapidement, une accumulation de P dans les sols et les sédiments lacustres et fluviaux du bassin entraînerait un export à l'exutoire. Si notre étude se veut une exploration du concept en utilisant une approche de substitution de l'espace pour le temps (« space for time substitution ») offrant des conclusions pertinentes, mais limitées (Pickett 1989), il serait intéressant de quantifier ce seuil de saturation pour des bassins contrastés en suivant l'accumulation sur le long terme.

Limites et incertitudes

L'étude de transferts de nutriments à de larges échelles spatiales et temporelles comporte inévitablement beaucoup d'incertitudes qui limitent, en partie, certaines conclusions ou applicabilités pouvant être tirées des résultats. Premièrement, nous reconnaissons que l'erreur autour des valeurs de NANI et NAPI puisse être considérable, compte tenu de l’existence de sources d’erreur dans chacun des facteurs du modèle (paramètres et variables) entrant dans l'estimation totale. Cependant, le calcul de propagation d'erreur dans nos modélisations NANI et NAPI fut impossible en raison de l’indisponibilité d’information sur l’étendue des valeurs potentielles des paramètres impliqués. Des études similaires à la nôtre ont tenté de résoudre ce problème (Chen et al. 2016; Hong et al. 2013) en attribuant un pourcentage de variabilité ou en créant une courbe de distribution pour chaque paramètre du modèle. Cependant, nous pensons que cette approche ne permet pas de réel gain d’information en raison de la subjectivité et facticité du taux de variabilité assigné aux paramètres du modèle.

À notre connaissance, deux études traitent de l’effet de l’incertitude des paramètres NANI et NAPI sur la relation entre surplus de nutriments au territoire et exports fluviaux. Suite à une analyse d’incertitude et un partitionnement de variance, McIsaac et al. (2001) montrent que 95% de la variance des valeurs prédites par un modèle d’export fluvial similaire à ceux développés dans les chapitres 1 et 2 (utilisant NANI et des exports fluviaux annuels) seraient dus à l’erreur statistique sur les paramètres de régression tandis que seulement 5% seraient dus à l’incertitude des paramètres NANI. Aussi, Hong et al. (2012) mettent en évidence le faible impact du choix de paramètre sur les valeurs finales de NANI et NAPI (~5% de différence). En incluant des paramètres de modélisation distincts pour chacune des 11 régions (pays) drainant la mer Baltique et en comparant les résultats obtenus avec ceux utilisant les mêmes paramètres pour toutes les régions, les auteurs observent que la variabilité régionale de NANI et NAPI est davantage déterminée par la distribution spatiale des variables du modèle (e.g. aires de plantes fixatrices de N, densité de populations animale et humaine) que par la variabilité des paramètres de celui-ci. Si ces deux études ne constituent en aucune sorte une preuve comme quoi l'erreur potentielle sur nos résultats finaux serait négligeable, nous considérons que ces démonstrations contribuent à valider la pertinence de nos résultats et de leur interprétation. De plus, puisque tous les budgets ont été construits de manière cohérente pour toutes les années et tous les bassins versants, les tendances spatiales et temporelles ici analysées demeurent représentatives même malgré l'incertitude associée aux estimations absolues.

Cette incertitude dans les valeurs NANI et NAPI découle aussi en grande partie de la qualité des données de base, soit majoritairement les recensements d'agriculture. On suppose que la précision des informations contenues dans ces documents diminue avec l'âge des données. En effet, les catégories d'animaux en 1901, par exemple, sont beaucoup plus sommaires qu'en 2011. Or, veaux, vaches laitières et bœuf de boucherie n'ont pas le même métabolisme point de vue ingestion et excrétion de nutriments. Cette discontinuité dans le niveau de détail des catégories était particulièrement importante au tournant des années 1931 et 1941. Pour pallier à cette perte d'information pour les années 1901-1931 par exemple, et pour rester constant dans nos méthodes de calcul lors d'assignation de différents paramètres, nous avons décomposé les catégories sommaires des années du début du siècle en catégories détaillées en appliquant les ratios de 1941. Ainsi, nous reconnaissons que l'incertitude autour des valeurs NANI et NAPI est d'autant plus importante au début du siècle.

Concernant l'incertitude autour de nos calculs de charges fluviales en nutriment (chapitres I et II), nous nous sommes assuré que les méthodes et les sources de données soient comparables à travers le temps. Pour cette raison, nous n'avons pas inclus les données, quoique disponibles, des années 1979-1985 puisque les méthodes d'échantillonnage et d'analyse des concentrations de N y étaient différentes de celles utilisées lors des années ultérieures (MDDEFP-BQMA; Environment Canada, 2014b). Concernant le chapitre II, nous sommes conscients de l'incertitude associée à l'interpolation annuelle de NANI et NAPI (calculé aux 5 ans) et de la perte d'information potentielle en terme de charge fluviale encourue par la modélisation sous la méthode LOADEST. En effet, la modélisation de charges fluviales tend probablement à sous-estimer l'export en nutriment lors de d'évènements de précipitations extrêmes. Nous pensons donc que cette 'simplification' des dynamiques de transfert de nutriments et l'incertitude associée aux valeurs NANI et NAPI participent au pouvoir prédictif limité de nos analyses, et ce particulièrement lors de nos analyses temporelles. Néanmoins, nos modélisations de charges sous la méthode LOADEST offrent une prédiction réaliste des charges réelles (observées). Les erreurs quadratiques moyennes (rmse; voir Annexe 5, Fig S1 pour la rivière Yamaska) et les intervalles de confiance autour des charges modélisées (Annexe 5, Fig S2) révèlent une faible marge d'erreur découlant de nos calculs de modélisation. Nous pensons donc que l'erreur résiduelle de nos analyses dans les chapitres II et III réside dans des phénomènes n'ayant pas été considérés ici, et non dans la marge d'erreur des calculs en amont.

Malgré l'incertitude reliée aux estimations, l'approche NANI/NAPI a été démontrée au fil du temps comme étant robuste pour la prédiction de charges fluviales en nutriments, confirmant ainsi sa validité et son intérêt (Boyer et al., 2002; Hayakawa et al. 2009, Howarth et al., 2012; Howarth et al., 1996; Hong et al., 2012; Swaney et al., 2012; Chen et al. 2015; Han et al 2012). En effet, nos estimations d'exports relatifs aux apports nets anthropiques s'accordent aux observations d'études précédentes. Aussi, la validité de nos études repose en partie sur la réplicabilité des résultats compte tenu de l'accessibilité aux données utilisées.

Perspectives

À la lumière de nos résultats et d'études précédentes, l'effet de legs historique pourrait jouer un rôle important au succès des efforts de restauration et pour l'intégrité des écosystèmes aquatiques (Carpenter 2005; McIsaac et al. 2001; Schlesinger 2009). Beaucoup d'incertitude demeure à propos des délais temporels impliqués et nous pensons que les connaissances à ce sujet doivent être approfondies, et ce particulièrement pour N. En effet, les recherches se sont jusqu'à maintenant penché prioritairement sur P concernant ces dynamiques de délais temporels. Par exemple, des analyses mesurant les nitrates dans les eaux souterraines ainsi que l'âge et la contribution de ces aquifères aux rivières pourraient aider à corroborer des études utilisant nos approches de bilans massiques.

Aussi, dans le Chapitre III, nous montrons que le concept de capacité tampon en P, préalablement utilisé uniquement à l'échelle des sols agricoles afin d'expliquer les concentrations de P dans les eaux interstitielles (Maguire and Sims 2002), peut être appliqué à d'autres échelles d'analyses, dont celle du bassin versant. Nous pensons que ce cadre conceptuel offre un potentiel additionnel pour l'étude des dynamiques de P dans les différents compartiments du bassin versant. Par exemple, l'étude présentée à l'Annexe IV montre pour sa part que les apports historiques de P au lac Saint-Pierre auraient contribué, par un effet de cascade, et ce avec un décalage temporel important, au déclin des populations de perchaudes par la détérioration de leur l'habitat suite à une transition d'un milieu riche en plantes aquatiques à des eaux plus turbides (Giacomazzo et al. in prep, 2018). En ce sens, il serait intéressant de quantifier la capacité tampon en nutriment de différents types de lacs et le point de rupture au-delà duquel le lac bascule vers un état dégradé. Bien que certaines études aient exploré cette idée d'états stables alternatifs dans les lacs (Carpenter 2005), peu ont tenté de quantifier la capacité tampon d'un lac et de ses sédiments ainsi que le seuil d'apport cumulatif en nutriment au-delà duquel le lac basculerait vers l'état alternatif des eaux turbides. Au-delà de l'identification des signes précurseurs d'un changement d'état de l'écosystème (Carpenter et al. 2011; Scheffer and Carpenter 2003), la quantification des seuils en dessous desquels les lacs et les bassins versants peuvent absorber les pressions en nutriments s'inscrit parfaitement dans le cadre des recherches foisonnantes sur la résilience des écosystèmes (Berkes et al. 2000; Folke et al. 2010) et représente un champ de recherche essentiel afin de dégager des informations pratiques à la gestion intégrée de nos systèmes socio-écologiques.

Dans le cadre des chapitres I et IV, nous avons aussi montré les relations importantes entre écosystèmes naturels et systèmes sociaux. De façon indirecte, nos études mettent en lumière la question de substitution entre les services écologiques et technologiques, question faisant l'objet de nombreux débats dans la littérature scientifique de la conservation (Ehrlich and Goulder 2007; Gómez-Baggethun et al. 2010; Helm 2014; Solow 1974). La transition observée d'une agriculture basée sur le recyclage des nutriments par processus écologiques vers un système presque entièrement dépendant de services technologiques permettant l'extraction minière de roches phosphatées et la synthèse de fertilisants azotés est un exemple parfait de cette question de substituabilité entre le capital naturel et le capital construit (technologique ou institutionnel) (Dietz and Neumayer 2007). Si plusieurs recherches

(Bouwman et al. 2013; Rockstrom et al. 2009; Steffen et al. 2007), dont les nôtres, ont montré que nos systèmes socio-écologiques ont basculé au cours du dernier siècle vers des systèmes inefficients au niveau de l'utilisation des ressources naturelles en substituant les services technologiques aux services de régulation et d'approvisionnement rendus par les écosystèmes, il semble être évident qu'une nouvelle révolution soit nécessaire, celle de l'équilibre et de la complémentarité entre les différents types de services ou de capitaux (naturels et construits). Bien que certains services technologiques puissent partiellement ou entièrement remplacer les services écologiques, la plupart permettent plutôt de soutenir ou d'amplifier leurs flux (Ehrlich and Goulder 2007; Fitter 2013; Raudsepp-Hearne et al. 2010). En ce sens, déterminer le point d'équilibre entre conservation et développement nécessitera, entre autres, l'utilisation de métriques communes aux différents types de services. Différentes approches ont été proposées permettant une comptabilisation holistique des empreintes environnementales, tels que la mesure de l'appropriation humaine de la production primaire (HANPP) (Haberl et al. 2009) ou celle de l'émergie (énergie utilisable contenue dans un bien ou un service, naturel ou construit) (Odum 1996). Ces approches semblent offrir des métriques objectives du point de vue biophysique, contrairement aux approches de monétarisation des services écologiques sujettes à la subjectivité sociale (Fourcade 2011). Ainsi, elles permettraient d'évaluer et de comparer la valeur des services écologiques et technologiques afin d'identifier où et quand ces services peuvent être complémentaires ou substituables. Cette question de substituabilité s'inscrit au cœur du concept de développement durable et représente un champ de recherche sous-exploité et prometteur pour l'analyse des compromis au nexus eau-alimentation.

En dressant un portrait historique d'une période charnière dans l'utilisation du territoire et de ses conséquences sur les ressources en eau, cette thèse met en évidence la complexité des processus régissant les flux de deux nutriments essentiels à la prospérité des populations humaines, l'azote et le phosphore. Face aux changements globaux (dont les changements climatiques), beaucoup d'incertitude demeure quant aux taux de transfert des nutriments le long des réseaux aquatiques. L'atténuation de l'eutrophisation demeure un enjeu contemporain qui nécessitera des solutions spécifiques à chaque région, aux contextes historiques et aux objectifs futurs de développement du territoire. Une nouvelle transition est nécessaire, celle de l’intégration du savoir entre disciplines et de l’adéquation entre développement et capacité de support des écosystèmes. Il s’agit d’un défi de taille, mais un défi incontournable faisant appel à toute la sagacité, le jugement et la créativité de l’espèce humaine.

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Annexe I. Les contaminants biologiques et chimiques en tant que moteurs du changement dans le bassin des Grands Lacs et du fleuve Saint-Laurent.

Biological and chemical contaminants as drivers of change in the Great Lakes-St. Lawrence River basin

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Contribution as co-(first-)author: Review of the literature, data synthesis and writing.

Annexe II. Quantification des effets des changements hydrologiques sur les tendances à long terme de la qualité de l'eau dans les réservoirs tempérés: aperçu d'une étude paléolimnologique multi-échelle

Quantifying the effects of hydrological changes on long-term water quality trends in temperate reservoirs: insights from a multi-scale, paleolimnological study

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Contribution as second author: Historical reconstructions of P surpluses in Saint-Francois watershed.

Annexe III. Capacité tampon de la pression en P par les bassins hydrographiques à l'échelle régionale, une comparaison dans l'espace et le temps

Watershed buffering of legacy phosphorus pressure at a regional scale, a comparison across space and time

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Contribution as second author: Project development, Data production and analysis

Annexe IV. La végétation aquatique submergée comme moteur de la dynamique des populations de poissons: un récit de soixante ans sur le déclin de la perchaude dans le lac Saint-Pierre (fleuve Saint-Laurent)

Submerged aquatic vegetation as a driver of fish population dynamics: a sixty years tale on yellow perch decline in Lake St. Pierre (St. Lawrence River)

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Contribution as second author: Data production and analysis

Annexe V. Marge d'erreur autour des modélisations de charges fluviales en nutriments sous la méthode LOADEST

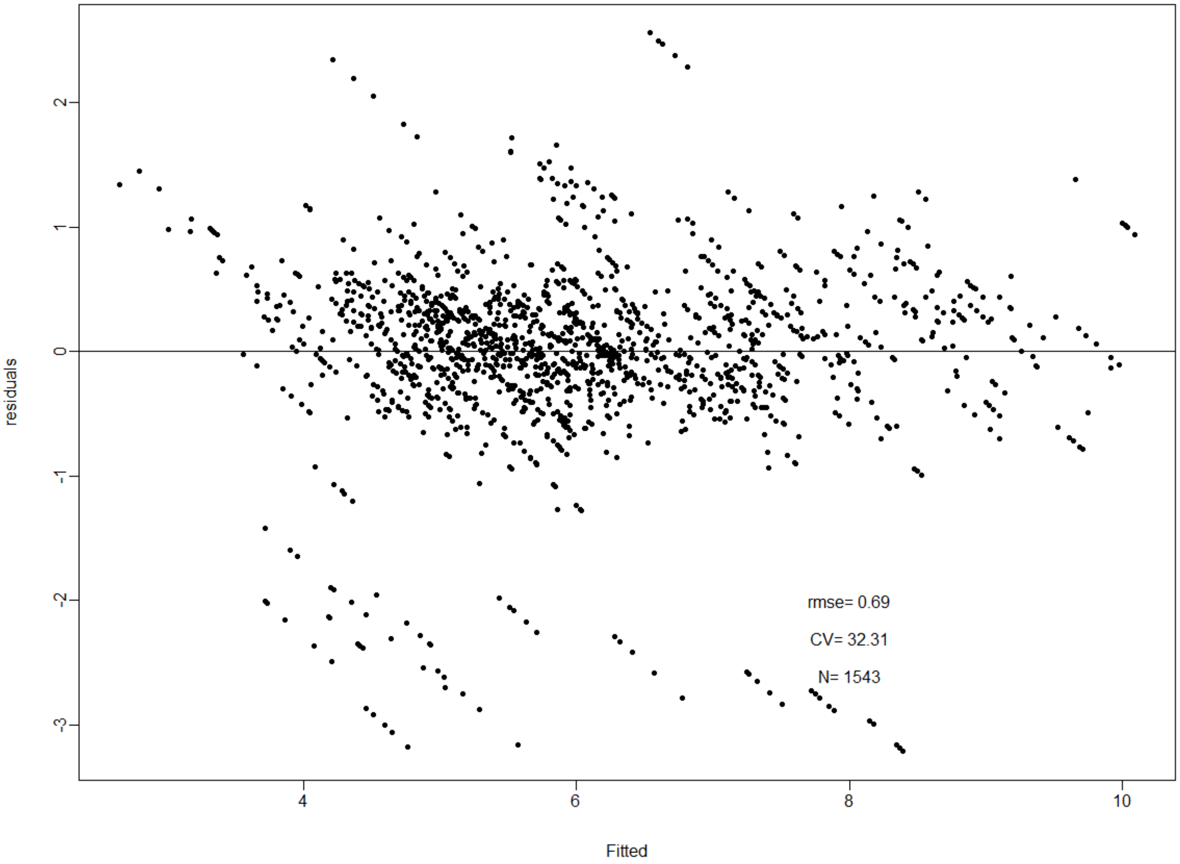

Figure S1. Performance of LOADEST models to predict observed TP loads in the Yamaska River over the 26 years period (1985-2011). Residuals versus fitted values are presented. LOADEST models were created (and calibrated) for each focal year on a 5 year window. RMSE values were computed for each model (each year). The mean and CV of RMSE values are reported.

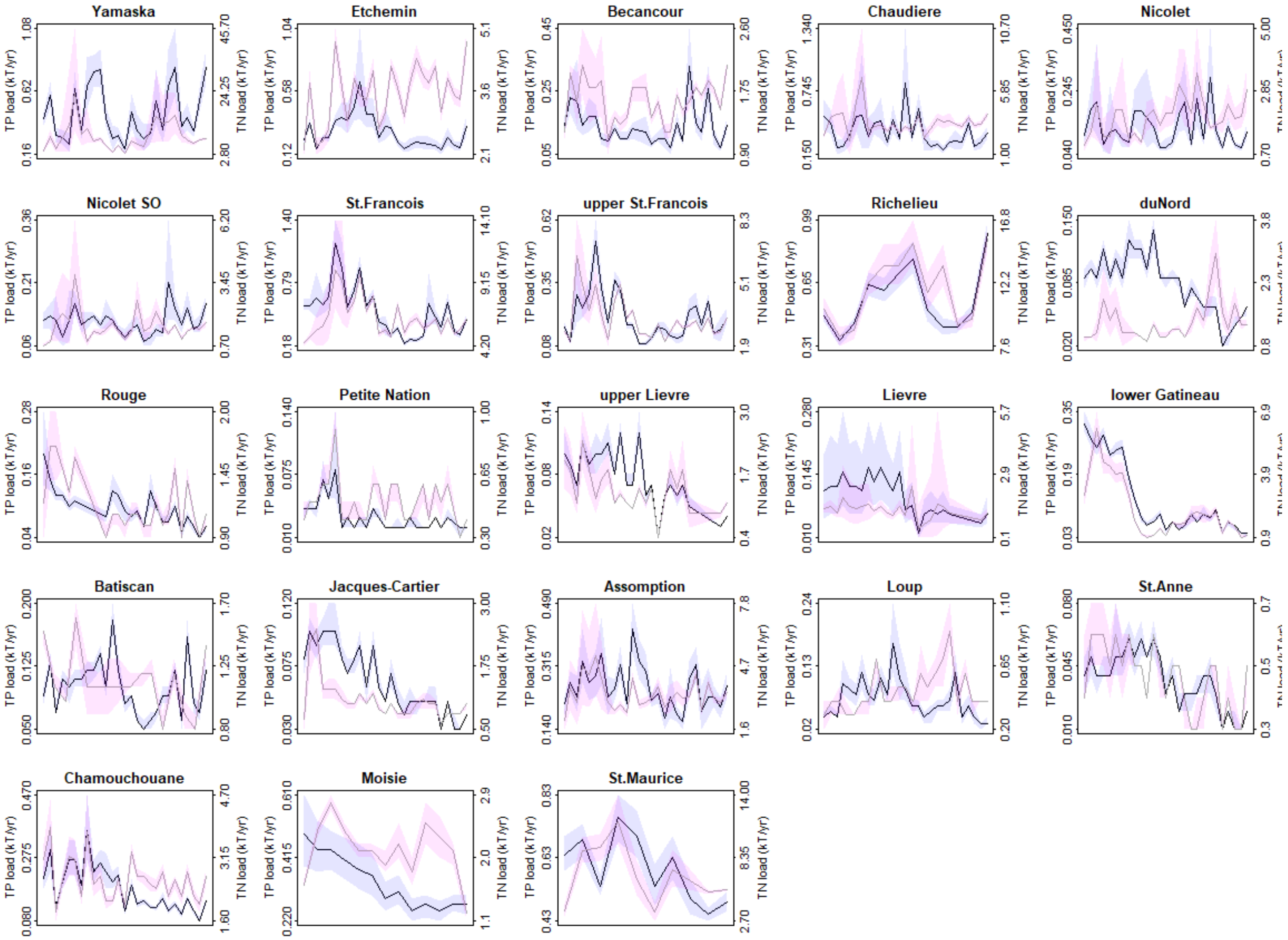

Figure S2. Annual riverine loads of TN (pink) and TP (blue) with their 95% confidence intervals as modeled through the LOADEST procedure. Note the different y axes for each panel.