Watershed Buffering of Anthropogenic Phosphorus Pressure: Landscape and Legacy

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Abstract

Phosphorus (P) is a non-renewable resource that is an essential element for agricultural crop production. However, when excess P enters fresh and coastal water systems, it can result in undesirable impacts such as the excessive growth of algae species and oxygen depletion. Millions of tonnes of P are applied to agricultural lands every year in the form of phosphate fertilizer to enhance crop growth and increase yields. While some of this P is taken up by crops, much is left on the land, and this P has a tendency to stay in the soil, which results in a build-up of P in agricultural landscapes that can last years or even centuries. This build-up of historic P inputs, also known as "legacy P", represents a threat to surrounding water bodies because erosion and runoff processes can transport P molecules and P-enriched soils to water systems.

The processes that transport P, including legacy P, from upland soils to water bodies are varied depending on the biological and biophysical features of the landscape, such as soil type and topography, as well as the human management features of the landscape, such as artificial drainage and riparian zone maintenance. Together, these features mediate the residence time of P in the soils and landscape. The ability of a watershed to retain historic P inputs is its "buffering capacity", its ability to buffer the water quality from the impact of current and historic P inputs to the watershed. In this thesis, I ask, "how does buffering capacity vary among watersheds in southern Quebec over a thirty-year period of intensive farming?" and "which watershed characteristics (be they geochemical, hydrological, or landscape) impact watersheds' buffering capacity and the transport of legacy P from land to water systems?"

I used two different methods to determine the buffering capacity of watersheds. One method, novel to this study, compares the long-term P accumulation of a watershed to current day riverine P flux values. I call this the Buffering Index (BI). The other method, known as Extended End-Member Mixing Analysis (E-EMMA) uses hydrological modeling to estimate the degree to which P is retained and released by watershed ecosystems as water moves through the landscape. These two values were calculated for sixteen different watersheds in the Saint Lawrence Basin, in Quebec, Canada, spanning a thirty-year period (1981-2011). I then compared these values to geochemical, hydrological, landscape, and socio-ecological factors to determine which factors are important in predicting buffering capacity.

All of the study watersheds have been accumulating P in their soils throughout the study period. My comparison of average riverine P flux values with average NAPI values showed that the study watersheds retained, on average, between 58% and 97% of net imported P in a given year. In general, watersheds with more P accumulation have higher riverine P flux; however, in many watersheds, riverine P flux has decreased over the study period, despite the fact that the amount of P accumulation in the watersheds has continued to mount over this time.

I found a range of BI and E-EMMA values among the watersheds, along with a range of geochemical, hydrological, landscape, and socio-ecological characteristics. There was no correlation between the two buffering metrics calculated for the watersheds suggesting that these two metrics measure different buffering phenomena. However, each of the buffering indicators correlate with various watershed characteristics, such as soil type, baseflow index, water yield, landuse composition and configuration metrics, population density, and the presence of artificial drainage. This suggests that geochemistry, hydrology, and landscape features may, indeed, play a role in determining various aspects of the overall buffering capacity of watersheds.

Determining which landscape features impact agricultural landscape buffering capacity can help us to understand how landscapes can be managed to increase their resilience to external pressure and identify leverage points for more holistic land management. A greater understanding of how buffering capacity is conferred on a watershed can also help identify which watersheds are particularly vulnerable to P pressure that could arise from changes in land use, including agricultural intensification and urbanization.

Résumé

Le phosphore (P) est une ressource non-renouvelable qui est essentiel pour la production agricole. Par contre, quand un surplus de P entre dans les systèmes d'eau douce et côtière il peut entrainer des effets indésirables tel une croissance accrue d'algues et une diminution d'oxygène. Des milliers de tonnes de P sont appliqués sur des terres agricoles à chaque année sous format de fertilisant de phosphate afin d'augmenter la production des récoltes. Malgré le fait qu'une portion de ce P est absorbé par les produits agricoles une grande portion de résidus reste dans le sol et tend à s'accumuler pendant plusieurs années. Cette accumulation de P historique, aussi connu sous le nom de « P d'héritage » peut menacer les cours d'eau environnantes dû à l'érosion et le ruissèlement de molécules de P et de sol enrichi par le P.

Les processus qui transportent le P et le P d'héritage des bassins versants vers les cours d'eau varient selon les conditions biologiques et biophysique du paysage. Le type de sol, la topographie, ainsi que des tactiques de gestion du territoire comme le drainage artificiel ou les zones riveraines, sont tous des exemples de ces conditions. Ensembles, ces conditions affectent le temps de résidence du P dans le sol et les paysages. La capacité d'un bassin versant de retenir le P historique se nomme la « capacité tampon ». Dans cette thèse, je demande « comment est-ce que la capacité tampon change des les bassins versant avec le temps ? » et « quels caractéristiques (géochimiques, hydrologiques et de la composition du paysage) de bassins versant influencent leur capacité tampon et le transport de P historique du sol vers les cours d'eau ? »

J'utilise deux méthodes différentes afin de détermine la capacité tampon des bassins versants. Une de ces méthodes, novatrice de cette étude, compare l'accumulation de P à long-terme

dans un bassin versant à la quantité moderne de P en fluctuation d'une rivière. Je nomme ceci L'index Tampon, ou IT. L'autre méthode, connu sous le nom de « Extended End-Member Mixing Analysis (E-EMMA) » Ces utilise la modélisation hydrologique pour estimé le degré de P retenue et relâché par un bassin versant lorsque l'eau se déplace à travers un paysage.

Ces deux valeurs ont été calculés sur une période de trente ans (1981-2011) dans 16 différents sous-bassins versant du grand bassin du Fleuve Saint Laurent, au Québec, Canada. J'ai ensuite comparé ces valeurs à des composantes géochimiques, hydrologiques, de composition du paysage et socio-écologiques afin de déterminer lesquels de ces facteurs sont d'importants prédicteurs de la capacité tampon.

J'ai trouvé une gamme de valeurs de IT et E-EMMA dans les bassins versant évalués, ainsi qu'une gamme de caractéristiques géochimiques, hydrologiques, du paysage et socio-écologiques. Il n'avait aucune corrélation entre les deux mesures de capacité tampon, ce qui suggère que ces deux indicateurs mesurent des phénomènes de tamponnage différents. Ceci étant dit, chacun des indicateurs de tamponnage sont corrélés avec divers caractéristiques de bassins versant, tel le type de sol, l'index d'écoulement de base, la quantité d'eau, la composition et configuration de l'utilisation du territoire et la présence de drainage artificiel. Ceci suggère que les caractéristiques géochimiques, hydrologiques et du paysage jouent effectivement un rôle au sein de la capacité tampon d'un bassin versant.

Déterminer quels facteurs influencent la capacité tampon de paysages agricoles peut nous aider à mieux comprendre comment les paysages peuvent être gérer pour augmenter leur résilience aux pressions externes. Une meilleure compréhension de comment la capacité tampon d'un bassin versant se forme peut aussi nous aider à identifier quels bassins sont particulièrement vulnérables au P et aux changements de P qui peuvent être causés par l'intensification agricole et l'urbanisation.

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Preface

This thesis is manuscript based. The two main chapters represent a literature review and a research-based paper. Within these two chapters, I aim to investigate the relationship among current and legacy phosphorus pressure, biophysical and social landscape characteristics, and water quality. Chapter 1 is a literature review that is not meant for publication at this time. Chapter 2 is prepared as a manuscript for submission to the journal *Ecosystems*, and is formatted according to this journal's style and guidelines.

In Chapter 1, I review the literature surrounding legacy phosphorus and phosphorus retention and transport mechanisms in agricultural watersheds. This begins with a review of the phosphorus cycle and the ways in which humans impact the global movement of phosphorus in terrestrial and aquatic ecosystems. I then discuss the causes and potential negative impacts of legacy phosphorus in agricultural watersheds. Following this, I present the idea of watershed "buffering capacity" as a conceptual framing to understand why and how different watersheds retain incoming phosphorus differently. This leads to a review of the main biophysical and social factors that contribute to watersheds' buffering capacity and then to a discussion relating the buffering capacity concept to a greater understanding of holistic watershed management, which considers the trade-offs between agricultural production and water quality protection through time at the watershed scale.

In Chapter 2, I present an empirical study that investigates the relationship between legacy phosphorus and current water quality, the buffering capacity concept, and the main landscape features that affect a watershed's ability to retain long-term and contemporary phosphorus pressure. This study examines 16 agricultural watersheds in southern Quebec, Canada throughout a thirty year period (1981-2011). This study includes multiple potential interpretations of the buffering capacity concept and considers a wide range of watershed characteristics that potentially impact the dynamics of phosphorus transport on the landscape.

Contributions of Authors

The candidate, Anna Kusmer, is responsible for leading the conceptualizing, data collection, analysis, and writing of both chapters.

Chapter 1 is a collaboration between Anna Kusmer and supervisor Dr. Elena Bennett. Chapter 2 was led by Anna Kusmer and included the contributions of a number of co-authors. Dr. Elena Bennett provided guidance throughout all stages of the conceptualization, research, and writing process. Dr. Graham MacDonald provided guidance throughout the research process, primarily with the conceptual framework and the analysis and interpretation of data. Dr. Paul Withers provided assistance with the conceptualization of the research project and provided insights and feedback throughout the course of the research. Jean-Olivier Goyette and Dr. Roxanne Maranger contributed an essential dataset on a century of phosphorus inputs in Quebec watersheds.

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Thesis Introduction

Cycles of elements such as phosphorus (P) and nitrogen (N) are important features of ecosystems that affect many key ecosystem processes. The presence and relative abundance of these nutrients drive growth and are often cited as being limiting factors for primary production, particularly in aquatic ecosystems (Ryther and Dunstan, 1971; Tyrrell, 1999). Due to the ecological significance of these elements, major changes in the nutrient content of aquatic ecosystems can cause significant changes in environmental functioning and structure, potentially shifting ecosystems to alternative states (Carpenter et al., 1998); in ecology, this is referred to as a regime shift (Folke et al., 2004). In the case of nutrient pollution, large additions of N or P into fresh or coastal waters can result in algae blooms and large-scale and deleterious oxygen depletion (Diaz, 2001; Diaz and Rosenberg, 2008; Rabalais et al., 2009; Diaz et al., 2010). Regime shifts in aquatic ecosystems are often unexpected and result in undesirable impacts for humans who rely on stable ecosystem functioning for their food, water, and livelihoods (Gordon et al., 2008).

Over the last two hundred years, human systems have significantly altered global nutrient cycles. In the case of P, large-scale mining operations extract millions of tons of P a year, and most of it is used for the creation of phosphate fertilizers that are spread across the world's croplands to enhance plant growth and increase agricultural yield (Smil, 2000; Bennett and Schipanski, 2013). This movement of P, from sedimentary rocks to agricultural landscapes, presents a threat to the stability of water systems, because P applied to land is often transported to water systems through soil erosion, leaching, and gravity (Allan, 2004; Bennett and Schipanski, 2013).

Once P is added to agricultural soils, it has a tendency to convert into less bioavailable forms and 'sorb to soil particles. Once applied, P can reside in agricultural ecosystems for up to decades or even centuries, and this long-term P storage is called "legacy P" (Sharpley et al., 2013). The accumulation of legacy P in agricultural soils and its subsequent transport to fresh and coastal waters represents the inefficient use of a non-renewable essential resource (P) and is a threat to water systems (Carpenter, 2005; Elser and Bennett, 2011). The slow release and movement of accumulated P from historically agricultural soils causes long term vulnerabilities to our water systems (Carpenter, 2005), and because of the substantial build-up of P throughout much the world's agricultural soils, many global water systems are at risk (MacDonald et al., 2011; Sattari et al., 2012; Withers et al., 2014).

Long-term residence of legacy P in agricultural soils also creates a delay between P accumulation in terrestrial landscapes and downstream water quality impacts, whereby agricultural watersheds can go through long phases of P accumulation when P inputs exceed outputs and significant time passes before terrestrial P transports to nearby waters (Powers et al., 2016). Legacy P has also been cited as one of the reasons that there is a significant delay between mitigation efforts that aim to halt the accumulation of P inputs and water quality improvements; this delay has been seen in many high profile case studies, exemplifying the fact that with nutrient pollution, particularly P, there is no quick fix (Meals et al., 2010; Kleinman et al., 2011; Jarvie et al., 2013; Sharpley et al., 2013).

The phenomenon of long-term P retention in agricultural watersheds results in the non-linear relationship between P inputs and decreasing water quality (Borbor-Cordova et al., 2006; Russell et al., 2008; Sobota et al., 2011). Watersheds vary widely in their ability to retain legacy P pressure. We refer to this ability as a watershed's "buffering capacity". A watershed's buffering capacity is a product of diverse biophysical characteristics, both innate and human-mediated (Doody et al., 2016). In this study, we consider different categories of watershed characteristics such as geochemical factors, such as soil type; hydrological factors such as baseflow index and water yield;

landscape factors such as the configuration of landuse; and socio-ecological factors such as population density and farm management.

In this study, we investigate these and other watershed characteristics that relate to a watershed's specific buffering capacity. The main questions guiding this research are: How do "buffering capacity" values vary among watersheds and within individual watersheds over time, and what can the changing nature of these buffering indicators tell us about the geochemical, hydrological, landscape and socio-ecological buffering capacity of specific watersheds? Which factors, or which types of factors (geochemical, hydrological, landscape, and socio-ecological), were most closely linked with the degree of watershed buffering observed across watersheds? To address these questions, we examine the relationship between buffering capacity indicators and spatial characteristics in large watersheds (~1000-10,000 ha) draining to the Saint Lawrence River, located in the province of Quebec, Canada, over a thirty year time span.

A greater understanding of P cycling and transport mechanisms in watersheds could increase the efficacy of mitigation strategies and help to manage the trade-off between agricultural production and water quality at different scales. Anthropogenic impacts on the P cycle and consequent aquatic degradation are symptoms of a wider problem of a lack of harmony between human systems of production and the land and water systems that humans critically rely on. A transition to sustainable P management will rely on a holistic perspective of land management and a greater integration between production and conservation goals on the landscape. Increased agricultural intensification and long-term sustainability of freshwater ecosystem services are incompatible unless we mitigate and confront the problem of P accumulation in our watersheds (Bennett et al., 2001).

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CHAPTER 1 Literature Review: Holistic watershed management and legacy phosphorus: reconciling production and conservation goals in agricultural landscapes

Introduction: The problem with phosphorus

Phosphorus (P) is both a freshwater pollutant and a vital, non-renewable resource for agricultural production. In agricultural systems, the use of P fertilizers enables dramatically increased crop yields throughout the world, which supports food production for a rapidly growing global population (Tilman, 1998). Because P is a limited nutrient in freshwater systems, its excessive introduction to aquatic ecosystems often results in eutrophication, an undesirable, expensive, and typically irreversible condition of over-fertilized lakes (Sharpley et al., 1994; Carpenter et al., 1998; Dodds et al., 2008; Selman et al., 2008; Keeler et al., 2012; Withers et al., 2014). Human activities have resulted in a significant increase in the cycling and mobilization of global P, and there is evidence to suggest that the human influence to the global P cycle has surpassed a tipping point with impacts to regional water systems throughout the biosphere (Cordell et al., 2009; Rockström et al., 2009; Carpenter and Bennett, 2011; Elser and Bennett, 2011). Studies show that hundreds of freshwater and coastal regions around the world are impacted by nutrient pollution (Diaz, 2001; Diaz and Rosenberg, 2008; Diaz et al., 2010), including culturally an economically important waters such as the Chesapeake Bay, the Baltic Sea, the Gulf of Mexico, and the Great Lakes (Selman et al., 2008; McCrackin et al., 2016). The management of P resources must take into consideration the long-term viability of both food and water systems –two systems essential to human life and global sustainability.

Human impacts on the global P cycle

Phosphorus, along with carbon and nitrogen, is an essential nutrient for the creation of biological structures and the persistence of life, although it represents only 0.11 percent of the earth's crust by mass (Sterner and Elser, 2002). Despite its relative scarcity, P is necessary for plant growth and is one of the requirements for soil fertility and the cultivation of crops (Bennett and Schipanski, 2013). Technological advancements and intensification of agricultural systems over the last two hundred years have led to an increase in human use of P as a means of increasing the fertility and productivity of agricultural soil (Smil, 2000).

Unmediated P cycle

Over ninety percent of global P exists in deep sea reservoirs, and the remaining 10 percent is spread widely throughout terrestrial and aquatic ecosystems throughout the world. At the civilizational time scale (~100-1,000 years), the P cycle generally consists of a linear flow from terrestrial sedimentary rock to the ocean; this process consists of the mineralization of P from sedimentary rocks into plant-available forms and its eventual erosion and runoff into water systems. On the geological time scale (10^7-10^8 years), deep ocean P reforms to sedimentary rock and tectonic uplift exposes P-rich sedimentary rocks to the surface, upon which the cycle continues (Smil, 2000).

Because P has no gaseous phase, its cycling is earthbound and strongly mediated by terrestrial processes, and its movement through ecosystems is significantly slower and more localized than other nutrients such as nitrogen and carbon (Smil, 2000; Bennett and Schipanski, 2013). Throughout its time in the biosphere, a majority of terrestrial P, around 86 percent, is found within plant materials; around 10 percent of terrestrial P is found within the soil (Smil, 2000). Within these ecosystems, there is a relatively local P cycle in which soil and aquatic microbiota and organisms utilize P for essential life processes and then decomposition allows for cycling, reuse, and continued growth (Smil, 2000).

Human-influenced P cycle

Over the last two hundred years, humans have become a major driver within the global P cycle. Studies have estimated that there has been a 2-3 times increase in the annual terrestrial flux of P since pre-industrial times (Smil, 2000; Bennett et al., 2001). The main way that humans increase the mobilization of global P is through large-scale extraction of P from sedimentary rock for the creation of phosphate fertilizers and feed supplements for livestock (Smil, 2000).

Beginning in the mid-20th century, a shift to input-intensive agriculture in many regions of the world (commonly referred to as the Green Revolution) resulted in a global increase in nutrient additions to agricultural fields in the form of synthetic fertilizers (Tilman, 1999). Between 1950 and 2000, humans applied around 550 Mt of P to global agricultural land (Smil, 2000). The advent of relatively cheap fertilizers around the 1950s decreased the incentive for farmers to seek local forms of nutrients such as manure and compost, which led to a trend of decoupling local nutrient production (animal manure) and demand (Oenema and Pietrzak, 2002).

Global P use remains high. Currently, annual phosphate mining removes up to 13-16 Mt of phosphate rock a year (Smil, 2000), ninety percent of which is used for agricultural production (Cordell et al., 2009). Much of the P applied to agricultural soil is taken up by crop plants and exported; however a large fraction (estimated at ~45 percent in 2005) of the P in agricultural systems stays in the agricultural landscapes, embedded in the soil (Cordell et al., 2009).

Phosphorus storage and export: The watershed as a key scale of analysis

The relationship between long-term terrestrial P accumulation and resulting water quality degradation is often best understood and managed for at the watershed scale. A watershed, also known as a catchment or a basin, is an area of land in which all water drains into a river system or some other body of water (Allan, 2004). A watershed's relatively contained nature makes it a natural scale at which to examine biogeochemical cycling and the connection between terrestrial and hydrological systems (Allan, 2004; Flotemersch et al., 2015). The global increase in P loading to surface waters throughout the last decades has increased the interest in P cycling at the watershed scale (Sharpley et al., 2009). With the watershed as a boundary, one can estimate the levels to which a nutrient, such as P, enters and exits the landscape, and then model its dynamics and interactions at this scale.

Different techniques have been developed to estimate and model the amount of P accumulating within a watershed and P dynamics at the watershed scale. Mass-balance approaches, known as 'nutrient budgets', are used to estimate differences in P inputs and outputs in agricultural croplands to determine the accumulated P building up within a watershed's agricultural soils (Smeltzer and Quinn, 1996; Bennett et al., 1999; MacDonald and Bennett, 2009). A more detailed technique, known as the 'net anthropogenic P input' (NAPI), includes the P embedded in food and detergent imports and thus accounts for a more complete model of net P accumulation in watersheds. In these models, P enters the watershed embedded either in synthetic fertilizer, non-food inputs, animal feed human food, and detergent, and P exits the watershed embedded in exported commodities (Russell et al., 2008; Han et al., 2011; Hong et al., 2012; Goyette et al., 2016). Models such as watershed nutrient budgets and NAPI calculations can improve nutrient management by increasing the understanding of the potential nutrient accumulation in watershed soils. Advanced models of P movement and retention, such as the extended end-member mixing analysis (E-EMMA), can increase understanding of the dynamics between long-term anthropogenic P pressure and ecological impact and determine the most strategic and effective management for current and future water quality protection (Jarvie et al., 2011).

However, while nutrient budgets and NAPI calculations can estimate the P surplus added to a basin in any particular year, their values do not necessarily accurately predict resulting water quality indicators of the same year. Across many regions, studies find that only a very small proportion of annual net P inputs to watersheds are detected in the surface water systems in the same year. For example, in the Great Lakes Region, Han et al. (2011) found that between 5 and 10 percent of annual watershed NAPI was exported to rivers in a given year. A study by Russell et al. (2008) found that the fractional export of P was 10 percent of NAPI in the Chesapeake Bay region of the USA. In the Central Valley of California, USA, Sobota et al. (2011) found that only 7 percent of P inputs were accounted for in their calculations of median fractional riverine export. In a study in the Sainte Lawrence Basin of Quebec, Canada, Goyette et al. (2016) calculated that, on average, 5 percent of annual NAPI was observed as riverine fractional export; however, among the 23 watersheds in the study, exports varied significantly, from 3 to 173 percent. The values from these various studies tell us that, in general, watersheds are retaining up to 90 percent of net P inputs in a given year, which suggests a massive build-up of soil P in these agricultural watersheds. Studies show that majority of the legacy P storage in watersheds happens in soils, surface water sediments, biomass, and occasionally in groundwater (Holman et al., 2008; Jarvie et al., 2013b; Sharpley et al., 2013; Chen et al., 2015a).

Legacy P: Nutrient retention in agricultural soils

Human changes to the global P cycle in the past 200 years have resulted in a dramatic increase in the accumulation of P in many agricultural soils. However, most soil P, around 80-90 percent, is found in an inorganic state known as "stable P" which is bound tightly to soil particles and less bioavailable to plants (Smil, 2000; Hansen et al., 2002). The low bioavailability this large amount of soil P contributes to the practice of continued application of P inputs to agricultural land despite high soil P levels (Hansen et al., 2002). The net input of P fertilizer and manures to agricultural land is as high as 11.5 Tg P per year, and over 70 percent of the world's croplands have net surplus of P due to human additions (MacDonald et al., 2011).

The steady build-up of P in agricultural soils due to fertilizers and manure inputs is known as P accumulation (Jarvie et al., 2013a; Chen et al., 2015a). P accumulation occurs whenever the P inputs in a region exceed the P exported from the same region in the form of crops. A study by Sattari et al. (2012) shows that, between the years 1965 and 2007, average soil P accumulation on global croplands was at 550 kg ha^{-1}, which amounts to a total of around 830 Tg of P.

However, the issue of P accumulation is not equally present in all agricultural regions (MacDonald et al., 2011). In eastern China, Ma et al. (2013) found that P accumulation in agricultural land ranged from 10 to 44.7 kg P ha^{-1} yr^{-1} (between the years 1984-2008); in Wisconsin, USA, Bundy and Sturgul (2001) recorded a that 16-50 percent of annual P inputs between 1970-1995 accumulated in agricultural soils; and Sattari et al. (2012) recorded 68 percent of annual P inputs accumulated in agricultural soils in their European study between the years 1965 and 2007. Some regions experience a net decrease in P accumulation and/or depletion, whereby soil P is exported at a faster rate than it is applied (MacDonald et al., 2011). Rates of P accumulation are variable due to a variety of factors such as fertilizer use rates, soil type, and the length of time the areas have been in agriculture (MacDonald et al., 2012).

The long-term residence of P in agricultural soils is referred to as 'legacy P' (Jarvie et al., 2013a; Sharpley et al., 2013). The build-up of legacy P in croplands increases the potential for P loss to surface waters through processes of soil erosion or leaching (Carpenter, 2005). Annual riverine TP flows usually consist of a combination of recently applied, contemporary P inputs in the form of manure or fertilizer as well as legacy P stores from previous years' inputs (Sharpley et al., 2013; Chen et al., 2015a).

The passage of legacy and contemporary P from terrestrial to aquatic ecosystems is often expedited by human-induced landscape changes and resulting soil loss (Smil, 2000; Bennett and Schipanski, 2013). Through landuse change, deforestation and intensive cultivation, humans have increased the rate at which P-rich soil is lost from terrestrial landscapes through increased rates of soil erosion. It is estimated that human-caused agricultural soil loss is as high as 20 t/ha, which implies a loss of between 10 – 15 kg of P per hectare from global croplands every year (Smil, 2000).

Legacy P may explain why there is often a significant delay between P accumulation in soils and ecological impact within water systems (Powers et al., 2016). Human-dominated river basins can go through a very long phase of P accumulation when inputs exceed outputs, and this accumulated P can have impacts on water quality years after the rate of P accumulation has waned or stopped all together (Powers et al., 2016). This explains why there is often a lower downstream ecological impact than expected in P-rich agricultural landscapes. Legacy P may also explain why there is often a delay between upstream mitigation measures and improvements in downstream water quality (Meals et al., 2010; Jarvie et al., 2013b).

Watershed Buffering: Retention and release of legacy P

Annual surplus P inputs in agricultural watersheds represent a threat to downstream aquatic ecosystems (Carpenter, 2005); however, a steady increase in upstream ecological pressure does not always result in a linear decrease in water quality (Allan, 2004; Flotemersch et al., 2015). Some studies find a significant correlation between annual NAPI values and yearly riverine P flux across watersheds (Han et al., 2011; Hong et al., 2012); however, many studies find no significant relationship between annual NAPI and riverine P flux across watersheds (Borbor-Cordova et al., 2006; Russell et al., 2008; Sobota et al., 2011). This suggests that, while riverine flux is directly influenced by annual P inputs, other factors mediate the relationship between pressure and impact besides the degree of pressure in any given year. Watersheds range in their ability to absorb and retain anthropogenic P inputs. This characteristic is known as a watershed's "buffering capacity" (Doody et al., 2016).

A watershed's specific buffering capacity is a product of diverse properties of its landscape, and it is also a property that can be dynamic through space and time (Burt, 2001; Doody et al., 2016). A watershed's buffering capacity is influenced by three main watershed characteristics: geochemical factors, such as soil properties (Kleinman et al., 2011); hydrological factors such as baseflow index and topography (Burt, 2001); and landscape factors, such as the composition and configuration of land use (Qiu and Turner, 2015). Buffering capacity is also impacted by socio-ecological factors such as population density, riparian management, and the presence of artificial soil drainage (Reed and Carpenter, 2002; Gentry et al., 2007).

Geochemical factors

Geochemical factors, such as soil type, play a major role in mediating P movement on the landscape, as soils are the one of the most common points of contact between P and the terrestrial landscape (Smil, 2000). When added to agricultural soils, P often binds to soil particles in a process called "P-fixation" (also known as P immobilization or retention). Various soil properties, such as current soil P content, soil texture, depth and chemistry, impact the degree to which incoming P binds to soil particles, which in turn impacts the amount of P potentially stored in a watershed's soil environment (Kleinman et al., 2011).

One of the major soil properties that impact its ability to retain incoming P is the amount of P already present in the soil. The capacity for soil to bind to P and convert it to stable forms decreases as the soil accumulates P (Kleinman et al., 2000). The degree to which soil's potential binding sites are occupied by P molecules is known as 'percent soil P saturation', and soils with low percent soil P saturation will be more likely to retain incoming P (Vadas et al., 2005).

Basic soil properties such as soil texture class can also have a significant impact retentive capacity of watershed soils (McDowell et al., 2003). The percent clay content within agricultural soils has an impact on rates of soil P retention. This is because, at the microscopic level, P binds readily to clay molecules due to high surface area and high levels of potential sites of adsorption on clay particles (Bennett and Schipanski, 2013). However, at the macroscopic level, the impermeability of clay dominated soils can potentially result in greater levels of runoff and suppressed baseflow, which can increase the transport of P to water bodies (Wilcock, 1997).

Other soil properties that impact the degree to which soils will retaining incoming P include a soil's mineral composition, organic matter content, and redox condition (McDowell et al., 2003).

High levels of humic material and iron and aluminum oxides also increase P retention in soils (Bennett and Schipanski, 2013). The pH of the soil can also impact P dynamics. Highly acidic and basic soils (pH <5 or >7) are associated with high levels of P adsorption (Wolf et al., 1987; Vaz et al., 1993), and slightly acidic and neutral soils (pH 5-7) are associated with higher levels of P bioavailability and movement through the soil profile (Wolf et al., 1987).

Hydrological factors

Hydrological factors may be some of the most powerful drivers of P retention and transport in watersheds (Burt, 2001; Kleinman et al., 2011). The hydrological conditions of a watershed such as baseflow index, water yield, and topography dictate the flow pathways for the nutrient as well as many potential mechanisms for potential retention (Gburek and Sharpley, 1998; McDowell et al., 2001; Kleinman et al., 2011).

Basic hydrological features, such as the average slope of a watershed, and the average water yield of a watershed, can potentially impact its retentive buffering capacity. In their study of 101 lakes in Iowa, USA, Fraterrigo and Downing (2008) found that slope was a relevant predictor of riverine P flux in watersheds with high levels of overland flow. Reed and Carpenter (2002) found that percent slope was the most strongly correlated with P flux in their study of six agricultural watersheds in Wisconsin, USA, with P flux increasing with increased slope. Studies also find that levels of river discharge can increase levels of riverine P flux (Borbor-Cordova et al., 2006).

Another key hydrological feature of watersheds that impact retentive capacity is relative contribution of groundwater to the flow of water through a watershed, which is measured by the baseflow index (Smakhtin, 2001). If a watershed has a high baseflow index value that means much of the water transported within the basin is below ground, which allows for more opportunities for

P retention within the soil matrix which can result in relatively lower rates of riverine P flux (Gburek and Sharpley, 1998). Watersheds with low baseflow index values contain more overland flow which contributes to higher rates of P loss through surface runoff. In these watersheds, specific locations within watersheds containing elevated levels of soil P (known as 'P hotspots") are at great risk for soil erosion, and in this case, P-laden soil particles end up in water systems (Pionke et al., 2000).

Landscape factors

Another key set of variables that impact the transport and retention of P in a watershed are landscape features such as the land use/land cover types found within a basin and the configuration (spatial location) of those land use/land cover types. Different land use classes can act as either a source of P to be released, such as agriculture, or a location for P retention, such as forest or wetlands (Allan, 2004). Many studies have found a significant link between agricultural land use and riverine P flux in watersheds (Fraterrigo and Downing, 2008; Jacobson et al., 2011; Qiu and Turner, 2015). This is due to the fact that most P coming into watersheds is applied to agricultural land where it has the potential to become a source of P release and nonpoint source pollution (Allan, 2004). Agricultural land throughout the world is found to have higher levels of soil P than nearby natural land covers (MacDonald et al., 2012). Besides agricultural land, researchers have also found that developed land in watersheds is a significant predictor in riverine P flux (Russell et al., 2008; Chen et al., 2015a). This is due to the fact that developed lands largely consist of impervious surfaces which increases the risk of surface runoff and developed lands contain less opportunities for infiltration and retention of P in soils (Sobota et al., 2011).

Wetlands, forests, grasslands, and other long-standing land cover types have the potential to counteract sources of P pollution and become 'sinks' or areas of P retention between source areas and waterways, thus potentially increasing the buffering capacity of a watershed. For example, wetlands have great potential to be a sink for P on the landscape; in a review study, Fisher and Acreman (2004) found that wetlands can retain 5-20 percent of watershed P flux, storing the nutrient within soils, vegetation, and plant litter. In Wisconsin's Yahara River Watershed, USA, Qiu and Turner (2015) found that P loading was negatively correlated with high percentages of natural land covers (such as forest, grasslands, and wetlands).

The spatial pattern of land use/land cover is also an important predictor of P flux across the landscape. Qiu and Turner (2015) found that high patch densities of wetlands and grasslands seemed to decrease P loss, as well as the amount of disaggregation in forest patches. In this study, P flow was also negatively associated with the contagion index, which is a general indication of land use heterogeneity, which means that a watershed with a more diverse set of land use may have more buffering potential.

Socio-ecological factors

Human and management factors within basins can also have a significant impact on the ability of the basin to retain incoming and legacy P inputs. Such factors include farm size, crop types, and on-farm management decision as well as larger-scale landscape alterations such as artificial soil drainage, river channelization and riparian management as well as demographic factors such as population density.

Socio-ecological factors significantly impact the way that P moves across landscapes by both creating source points of nutrients within watersheds, and by altering critical ecosystem processes. One major human alteration of the landscape regarding the passage of nutrients into surface waters is via tile drainage. Tile drainage is a process by which perforated pipes are laid 1-2 meters below poorly drained soils, and moisture from the land is drained through these pipes to surrounding drainage ditches and eventually to surrounding surface waters (Gentry et al., 2007). This practice allows drainage in perennially water-logged soils making them viable for agriculture. But it also increases the hydrological connectivity of the landscape by streamlining water, often heavily laden with nutrients, from agricultural fields to water systems (Gentry et al., 2007). This piping allows nutrients to flow directly into aquatic ecosystems by surpassing soil and other landscape processes that may otherwise retain excess nutrients from agricultural fields. A study on streams in Illinois, USA found that tile drainage was a significant source of P to surface waters (Gentry et al., 2007), and studies in watersheds in Delaware, Indiana and Canada confirm that tile drainage is important source of P export from agricultural fields (Sims et al., 1998). In their study, Chen et al. (2015a) also found that percentage drained agricultural land significantly correlated with riverine P flux.

Another human management decision that can impact P cycling is the management of riparian zones, the land directly adjacent to water bodies. Fraterrigo and Downing (2008) found that variables representing agricultural and urban land use within 100 meters of lakes were relevant in explaining P flux into lakes in watersheds with 'low transport capacity', which refers to watersheds that have relatively low rates of nutrient transport. This suggests that non-retentive land covers in riparian zones, such as developed land or exposed agricultural land, can significantly increase the amount of nutrient flux in watersheds that are otherwise fairly retentive. Reed and Carpenter (2002) looked at buffer composition and configuration in six watersheds in Wisconsin, USA, and found that the variability in riparian patch size was closely correlated with daily P-yield. Characteristics of the riparian buffers such as the percent wetland cover and the continuity of the riparian areas were closely correlated with the variability in P yield (Reed and Carpenter, 2002). Other studies considering the importance of riparian zones show mixed results or are inconclusive, illustrating the fact that this is an landscape ecology question still in play (Osborne and Kovacic, 1993; Sliva and Williams, 2001).

The number of people in a watershed and their density on the landscape can impact the incoming P because large populations of humans import food and produce large quantities of P-rich waste. Population density was considered a significant predictor of riverine P export in the Russell et al. (2008) study in the Chesapeake Bay Region of the US, and other studies confirm this relationship (Beusen et al., 1995; Caraco, 1995). Riverine P flux is also impacted by the degree and nature of legacy P present in watersheds (Chen et al., 2015a; Chen et al., 2015b).

These various watershed characteristics, geochemical, hydrological, landscape, and socio-ecological, potentially play a role in mediating the retention, release, and transport of terrestrial P to receiving water bodies. The specific set of these various features together determine a watershed's buffering capacity and the level to which watersheds will retain historic P inputs. The relative importance of these features and the impacts of their diverse interactions is currently unknown.

Holistic Watershed Management: Managing trade-offs between water quality and agricultural production

P is an essential input in agricultural production systems; however, the long-term P accumulation that occurs in most agricultural systems presents a latent threat to current and future water quality (Carpenter, 2005). Additionally, the diffuse nature of P transport processes and the variable time lag between initial P inputs on the landscape and its eventually impact on water quality make managing for water quality difficult. A greater understanding of mechanisms of legacy P transport in water systems will increase the level of certainty about which management strategies will yield the best results. A future where high water quality standards and thriving agricultural industry can co-exist in the same watersheds requires a holistic understanding of the trade-offs between these two ecosystem services at different scales as well as an understanding of how nutrients interact with the surrounding landscape to either prevent or exacerbate the vulnerabilities of water systems, and for those who rely on local food and water ecosystem services, the stakes are high (Jarvie et al., 2013b; Doody et al., 2016).

An understanding of watershed buffering capacity can help consider the trade-offs inherent in watershed management and help land managers achieve specific goals on the landscape. It can help to determine the vulnerability of landscapes to nutrient pressure and can be used to model the potential consequences of changes in land use or land management in watersheds (Jarvie et al., 2011). Watershed management can improve by realizing which specific levers can increase an ecosystem's ability to retain overland P runoff (Burt, 2001). Knowledge of watershed buffering capacity can also aid in deciding which watersheds can sustain increased agricultural intensification and which watersheds would benefit from increased conservation measures (Doody et al., 2016); this will potentially help land managers to avoid the crossing of irreversible thresholds in P loading to surface waters (Burt, 2001; Gordon et al., 2008). Improved models of watershed vulnerability will also aid in managing expectations between mitigation actions and ecological improvements (Bolinder et al., 2000; Meals et al., 2010; Jarvie et al., 2013b).

Conclusion

P is a good example of the complex challenges for the relationship between humans and nature in the Anthropocene. Many productive agricultural regions have prioritized provisioning services such as crop production at the expense of slower-acting services such as the water quality regulation performed by forests or wetlands (Raudsepp-Hearne et al., 2010). If the trade-offs between these services are not specifically addressed and managed for, the long-term consequences of agricultural run-off will continue to impact fresh and coastal water systems and the people who rely on them. The problem of eutrophication is being seen more frequently and at a larger scale than ever before, it may be exacerbated by climate change (Michalak, 2016). Eutrophication and the negative consequences of P pollution are also expected increase due to projections of global population growth and general trends of increased agricultural intensification (Tilman et al., 2001). Sustainable agricultural production on the landscape must incorporate processes of drawing down P-saturated soils, and land managers must prioritize protecting soils and the nutrients they contain.

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Chapter 1 to Chapter 2 Connecting Statement

In chapter 1, I reviewed the issue of anthropogenic changes to the global P cycle, the build-up of P in agricultural watersheds, and the potential impact of this phenomenon on fresh water and coastal ecosystems. This chapter also covered the literature regarding the relationship between long-term legacy P retention and processes of P release and transport on the landscape. I also considered the factors that potentially impact the degree to which watersheds retain P for long periods of time, including geochemical, hydrological, landscape, and socio-ecological factors.

In chapter 2, I apply this knowledge to research into the relationship between legacy P accumulation and current and historic water quality indicators in 16 agricultural watersheds in Quebec, Canada, across a thirty year time span (1981-2011). Here, I use multiple indicators to estimate the specific "buffering capacity" of these watersheds and then compare the buffering capacity indicators to a diversity of watersheds characteristics that may play a role in impacting the transport of P within watersheds such as soil type, water yield, landscape configuration, and the presence of artificial drainage, among others. This study includes multiple potential interpretations of the buffering capacity concept, and considers a wide range of watershed characteristics that potentially impact the dynamics of phosphorus transport on the landscape.

CHAPTER 2 Watershed buffering of anthropogenic phosphorus pressure at a regional scale, a comparison across space and time

Introduction

Phosphorus (P) is a non-renewable resource essential for agricultural production, and millions of tonnes are applied to agricultural fields worldwide in the form of phosphate fertilizers (Bennett et al., 2001). Due to the soil's capacity to adsorb P and its propensity to exist in less bioavailable forms (i.e. through P-fixation), many agricultural watersheds have become enriched with P from years P inputs in fertilisers and manures that are greater than the amount of P removed in harvest (Hansen et al., 2002; Jarvie et al., 2013). Long-term residence of P in agricultural landscapes (known as 'legacy P') and its slow release from soil provides an endemic and delayed source of P inputs to receiving water bodies (Powers et al., 2016; Rowe et al., 2016).

Excess agricultural P is a major source of pollution in fresh and coastal waters, and therefore, P-enriched landscapes present a long-term threat to water quality (Allan, 2004; Carpenter, 2005). The two major symptoms of over-enriched water bodies of particular societal concern include oxygen depletion (known as hypoxia) and toxic blue-green algal blooms, which can be dangerous to human health, expensive, and are often irreversible (Dodds et al., 2008; Rabalais et al., 2009; Keeler et al., 2012). Accumulation of P in agricultural soils, and its movement to fresh and coastal water systems, is a global phenomenon in the Anthropocene (Elser and Bennett, 2011; MacDonald et al., 2011); and many regions around the world are impacted by eutrophication (Diaz, 2001; Diaz and Rosenberg, 2008; Diaz et al., 2010; McCrackin et al., 2016).

While eutrophication and the resulting hypoxia are an inevitable consequence of excessive nutrient inputs, the amount of P accumulated in upstream ecosystems is not always a good predictor of cascading downstream water quality impacts (Borbor-Cordova et al., 2006; Russell et al., 2008; Sobota et al., 2011). This is due to the non-linear relationship between anthropogenic P pressure and water quality impacts, one aspect of which is landscapes' ability to retain P for decades to centuries, delaying its transport to aquatic ecosystems (Carpenter, 2005; Powers et al., 2016). Due in part to the dynamics of legacy P in watersheds, the relationship between P inputs on the landscape and P loading into surface waters often shows significant variation depending on the a watershed's ability to retain added P (Allan, 2004; Jarvie et al., 2011). This ability is known as the watershed's "buffering capacity".

Buffering capacity is a product of the diverse properties of the landscape, both ecological and social, and is dynamic through space and time (Doody et al., 2016). A watershed's buffering capacity is influenced by three main watershed characteristics: geochemical factors, such as soil characteristics (Vaz et al., 1993; McDowell et al., 2003; Kleinman et al., 2011); hydrological characteristics, such as water yield or topography (Reed and Carpenter, 2002; Borbor-Cordova et al., 2006); and aspects of the landscape, such as the composition and configuration of land use (Fraterrigo and Downing, 2008; Qiu and Turner, 2015). Buffering capacity is further impacted by land management decisions, such as riparian zone maintenance, artificial drainage, the nature and timing of nutrient applications, as well as the amount and configuration of above-ground biomass (Osborne and Kovacic, 1993; Reed and Carpenter, 2002; Gentry et al., 2007).

These diverse biophysical and social characteristics govern the quantity of P that watershed ecosystems are able to absorb, and can therefore potentially be used to predict how much P a watershed will retain and for how long. Watershed buffering can potentially create a delay between P accumulation in terrestrial ecosystems and resulting water quality degradation –which is an opportunity and also a risk for watershed management (Carpenter, 2005; Rowe et al., 2016).

Determining which landscape features impact agricultural landscape buffering capacity can help us to understand how landscapes can be managed to increase their resilience to external pressure and identify leverage points for more holistic land management (Flotemersch et al., 2015; Doody et al., 2016). A greater understanding of how buffering capacity is conferred on a watershed can also help identify which watersheds are particularly vulnerable to P pressure that could arise from changes in land use, including agricultural intensification and urbanization.

In this study, we measure the buffering capacity of large, agricultural watersheds in southern Quebec, Canada, using two different methods and investigate the landscape factors most closely associated with buffering capacity (Figure 1). The first method (Buffering Index) uses long-term net anthropogenic P input and riverine P flux data to quantify the degree to which watersheds retain accumulated nutrients through time; it was developed based on previous attempts to understand how P legacy impacts current-day water quality (Sharpley et al., 2013; Chen et al., 2015). The second method (Extended End-Member Mixing Analysis, E-EMMA) uses hydrological modeling to estimate the degree to which P is retained and released as water moves through watersheds (Jarvie et al. 2011).

These methods capture two different aspects of watershed buffering capacity. The buffering index is based on century-long datasets and represents the level to which a watershed has acted as a sink for *historically accumulated* TP inputs (i.e. focuses on legacy P). The E-EMMA values, on the other hand, are based on flow-nutrient dynamics and represent the degree to which the landscape traps P mobilized by moving water across the land-water continuum. Thus, the buffering index is an indicator of the long term buffering capacity of a watershed; whereas, the E-EMMA retention value is an indicator of the short-term retention of mobilized TP.

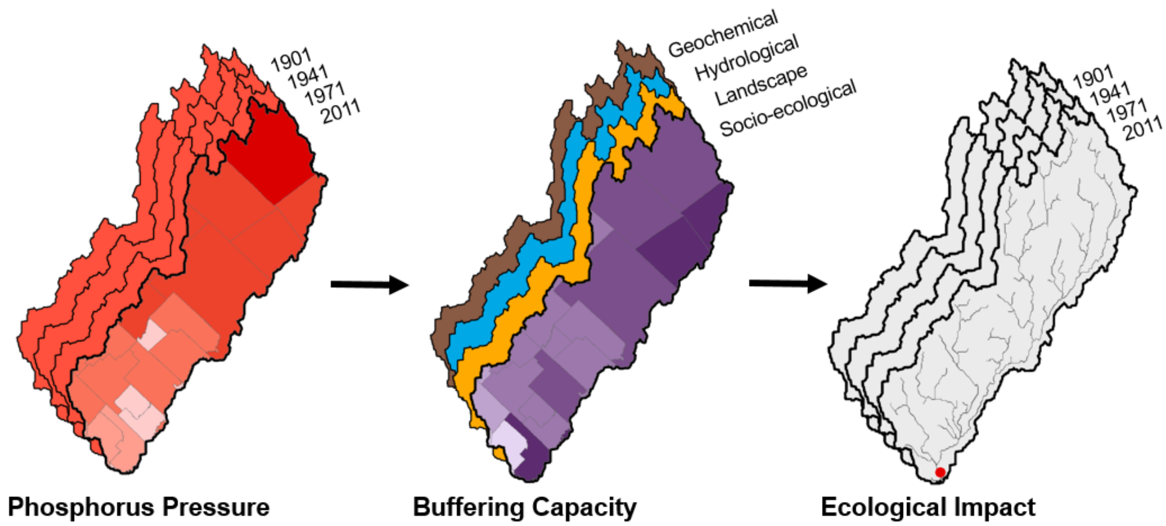

Figure 1: Conceptual model of study. Conceptual model outlining factors that could mediate the relationship between P pressure and ecological impact by affecting buffering capacity. We hypothesize that watersheds have innate buffering capacities based on their geochemical, hydrological and landscape characteristics, and human activities and management impact this dynamic. The watershed's ultimate capacity to buffer increasing P pressure is dictated by a combination of innate landscape features, cumulative pressure, and human management.

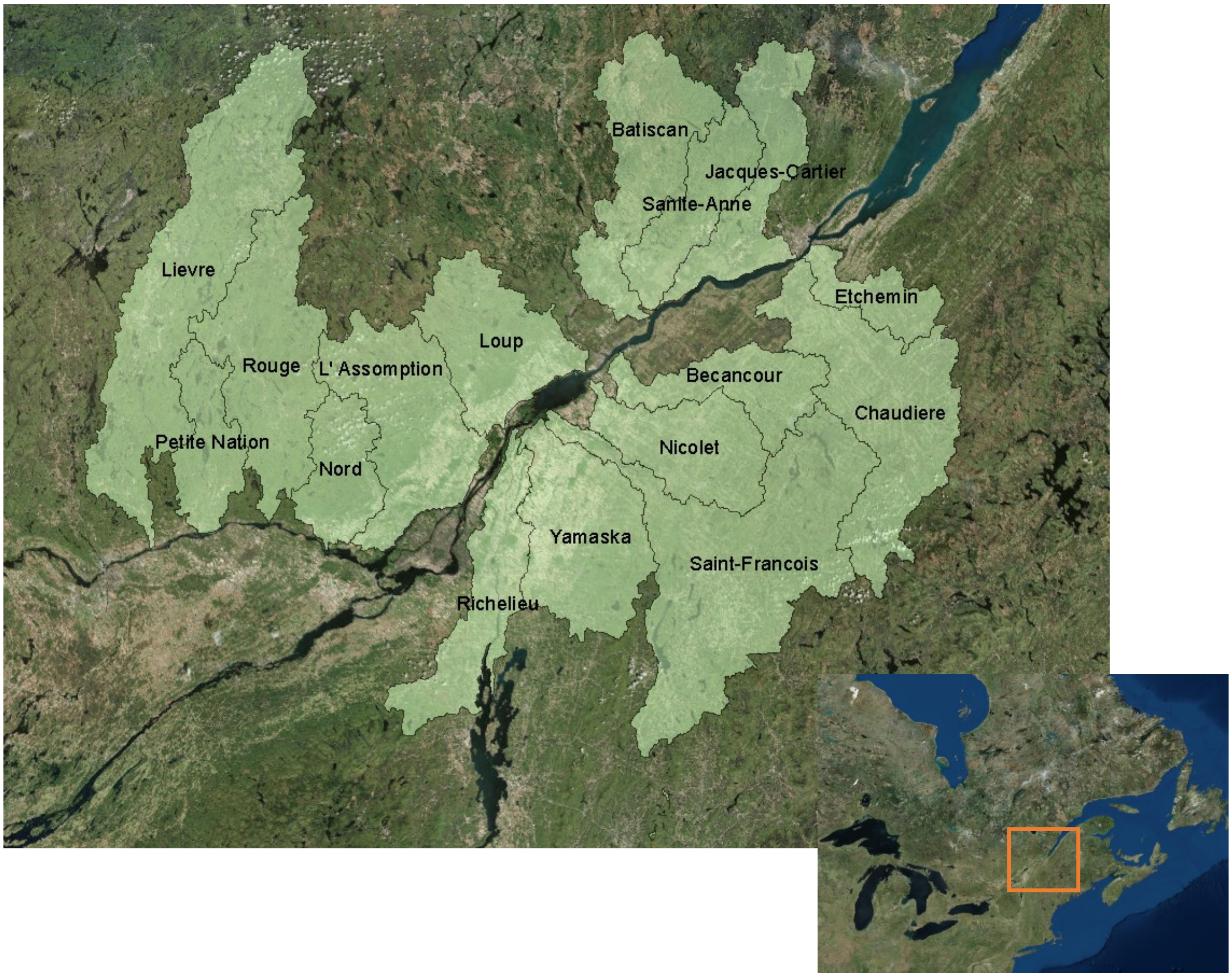

Figure 2: Map of study area. This maps shows the 16 watersheds located in Quebec, Canada that were examined in this study. The study area surrounds the City of Montreal in the west, and Quebec City, in the east. The dominant land cover in these basins includes agriculture, forest and developed (built up) land. These watersheds all drain into the Saint Lawrence River, which culminates in the Lower Saint Lawrence Estuary to the east (see inset map).

Study Site

The sixteen watersheds examined in this study lay within the greater Saint Lawrence River Basin in Southern Quebec (QC), Canada (at 46°7'N, 72°42'W). These watersheds are home to approximately 4 million people and drain a total land area of ~73,000 km^2 (Figure 2). The dominant historical land cover is temperate forest; however, agricultural expansion starting around the end of the 19th Century reduced forest cover, with agricultural intensification starting primarily during the 1970s (MacDonald and Bennett, 2009). The most common land uses include intensive cash cropping, swine and dairy production, forage cropping, nature recreation, maple syrup production, as well as residential and urban development (Environment and Development, 2001; MacDonald and Bennett, 2009; Raudsepp-Hearne et al., 2010). Annual average precipitation ranges between 800-950 mm (Environment Canada, 2016). The region is relatively flat, with an average slope of around 10 percent. The dominant soil type in the region is a strongly acidic sandy podzol. Other common soil types include weakly acidic clay gleysol and weakly acidic brunisol (Shields, 1991). Multiple studies have estimated high levels of soil P enrichment in the region's agricultural soils related to historic P inputs from agriculture (MacDonald and Bennett, 2009; van Bochove et al., 2012; Goyette et al., 2016).

The sixteen watersheds all contain major rivers that drain to the north-flowing Saint Lawrence River. The Saint Lawrence River drains to the Lower Saint Lawrence Estuary (LSLE) which is the second largest freshwater discharge in North America (Bourgault and Koutitonsky, 1999). The LSLE has seen diminishing levels of deep-water oxygen over the last century, and it is speculated that this could be partly attributed to increased nutrient loadings into the estuary from the upstream watersheds, such as the ones considered in this study (Gilbert et al., 2005; Thibodeau et al., 2006).

Methods

To quantify buffering capacity, we obtained and analysed long-term data on P pressure (P input to watersheds, 1901-2011), historic river flow data, and water quality data in 16 agricultural watersheds in southern Quebec. We then compared two indicators of watershed buffering capacity with various landscape characteristics to determine the major factors that mediate P buffering at the watershed scale.

P Input data

We compiled P input data from Goyette et al. (2016), who calculated net anthropogenic P input (NAPI) values for all river watersheds draining directly to the Saint Lawrence River on a decadal or bi-decadal basis between the years 1901 and 2011. The NAPI values correspond to the difference between P inputs and outputs and thus indicate the amount of P accumulated in each watershed for each of the study years (Figure 3). NAPI inputs include the P embedded in fertilizer imports, as well as P imported as food, animal feed, and detergent; P outputs in NAPI are the P embedded in exported crops (Russell et al., 2008). Net cropland P input was calculated based on the difference between the P embedded in inputs to croplands on each given year (fertilizer and manures) minus the P embedded in exports from croplands on each given year (crops). Because NAPI data only exists for 10- or 5- year time steps, the total net input values between time steps were interpolated to estimate annual values throughout the century. Annual net P input values were added together to determine amount of P accumulated in each watershed between 1901 and each subsequent year of the study.

Water quality data

We obtained monthly riverine P concentration data and daily water flow data between the years 1979 to 2011 collected by two Quebec water monitoring agencies: *Banque de données sur la* *qualité du milieu aquatique* (BQMA) and *Centre d'expertise hydrique du Québec* (CEHQ). To convert P concentration (mg/L) to riverine flux (kg/yr), we calculated the annual flow-weighted P concentrations (FWPC), and then estimated annual P loading based on the FWPC and water discharge using the U.S. Army Corps of Engineers' FLUX32 software (Walker, 1999). The software uses a jackknife approach to calculate variance, and the variance calculated then represents the weight of a single data point on the resulting values. Using this FLUX32 software, we calculated annual P flux values for each of the 16 watersheds for each year between 1979 and 2011 (Figure 3). River P data was limited to this time period as there were no previous measurements before 1979. We then aggregated these annual values into seven 5-year time-steps between the years 1981 and 2011 to correspond with the time scale of the NAPI data. Flux calculations were divided by the total watershed area to determine the kilograms of P flux per area per year of study ($kg/km^2/yr$).

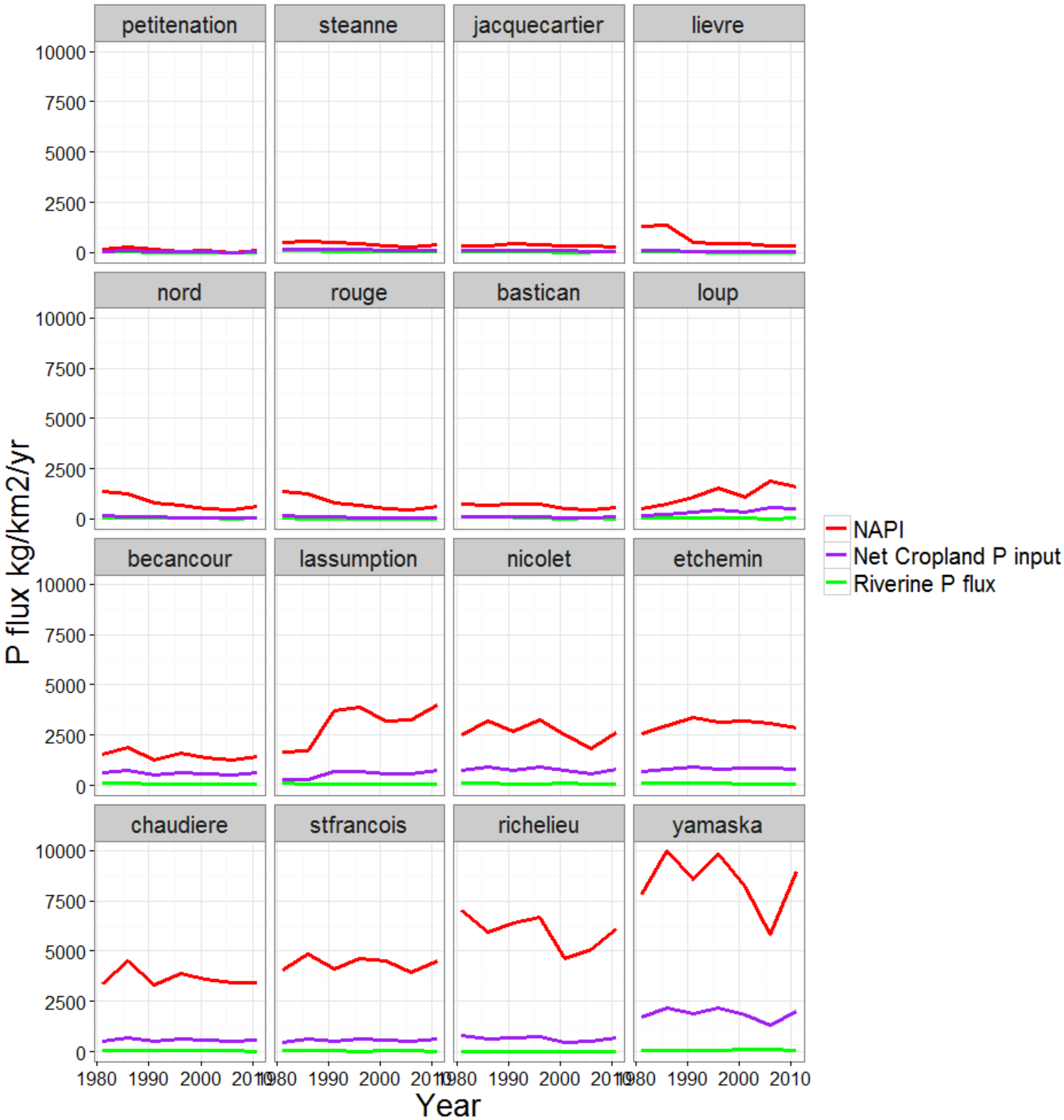

Figure 3: Summary of P flux across watersheds. The 16 watersheds show varying levels of overall P input data (NAPI), net cropland input data (fertilizer and animal feed inputs minus crop outputs) as well as riverine P flux over the 35-year study period. The 'gap' between the NAPI (red) and riverine P flux (green) lines represents the amount of P that has accumulated within the total watershed area in each year. The 'gap between the net cropland P inputs (purple) and riverine P flux (green) lines represents the amount of P that has accumulated within watershed croplands in each year.

Buffering Method # 1: Calculating "Buffering Index" (BI)

We estimated a "buffering index" (BI) for each watershed by determining what percentage of historically accumulated P was being retained by a watershed in each study year. The BI value is an indication of the *capacity* of the watershed to absorb net P pressure and hypothesizes that some watersheds retain higher levels of accumulated P than others before releasing this P to the river. Retention was calculated as the difference between watershed inputs and P flux to the river. In order to resolve the magnitude of difference between these two values, we calculated the relative degree of retention using the log-scaled accumulated P and riverine TP flux values:

$$BI = (1 - \frac{\log(Riverine\ TP\ flux\ (kg \cdot km^{-2} \cdot yr^{-1}))}{\log(cumulative\ NAPI\ (kg \cdot km^{-2} \cdot yr^{-1}))})$$

Buffering Method # 2: Extended End-Member Mixing Analysis (E-EMMA)

We used the extended end-member mixing analysis (E-EMMA, Jarvie et al. 2011) to further investigate the level of P retention in each of the study watersheds. The E-EMMA methodology is used to estimate what percentage of P is retained by upstream ecosystem processes as water flows through the watershed by capturing the degree of non-linearity in the relationship between watershed flow and P flux in a watershed over time (Neal et al., 2010; Jarvie et al., 2011; Jarvie et al., 2014). When the relationship between watershed flow and P flux is linear, this denotes there is a relatively small amount of terrestrial retention and in-stream uptake because it means that there is a relatively proportional relationship between the amount of water moving across the landscape and the amount of P transported in that water. In contrast, a non-linear relationship between watershed flow and riverine P flux denotes more retention of P within the watershed because it means that as water moves across the landscape, there are relatively more opportunities for P molecules to be trapped and retained by terrestrial and aquatic ecosystems; this means that less P is delivered to waterbodies in the near term, and it also means that there is more P being stored in the watershed for later delivery.

This modeling process assumes that the two main sources of riverine P are 'baseflow end-member sources' which come from groundwater sources and effluent, and 'stormwater end-member sources' which come from overland non-point runoff (Jarvie et al., 2011). The lowest flow values for the watershed are assumed to represent the baseflow end-member source, and the highest flow values are assumed to represent the stormwater end-member source. With the E-EMMA methodology, we compared observed non-linear relationships between river flow and P flux observations with a theoretical linear relationship between baseflow and stormwater P flux values to estimate the amount of P retention within each of the watersheds; we were unable to perform the E-EMMA analysis for the Lievre watershed due to an insufficient variation in river flow values in this watershed over the study period.

Watershed data

We determined watershed boundaries and we collected geochemical, hydrological, landscape, and socio-ecological spatially explicit information for the 16 QC watersheds from a variety of sources (Table 1). These values were then used to investigate which watershed characteristics are most closely associated with P buffering capacity.

Watershed Boundaries. We obtained watershed boundaries for the global HydroSHEDS dataset (Lehner and Grill, 2013) Level 7 (corresponding to watersheds roughly between 1000 to 7000 ha) because it matched most closely with the scale of the NAPI data (Goyette et al., 2016).

In two of our study watersheds (Lievre and Saint-Francois), sub- watersheds representing "upper" and "lower" halves were combined so as to correspond with the NAPI data.

Geochemical Characteristics. Soil P data were collected between the years 1995 and 2011 (kg P ha^{-1}; Mehlich-3 derived, taken at a 20-cm depth) (Beaudet et al., 2003). We aggregated municipal-level P data and partitioned it to the corresponding watershed. Soil characteristics, such as texture and pH, were summarized for each watershed to determine dominant soil qualities.

Hydrological Characteristics. To calculate water yield for watersheds, we obtained streamflow data (m^3/sec daily throughout the study years) at the outflow point of each watershed. We calculated a simple average annual stream flow and divided this by the area of the watershed to determine the water yield per km^2. We calculated the baseflow index for each watershed through time using the web-based hydrograph analysis tool (WHAT) developed by Lim et al. (2005). This tool interprets streamflow data using signal analysis to separate high and low frequencies within the data. High frequency waves have been associated with direct runoff, and low frequency waves have been associated with baseflow (Eckhardt, 2005). We calculated mean percent slope of the total watershed area, as well as the sinuosity of the major rivers within each of the watersheds in ArcGIS v. 10.1 (ESRI, 2012).

Landscape characteristics. To determine the degree of vegetative cover for each watershed, we calculated the normalized difference vegetation index (NDVI) for each study year between 1981 and 2011 (Weier and Herring, 2000). Higher NDVI values indicate greater vegetative cover. Landsat data with <10% cloud cover was aggregated in the years preceding each study year to create composite cloud-free satellite images. We repeated the NDVI calculation for the 100-meter buffer regions around major rivers in each watershed as an indication of riparian vegetate cover.

To determine the land use/land cover of watersheds, we consolidated 145 land use classes into eight broad categories to determine the land use trends of the area; this data was made available from the *Quebec Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques* (Bissonnette and Lavoie, 2015). In a rasterized format, we calculated percent land cover types in each watershed. We recalculated percent land cover for the 100-meter buffer regions around major rivers in each watershed to get an indication of riparian land use. To calculate metrics of landscape configuration, we used FRAGSTATS 4.0 (McGarigal et al., 2012). We selected a set of landscape configuration metrics that were ecologically relevant to P transport mechanisms, including fragmentation indices (patch density [PD] and edge density [ED]), and connectivity indices (patch cohesion [COHESION] and probability of adjacency [PLADJ]), as well as an interspersion index, known as contagion [CONTAG] (McGarigal et al., 2012; Qiu and Turner, 2015).

Socio-ecological Characteristics. We calculated watershed population density by partitioning municipality-scaled population density values to watershed boundaries. To calculate average field size in each watershed, we calculated the size of each farm in the study area using a polygon map of all of QC farms available from *La Financiere agricole Quebec*. We calculated the market capital value of farms (dollars per farm) for each watershed by divided the total market value (TMV) of all of the farms in each census subdivision by the total number of farms, and then we partitioned TMV to watershed boundaries; this data was available from the Quebec Agricultural Census.

The process of sub-surface drainage (also known as tile drainage) is important because it involves the piping of water from agricultural fields directly into water courses, which is a potential pathway of P mobilization in agricultural watersheds (Gentry et al., 2007). However, no complete dataset exists on the presence and location of sub-surface drainage in Quebec. We estimated the presence of drained land using inference from the combination of land use data and soil type data. We assumed that if there are row crops being cultivated on areas of poorly drained soil (as indicated by the Soil Landscapes of Canada database), there is a very high probability that there is a sub-surface drainage system on that farm land (Sugg, 2007). To estimate this, we overlaid agricultural land use and soils spatial data (from *La Financiere agricole Quebec*) in ArcGIS and calculated the amount of land in each watershed where row cropping was happening in very poor (VP), poor (P), or imperfectly drained (I) soils, assuming that these areas would have sub-surface drainage in order to be cultivated. With this information, we calculated the percent of total agricultural land that is likely drained.

Data Analysis

We used Pearson's correlation coefficients to estimate the relationship between buffering indicators and various watershed characteristics. For the correlation analysis, we omitted two outlying E-EMMA values (Richelieu and Petite Nation).

We also performed simple regressions between watershed characteristics, legacy P values, and riverine P flux values to determine whether landscape characteristics or legacy P had more explanatory power over riverine P flux.

Results

P accumulation and flux

All of the study watersheds have been accumulating P in their soils since the beginning of the 20^{th} century. Since 1981, among the sixteen watersheds in this study, total P imports (including agricultural, food, and detergent inputs) have exceeded exports by an average of between 125 kg/km^2/yr (Petite Nation) and 8,460 kg/km^2/yr (Yamaska) (Figure 3). The estimated net inputs on *croplands* (fertilizer and feed inputs minus crop exports) shows a lower range with a low of 85 kg/km^2/yr (Lievre) and a high of 2,386 kg/km^2/yr (Yamaska). By our most recent study year, 2011, long-term cumulative net P inputs (total P accumulation) in the soils of these watersheds could range from ~6,000 (Lievre) to ~100,000 kg/km^2 (Yamaska), with an average of ~29,000 kg/km^2 across the entire study area since initial measurements in 1901.

The level of riverine P flux ranged from an average of 16.4 kg/km^2/yr (Petite Nation) to 84.74 kg/km^2/yr (Etchemin). Comparison of average riverine P flux values with average NAPI values showed that the study watersheds retained, on average, between 58 % and 97 % of the net imported P in a given year (Nord and Richelieu, respectively).

In general, watersheds with more P accumulation have higher riverine P flux values. Within any given year, across the watersheds, higher P accumulation significantly correlate with higher riverine P flux values (Figure 4). Analysis revealed that the slopes of these relationships significantly varied among study years. Unexpectedly, riverine P flux has decreased over the study period in many watersheds, despite the fact that the amount of P accumulation in the watersheds has continued to mount over this time (Figure 5).

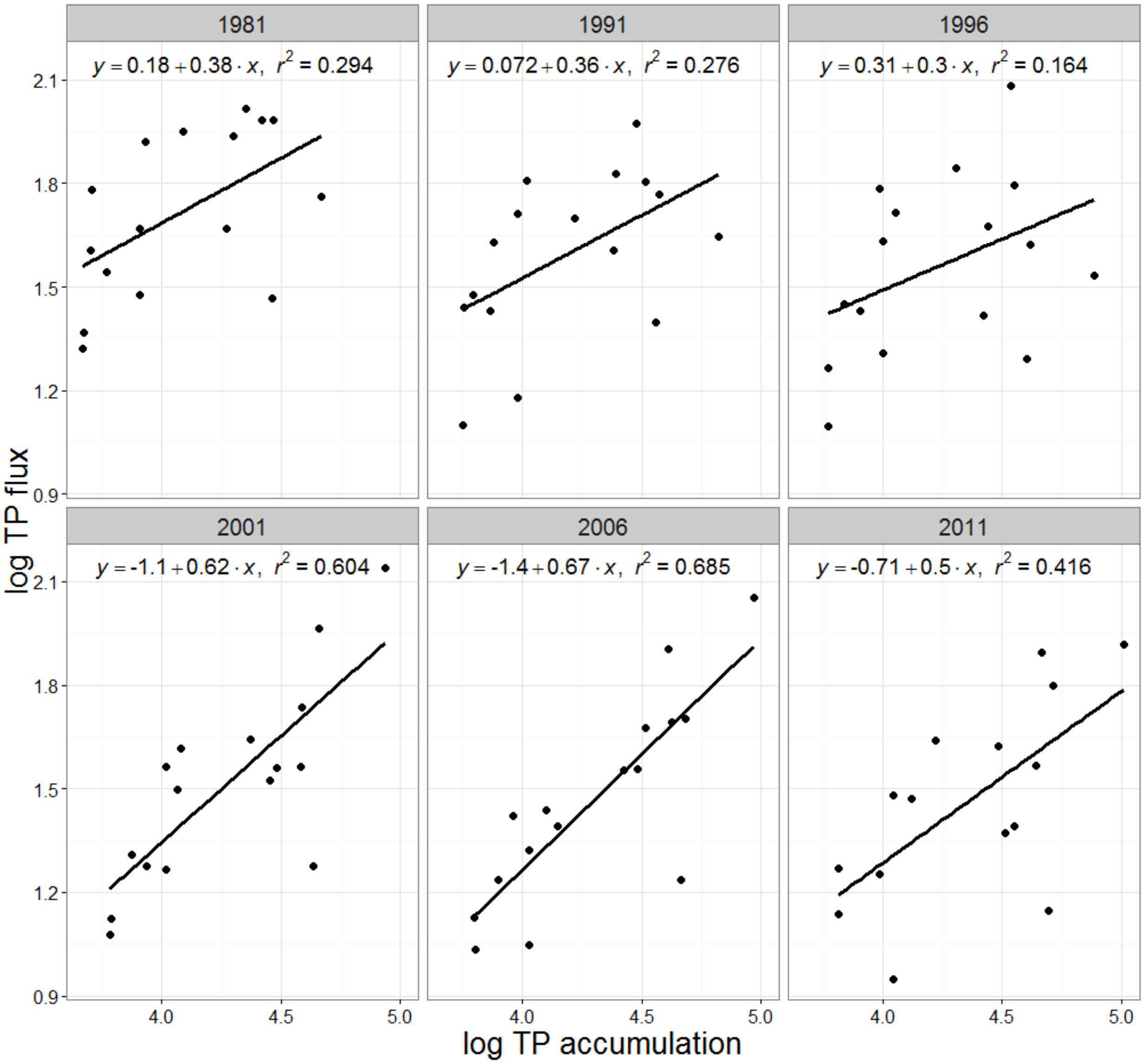

Figure 4: Relationship between P accumulation and TP flux across study years. The relationship between cumulative P inputs (since 1901) and P flux in each year of the study period (1981, 1991, 1996, 2001, 2005, and 2011) for each of the 16 watersheds. Across watersheds, within each study year, increased P accumulation results in a general increase in riverine P flux. ANCOVA results show that the slopes of the lines are significantly different ($F=5.86$, $P<0.0001$). The overall model with main effect has an $R^2= 0.20$ at $P<0.0001$.

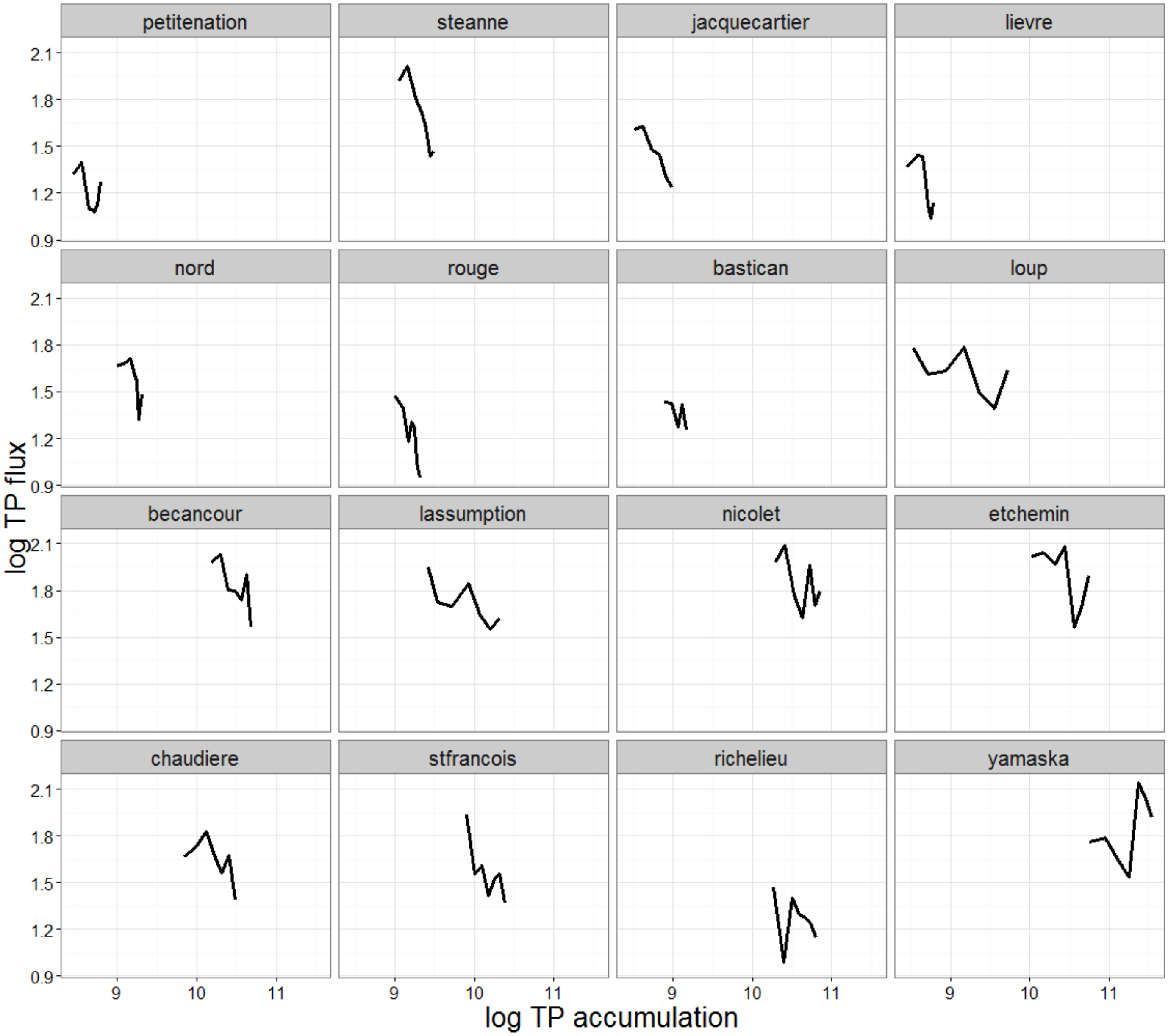

Figure 5: Relationship between P accumulation and TP flux across watersheds. These graphs show the relationship between P accumulation (since 1901) and annual riverine P flux for each watersheds within the study years. Many watersheds show a decrease in riverine P flux as their total P accumulation increases.

Buffering capacity estimates

We found a range of BI and E-EMMA values among the watersheds (Table 2; Figure 6; Figure S1). The watersheds with the highest average BIs over the study period are Richelieu, Rouge, Petite Nation, and Lievre. The watersheds with the lowest average BIs include Loup, Etchemin, and Sainte-Anne. The average BI value was 0.63 with a standard deviation of 0.06. The BI retention values significantly increase through time in a majority of watersheds because riverine fluxes have generally decreased, even as cumulative net P inputs have increased. This indicates that as P accumulation continues on landscapes, the ecosystem buffering continues to increase as well. The watersheds with the highest average E-EMMA retention values were Becancour, Yamaska, and Sainte-Anne, which retained 81%, 78%, and 77% of total watershed P, respectively; the watersheds with the lowest E-EMMA retention values were Richelieu and Petite Nation, both of which were found to have net P release, with retention values of -19%, and -11%, respectively. These negative retention values may be due to the fact that riverine P flux values in these watersheds are very low, which results in P retention values being also low; it is also potentially due to high levels of P release in these watersheds. The average E-EMMA percent P retention across the watersheds was 61 % with a standard deviation of 15. E-EMMA retention values did not change significantly through time.

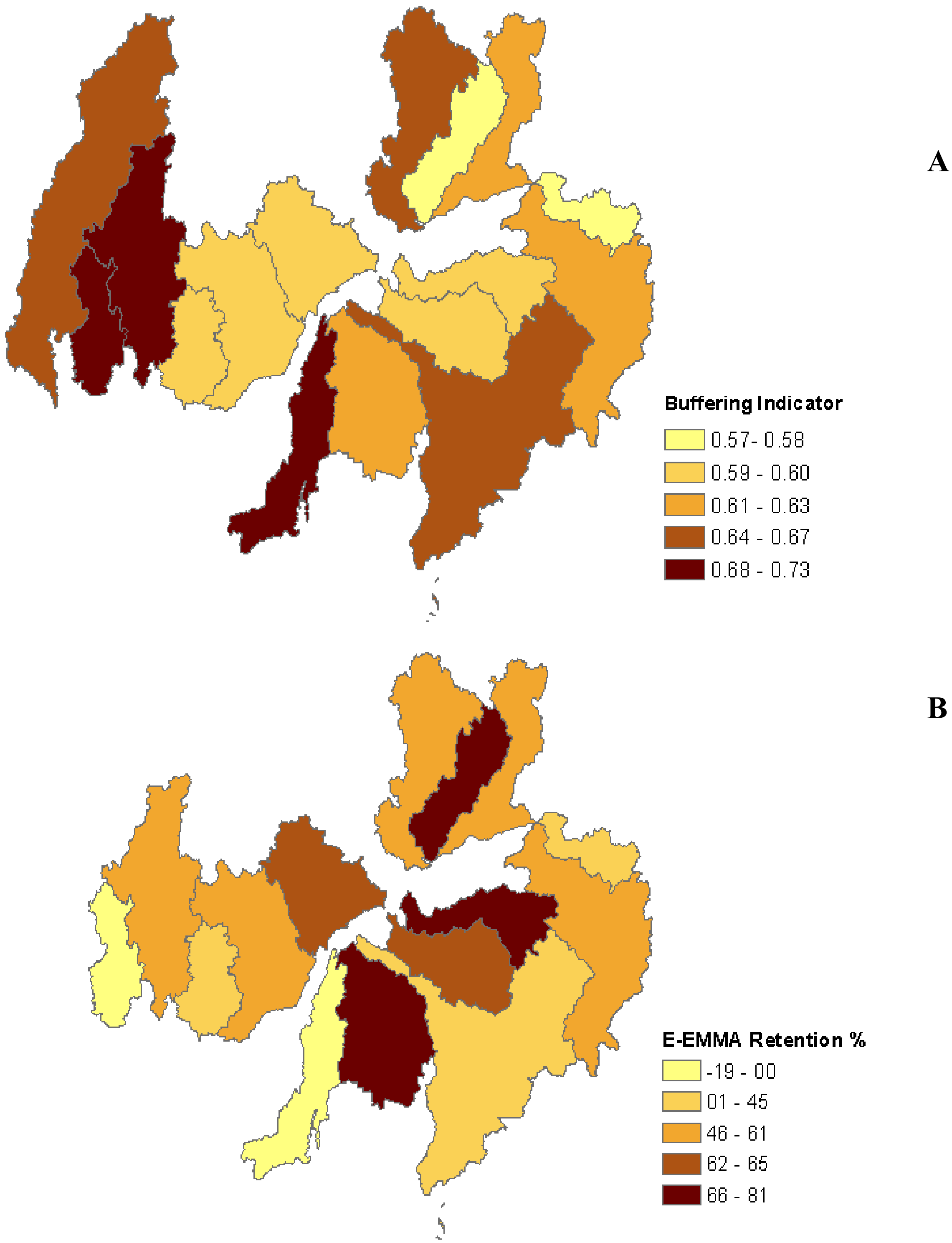

Figure 6: Maps of average buffering values in study watersheds. Average P buffering capacity estimates for each of the study watersheds using the (A) Buffering Index and (B) E-EMMA methodology.

Trends in watershed characteristics

The sixteen watersheds showed a diverse range of geochemical, hydrological, landscape, and socio-ecological characteristics that might be used to explain differences in watershed buffering capacity (Tables 2, 3, 4, Figure 7).

Geochemically, this region is generally dominated by acidic, sandy soils and these two soil qualities are positively correlated in the watersheds (r=0.62). Highest clay content in the region was 41% in Richelieu. Soil test P values were highest in historically agricultural watersheds and were positively correlated with percent agricultural land cover (r=0.72). The highest average soil test P value was 204 kg/ha in Yamaska.

The watersheds also ranged in their hydrological landscape features. Watershed percent slope values are relatively low in this region, mostly under 20 percent. Watersheds with relatively low mean percent slope were positively correlated with low values of water yield (r=0.65). Baseflow index, an indication of the relative contribution of groundwater to the water flow within the watershed, also ranged significantly across the study sites (range from .59 and .99); watersheds with high baseflow values were generally less steep and had lower water yield.

There was high degree of co-linearity among watershed landscape composition and configuration variables due to common trends of development and landuse in QC. All of the watersheds consist mostly of agriculture and forested land cover. However, only two of the watersheds are majority agricultural land cover, the Richelieu (68 %) and the Yamaska (55%). Most of the watersheds had relatively small amounts of developed (built-up) land (10 percent or less). This developed land was strongly positively correlated with population density (r=0.66). Tile-drained agricultural land is quite common in the Quebec landscape; in about half of the watersheds, we estimated that upwards of 80 percent of agricultural croplands contain artificial drainage (with a range of 0 and 35 percent of total watershed area).

Role of watershed characteristics in explaining buffering index and E-EMMA

There was no correlation between the two buffering metrics calculated for the watersheds suggesting that these two metrics measure different buffering phenomena (r=-0.03). However, each of the buffering indicators correlate with various watershed characteristics, such as soil type, baseflow index and landuse configuration metrics. This suggests that geochemistry, hydrology and landscape features may, indeed, play a role in determining the overall buffering capacity of watersheds (Tables 3 and 4).

For geochemical characteristics, we observed a negative correlation between E-EMMA P retention values with percent clay values (r=-0.26) which suggests that heavier, more poorly drained soils may result in faster overland flow and increased P runoff (Wilcock, 1997). Percent clay values also correlated strongly with watershed soil P values, which confirms that clay soils may contain higher levels of historically accumulated P (Ballard and Fiskell, 1974).

Both the buffering index and the E-EMMA retention values were most strongly correlated with hydrological variables, which indicates that watershed hydrology may be one of the most powerful buffering agents within watersheds. Both E-EMMA and the BI were negatively correlated with mean percent slope values (r=-0.35 and r=-0.28) and water yield values (r=-0.38 and r=-0.27), which suggests that watersheds with steeper topography and more river flow may have an overall lower buffering capacity. Both E-EMMA and the BI values correlated positively with baseflow index values (r=0.36 and r=0.48). This finding suggests that watersheds with relatively less overland flow have greater buffering capacities. The BI values were also positively correlated with watershed size suggesting that larger watersheds may buffer more anthropogenic P than smaller watersheds (r=0.23).

Landscape composition and configuration variables were also correlated with buffering indicators. Counterintuitively, E-EMMA retention values were positively correlated with percent agricultural cover (r=0.33). This finding potentially indicates the fact the mass mobilization of P on agricultural land also acts as a process of P uptake and retention in the landscape. E-EMMA retention values were also negatively correlated with percent developed land (r=-0.24) which could be due to increased levels of sewage effluent being exported from urban spaces. In contrast, the BI was positively correlated with percent wetland cover (r=0.17), which is expected because wetlands are well established as sources of P retention on the landscape (Qiu and Turner, 2015). For configuration variables, we found E-EMMA retention values to be positively correlated with agricultural edge density (ED) (r=0.17), which perhaps signifies that dispersed agricultural land can increase the landscapes ability to retain mobilized P. The BI indicator was negatively correlated with agricultural cohesion (r=-0.28), which indicates that well connected agricultural land may undermine buffering capacity. Both the E-EMMA and BI values were weakly negatively correlated with the Forest Probability of Adjacency (PLADJ) indicator (r=-0.24 and r=-0.18), which suggests that landscapes with higher levels of forest connectivity have greater abilities to buffer P pressure.

The buffering indicators also had some correlations with socio-ecological landscape characteristics. The buffering index values were weakly negatively correlated with population density (r=-0.16), which is probably due to the increased levels of sewage effluent associated with higher population densities. One interesting positive correlation was between the BI values and "market capital", which is a measure of the relative wealth of farms on the landscape (r=0.41).

This correlation suggests that landscapes containing farmers with more assets and capabilities can potentially increase the ability of farms on the landscape to collectively “buffer” P; this could be due to an increased ability to afford infrastructure such as manure pits and fencing, or an increased ability to opt for potentially expensive management options such as riparian buffer strips. Higher levels of capital could also allow farmers greater access to agronomic expertise and planning. E-EMMA values were positively correlated with average field size values, which may also be an indication of wealthier farms with greater abilities to invest in “best management practices” (r=0.32). E-EMMA retention values were positively correlated with percent tile-drained agricultural land in the watersheds (r=0.43). The BI values were, however, negatively correlated with percent agricultural tile-drainage (r=-0.26). Most of the correlations between buffering capacity and watershed characteristics in this study are relatively poor (r <.30); this is presumably due to the fact that buffering capacity is a complex mixture of a number of watershed variables.

Many watershed characteristics correlated with TP riverine flux, such as the geochemical variable pH (r=-0.37), the hydrological variable baseflow index (r=-0.52), the landscape variable percent agriculture (r=0.35), and the socio-ecological variable percent tile drainage (r=0.35). We also found a TP riverine flux was highly correlated with levels of historic P accumulation. We found that the best predictor of riverine TP flux was a model accounting for both P accumulation and baseflow index (Table 5). This signifies that while both knowledge of legacy P and watershed characteristics can be used to understand water quality parameters, when looked at together, they tell a much more comprehensive story.

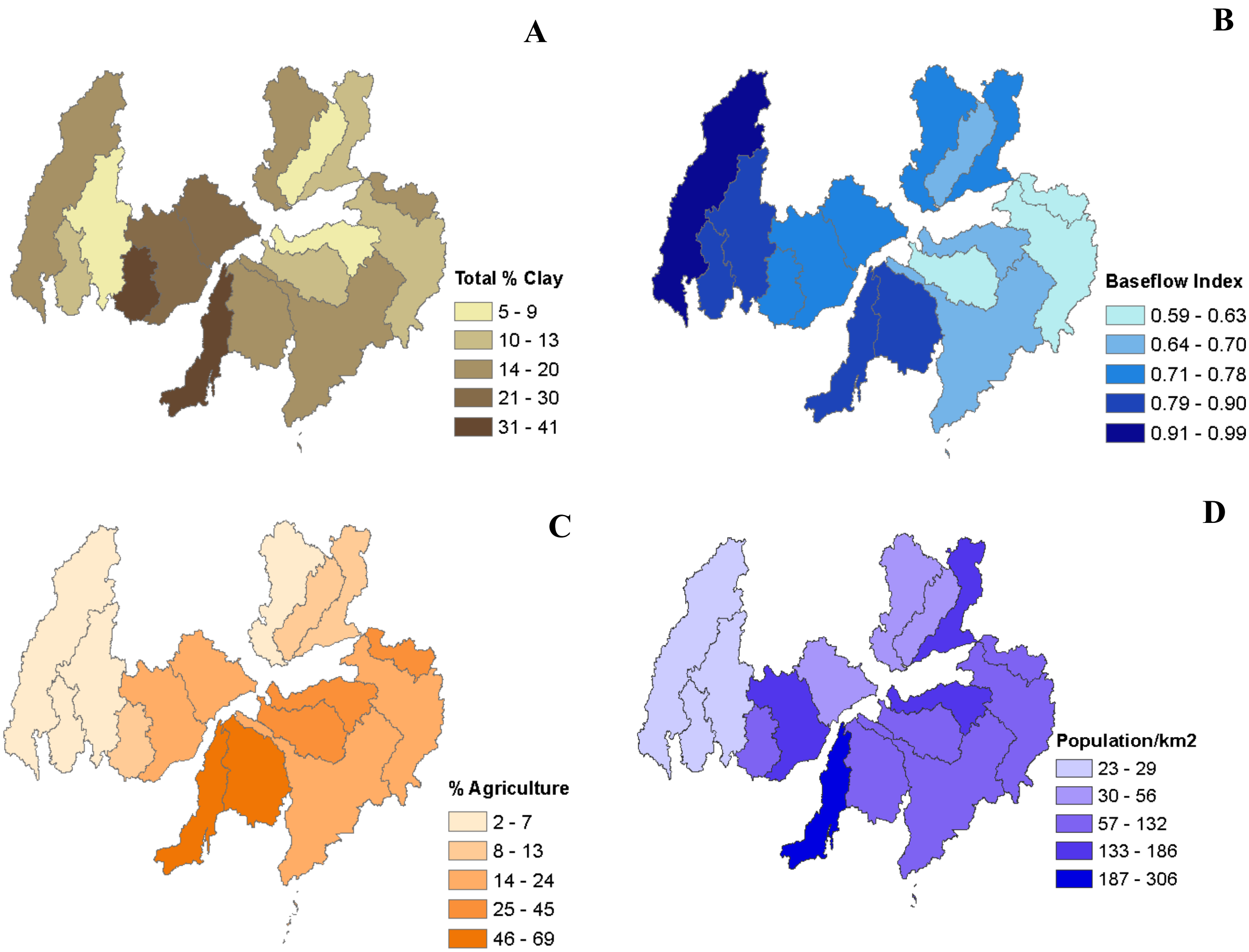

Figure 7: Maps of selected geochemical, hydrological, landscape, and socio-ecological characteristics for each of the 16 study watersheds. (A) Total percent clay (B) Baseflow Index (C) Percent Agricultural Landuse (D) Population Density.

Discussion

P accumulation and flux

Our results show that, across the study region, watersheds with more historic P pressure experience greater levels of riverine P flux. At the same time, almost all of the study watersheds individually experienced decreasing rates of riverine P flux over the study period despite continued P accumulation. Reductions in riverine P flux despite continued landscape P pressure could be due to either improvements in watershed P management in the form of better nutrient management regulation or upgraded sewage treatment infrastructure (Mailhot et al., 2002; van Bochove et al., 2012). The fact that riverine P flux decreased despite continued watershed P accumulation indicates a potential delay between large scale terrestrial P accumulation and water quality impairment that can last decades (Carpenter, 2005).

This delay between P accumulation and riverine flux is both a risk and an opportunity for watershed P management. It is a risk because long time lags between pressure and impact reduce our ability to perceive the threat of the pressure and makes our system prone to ecological surprises (Gordon et al., 2008). In systems with significant delays, like this one, measures of the ultimate impact can be a misleading indicator of the state of the system. An ecosystem assessment that only considers water quality indicators may conclude that the vulnerability of the waters is decreasing; however, steady increases in pressure indicators show that, in fact, the opposite is true. Increasing the delay between pressure and impact is also an opportunity because retaining watershed P in agricultural soils opens up the prospect for remediation strategies and the drawdown of P saturated soils (Penn et al., 2014; Rowe et al., 2016).

Besides terrestrial P retention, there are other potential explanations of why water quality improvements were recorded despite continued upstream P pressure. One key reason for water quality improvements among the watersheds is the fact that although total P accumulation continued to increase over these years, annual fertilizer and manure input levels decreased during this time. That is, while accumulation continued, the rate of accumulation decreased. In their study of historic nutrient trends in the Saint Lawrence Basin over the 20th C, MacDonald and Bennett (2009) found that annual P surpluses on croplands decreased by almost half between the years 1981 and 2001, which is a trend also observed in some of the watersheds in this study.

The relative decrease of annual P inputs into the watersheds at this time and resulting reductions in riverine P flux were likely due to changes in Quebec nutrient management legislation as well as a general trend of increased nutrient use efficiency in agriculture at this time (van Bochove et al., 2012). Starting in the mid-1980s, QC began passing legislation measures specifically targeting nutrient pollution from agricultural land. In 1981, the provincial government passed the "*Regulation respecting the prevention of water pollution from livestock operations (RPPEEPA)*" which mandated greater protection of manure storage facilities. In 1997, QC passed a law called the "*Reduction of Pollution from Agricultural Sources*" which was updated in 2002 and renamed "*Regulations on Agricultural Exploitations*" (Q.c.Q-2,r.18.2). This law's most notable elements included: mandatory nutrient management plans on all farms, strictly limiting surplus P inputs into saturated soils; infrastructure for the storage of manure to prevent on-site leaching; as well as strict record-keeping of manure on farms to ensure its safe and legal disposal or reintegration to agricultural land (Montpetit and Coleman, 1999; Boutin, 2005). During these years, QC also promoted programs designed to increase the environmental awareness of producers, such as education initiatives, technology transfer activities, and the formation of 'agri-environmental advisory clubs' (Boutin, 2005). The years between 1980 and 2010 also saw general trends of greater P use efficiency on farms in North America and Europe due to improved agricultural technology and practices, such as the widespread use of the animal feed additive phytase, an enzyme that breaks down otherwise insoluble phosphorus compounds in animal feed and allows animals to grow with less P in their feed (Withers et al., 2001; Dobermann and Cassman, 2002; van Bochove et al., 2012).

Another key explanation for the increases in water quality over the time period was an increase in wastewater treatment infrastructure in QC. In 1978, the QC provincial government started a clean water program called the *Programme d'assainissement des eaux du Québec* (PAEQ) which focused primarily on municipal wastewater processing and treatment. This program resulted in the construction of many wastewater treatment plants (WWTP) in the province in the 1980s and 1990s and is estimated to have a dramatic impact on Quebec water quality (Painchaud, 1997). In one of the study watersheds, Chaudiere, 35 WWTP were constructed between 1985 and 1999. During this time, the number of people connected to the wastewater treatment network in Chaudiere increased by over 500% in response to the new legislation, and these changes are estimated to have removed up to 40% of riverine P flux in the watershed (Mailhot et al., 2002).

The reduction in riverine P flux in the 1980s and 90s following QC wastewater treatment improvements and decreased fertilizer inputs shows that riverine P fluxes are very responsive in the short-term to reductions in effluent controls and cropland inputs. Legacy P in agricultural soils, however, poses a long-term risk to water bodies as the slow flux of P from agricultural soils is one of the main drivers of eutrophication in historically agricultural landscapes. The more nutrients accumulated in cultivated soils, the more vulnerable our waters are to eventual pollution (Carpenter, 2005; van Bochove et al., 2007). Mitigating the risk of the passage of accumulated terrestrial P into surface waters through land-based mitigation methods such as nutrient management policies are a relatively long-term control option due to geochemical, hydrological and landscape buffering processes which create a delay between control actions and water quality results (Meals et al., 2010).

Exploring buffering capacity

The buffering capacity of watersheds- the process by which landscapes retain P for varying amounts of time – is one of the major mechanisms which drives the delay between P pressure and water quality impacts. This buffering capacity can lead to temporal disconnections between cause (P accumulation) and effect (water quality reductions). However, results from this study show that buffering capacity can be defined and measured in many different ways and is difficult to quantify due to the complexity of the mechanisms driving P retention at the watershed scale.

The two buffering capacity metrics used in this study examine two different mechanisms of terrestrial P retention, and the relationships of the indices to landscape characteristics give us a particular insight into the merits of each approach. Results from this study confirm that the BI metric is more focused on describing a watershed's ability to retain long-term legacy P; whereas the E-EMMA value is focused on describing the short-term ability of a landscape to trap or retain P molecules that are cycling within the terrestrial and aquatic watershed ecosystems as water moves through the landscape. Because the BI method captures a century-long process of P accumulation and retention, its values are potentially valuable predictors of the delay between terrestrial P accumulation and water quality degradation, discussed earlier. E-EMMA, on the other hand, may be a better indicator of inter-annual variation.

This difference is exemplified by the differences in the landscape characteristics that correlate with the buffering indicators. For example, the buffering index is positively correlated with high percent clay soils because clay soils have a greater total P adsorption capacity; whereas E-EMMA retention values are negatively correlated with high percent clay soils. Due to its propensity to bind tightly to P molecules, on the long term, watersheds with high clay content will retain larger volumes of P inputs (Ballard and Fiskell, 1974). However, due to its relative impenetrability, high clay soils may see higher levels of overland runoff on the short term (Wilcock, 1997). In the long-term, high clay content may increase the watershed P retention, but on the short term, it may increase risks for non-point P pollution.

Another finding that exemplifies the difference between the BI and the E-EMMA buffering method is their diverging relationship to the presence of artificial drainage on agricultural land. The buffering index is negatively correlated with agricultural tile drainage, and this is likely due to the fact that, in watersheds, tile drainage potentially increases the discharge of water into receiving waters by up to 25 percent (Tomer et al., 2005). The presence of tile drainage pathways can potentially increase P transport into receiving water bodies in soils with low P sorption capacity (Gburek and Sharpley, 1998). The presence of drain pipes allows P to bypass soil infiltration and retention processes and pass directly into water systems, which undermines long-term soil P retention (Gentry et al., 2007; Smith et al., 2015). However, the E-EMMA retention values were positively correlated with percent tile-drained agricultural land in the watersheds, and this is likely due to the fact that during a high flow event, drain pipes redirect water that would otherwise contribute to surface runoff into below-ground channels. This potentially increases retention as there are more opportunities for P absorption and retention in drain-flows than there are in surface runoff (Haygarth et al., 1998; Withers et al., 2009). The E-EMMA finding highlights the potential for artificial drainage systems to trap P as water moves it through the landscape; whereas the buffering index captures a longer-term impact of artificial drainage on the retentive capacity of the landscape.

The fact that the two indicators had, in general, the same relationships with hydrological variables such as water yield, baseflow index, and mean percent slope, shows that innate hydrological factors may be the most powerful drivers of both short and long term P retention processes. The story is less clear for land use / land cover, both in terms of composition and configuration. Early findings show that that characteristics such as landscape connectivity and heterogeneity do matter, but high degrees of co-linearity among composition and configuration metrics make it difficult to identify the most powerful indicators of P retention among these variables. However, since land use/land cover is easy to adjust (relative to mean percent slope, say), a more in depth study on land use/ land cover impacts on watershed P retention would be worthwhile. Knowledge about these landscape features which mediate the relationship between P pressure and resulting water quality degradation can also help us to manage our expectations concerning the state of our systems and know when to expect delays between mitigation actions and results (Meals et al., 2010; Sharpley et al., 2013).

Transport of P across the agricultural landscape is a result of both the degree and nature of legacy P stores as well as the watershed characteristics that impact the transport of P across the landscape. We find in this study that the most comprehensive picture of landscape vulnerability comes when we look at both legacy P indicators as well as the biophysical characteristics, such as the baseflow index, that mediate the release and transport of legacy P.

Buffering capacity insights for watershed management

New insights into release and transport processes of legacy P within watersheds, as well as a greater knowledge of the landscape characteristics that determine a watershed's specific buffering capacity, can increase the effectiveness of landscape management both on a local and a regional scale. Locally, this information can provide specific ways in which land managers can increase a watershed's resilience to P pressure and decrease the vulnerability of water systems. Regionally, this information be used to identify which watersheds are more or less vulnerable to increased P pressure arising from agricultural development or urbanization.

Within watersheds, land managers can use knowledge about the factors that impact buffering capacity to promote either practices that may increase P retention on the landscape (in order to protect water bodies) or practices that may decrease P retention on the landscape and expedite the transport of P (in order to prevent P accumulation in soils). Land managers can prioritize characteristics that are potentially adjustable by humans (such as forest connectivity, landscape configuration, and tile drainage) to achieve landscape goals.

At the inter-watershed scale, watersheds' varying buffering capacities can be used to make suggestions about which watersheds can cope with more intensive agriculture sustainably (at least in terms of P), and which may be particularly vulnerable to increased P pressure. For example, a watershed that has been determined as having a low buffering capacity is relatively worse at retaining P inputs, and increased agricultural development will have a proportionally higher level of impact on water quality. Therefore, if protecting water bodies is the goal of landscape managers, areas of low buffering capacity are best left uncultivated; whereas watersheds with high buffering capacity may be better suited for agricultural development.

Conclusion

This study explores the complex, and often counterintuitive, relationship between soil P accumulation and water quality indicators. We find that the capacity for a watershed to retain P for long periods can result in significant delays between initial accumulation and riverine P flux. This can result in a simultaneous increase in water quality indicators even as waters become more vulnerable to long-term degradation. This delay represents both a long-term risk to water systems due to inevitable P transport as well as a potential opportunity for soil P utilization and drawdown.

This study also proposes that multiple methods and measurements are needed to understand a watershed's buffering capacity and vulnerability to P pressure. Buffering capacity is a product diverse variables which interact at various scales. Different methods of measuring this watershed property help to reveal the exact nature of P retention and movement on the landscape at different time scales and under different conditions. This study shows that with multiple indicators, it may be possible to separately predict a watershed's long- and short- term vulnerability to P inputs which is a process mediated by a diverse picture of watershed characteristics.

Table 1: Sources of spatial data

Component of Buffering capacity	Indicator of P buffering capacity and unit	Spatial Resolution	Temporal Resolution	Data Source
Geochemical	Percent clay	~ 1 km	Single value (~2001)	Soil landscapes of Canada
	pH (measured in calcium chloride)	~ 1 km	Single value (~2001)	Soil landscapes of Canada
	Soil P levels (kg/ha)	QC Municipalities	Single value (~2001)	MAPAQ
Hydrological	Watershed size (km^2)	15 sec	Single value	HydroSHEDS, HydroBASINS with lakes - level 7
	Percent slope	3 sec	Single value	HydroSHEDS, void-filled elevation
	Water yield (m^3/km^2/year)	NA	Daily values (1979-2011)	CEHQ
	Baseflow index	NA	Annual values (1979-2011)	CEHQ
	Sinuosity ratio	15 sec	Single value	HydroSHEDS, river network
Landscape and socio-ecological	Vegetative cover (NDVI)	~30 m	Annual values (1985-2011)	Landsat remote sensing
	% Land use classes	-30 m	Single value (~2010)	MDDELCC
	Landscape configuration metrics	-30 m	Single value (~2010)	MDDELCC
	Population density	QC Municipalities	Bi-decadal census years (1981-2011)	Quebec population census
	Average field size (km^2)	~.5 m	Single value (~2008)	La Financiere agricole Quebec
	Average market capital ($/farm)	QC Municipalities	Bi-decadal census years (1981-2011)	Quebec agricultural census
	% Agricultural tile drainage	~1 km	Single value ~2011	Soil landscapes of Canada La Financiere agricole Quebec
P flux	NAPI	QC Municipalities	Decadal and bi-decadal census years (1981-2011)	Goyette et al. (2016)
	Riverine P flux	NA	~Monthly values (1979-2011) ~Daily values (1979-2011)	MDDEFP-BQMA (concentration) CEHQ (flow)

Table 2: Indicators of P buffering capacity and geochemical, hydrological, landscape, and socio-ecological characteristics in the 16 study watersheds.

	Geochemical Indicators				Hydrological Indicators				Landscape and Socio-ecological Indicators						P flux		
Watershed	Soil test P (kg/ha)	% clay	pH	Mean % slope	Mean H_2O yield ($m^3/km^2/sec$)	Baseflow index	Sinuosity index	Basin area (ha)	% Agriculture	% Forest	% Wetlands	% agriculture tile-drained	Population density (pop/ha)	Average NAPI (kg/ha/yr)	Average TP riverine flux (kg/ha/yr)	Buffering index	E-EMMA % P retention
Richelieu	160.57	41.01	5.86	6.08	.018	0.901	0.791	3568.09	68.16	16.27	3.74	91.79	306.13	692.11	19.14	0.725	-19.44
Rouge	76.76	4.74	5.55	10.70	.020	0.799	0.828	5610.44	2.19	80.92	8.93	0	25.95	102.23	18.35	0.691	59.04
Petite Nation	102.42	10.95	5.40	10.08	.017	0.85	0.840	2240.17	7.36	75.58	7.16	16.46	23.40	65.52	16.38	0.681	-11.33
Lievre	80.34	15.90	5.40	9.41	.026	0.995	0.834	9564.14	2.82	79.64	8.51	0.56	29.41	62.62	19.27	0.665	NA
Yamaska	204.11	20.69	5.37	5.04	.012	0.853	0.824	4944.05	55.09	33.83	5.54	85.93	122.57	1828.83	75.91	0.623	78.43
Batiscan	69.26	16.50	5.23	11.55	.021	0.783	0.813	4732.56	5.83	77.91	6.82	48.23	52.25	126.37	25.34	0.643	60.78
St. Francois	123.51	15.94	4.98	6.30	.025	0.691	0.859	10426.3	21.6	60.85	13.5	32.32	103.71	410.78	40.19	0.645	43.84
Chaudiere	121.35	13.29	4.83	5.56	.020	0.612	0.850	6604.29	22.01	64.13	9.25	23.64	96.43	553.37	46.13	0.628	60.60
Jacque-Cartier	155.48	10.92	5.08	18.08	.031	0.738	0.848	3362.49	10.72	70.64	4.69	29.3	186.59	112.46	29.80	0.618	62.02
Nord	119.89	38.58	5.55	8.46	.022	0.727	0.823	2284.68	13.35	67.94	7.9	91.08	119.27	102.23	39.62	0.603	44.46
Loup	156.61	30.65	5.49	9.79	.018	0.744	0.826	4002.81	24.02	63.36	4.89	83.74	56.80	368.39	43.54	0.590	63.93
L'assomption	178.60	25.28	5.70	11.63	.019	0.737	0.815	5114.49	22.69	60.57	4.04	84.91	161.00	586.29	54.74	0.598	61.65
Nicolet	136.78	10.13	5.13	9.51	.022	0.585	0.827	3377.9	45.08	44.33	4.22	89.27	117.09	733.89	75.14	0.598	65.30
Becancour	126.52	8.54	5.10	9.05	.022	0.665	0.816	2698.66	33.01	52.16	7.22	89.27	154.25	576.29	71.53	0.596	80.52
Ste. Anne	91.87	7.87	5.09	12.69	.032	0.704	0.851	2759.37	10.23	75.84	4.43	59.68	51.23	155.28	57.31	0.575	76.81
Etchemin	161.45	15.14	4.81	20.87	.031	0.633	0.819	1547.08	30.69	55.54	6.27	25.13	132.38	771.51	84.74	0.598	34.13

Table 3: Correlation between P flux variables and geochemical, hydrological, and socio-ecological watershed characteristics

	Buffer index	E-EMMA	TP Flux	% Clay	pH	Soil P	% Slope	H2O yield	Baseflow index	sinuosity	Watershed size	NDVI	NDVI 100m	Pop density	Field size	Market capital	% tile drained
Buffer index	1																
E-EMMA	-0.03	1															
TP Flux	-0.80	0.10	1														
% Clay	0.10	-0.26	-0.12	1													
pH	0.35	0.18	-0.37	0.62	1												
Soil P	-0.20	0.13	0.42	0.42	0.11	1											
% Slope	-0.28	-0.35	0.15	-0.31	-0.33	0.00	1										
H2O yield	-0.27	-0.38	0.13	-0.35	-0.51	-0.27	0.65	1									
Baseflow index	0.48	0.36	-0.52	0.25	0.59	-0.13	-0.21	-0.34	1								
Sinuosity	-0.15	-0.09	-0.05	-0.55	-0.58	-0.27	0.04	0.37	-0.23	1							
Watershed size	0.23	-0.13	-0.24	-0.10	-0.05	-0.23	-0.44	-0.06	0.26	0.39	1						
NDVI	0.03	-0.08	-0.20	-0.18	0.07	-0.38	-0.06	-0.06	0.11	0.23	0.11	1					
NDVI 100m	-0.04	0.00	-0.07	-0.15	-0.02	-0.18	-0.09	-0.07	-0.01	0.23	0.04	0.94	1				
Pop density	-0.17	0.02	0.25	0.40	0.17	0.51	-0.02	-0.08	-0.01	-0.40	-0.19	-0.43	-0.28	1			
Field size	0.05	0.32	0.06	0.60	0.57	0.26	-0.43	-0.42	0.24	-0.57	-0.09	-0.15	-0.06	0.21	1		
Market capital	0.41	0.01	-0.13	0.25	0.19	0.26	-0.12	-0.04	-0.06	-0.24	-0.06	-0.14	-0.07	-0.17	0.26	1	
% tile drained	-0.26	0.43	0.35	0.57	0.34	0.55	-0.30	-0.33	-0.19	-0.52	-0.41	-0.25	-0.09	0.42	0.74	0.26	1

*shaded boxes indicate r-values >0.30 or <-0.30

Table 4: Correlation between P flux variables and landscape composition and configuration characteristics

	Buffer index	E-EMMA	TP flux	% Ag	% Forest	% Devel oped	% Ag 100m	% Forest 100m	% devel oped 100m	% wetland	ED Ag	ED Devel oped	Cohesion Ag	Cohesion Developed	PD Forest	PD wetland	PLADJ forest	Contag
Buffer index	1																	
E-EMMA	-0.03	1																
TP Flux	-0.80	0.10	1															
% Ag	0.04	0.33	0.35	1														
% Forest	-0.09	-0.29	-0.30	-0.99	1													
% Developed	0.03	-0.24	0.09	0.57	-0.64	1												
% Ag 100m	0.03	0.35	0.34	0.99	-0.98	0.57	1											
% Forest 100m	-0.05	-0.19	-0.33	-0.98	0.99	-0.69	-0.98	1										
% Developed 100m	0.01	-0.37	0.04	0.35	-0.42	0.93	0.34	-0.51	1									
% Wetlands	0.17	-0.43	-0.19	-0.39	0.36	-0.29	-0.45	0.32	-0.06	1								
ED Ag	-0.14	0.17	0.53	0.87	-0.84	0.41	0.83	-0.85	0.27	-0.11	1							
ED Developed	-0.07	-0.21	0.16	0.53	-0.58	0.95	0.53	-0.66	0.95	-0.20	0.43	1						
Cohesion Ag	-0.29	0.04	0.41	0.58	-0.58	0.51	0.58	-0.59	0.37	-0.34	0.58	0.49	1					
Cohesion Developed	-0.16	-0.10	0.30	0.57	-0.60	0.73	0.53	-0.62	0.64	-0.15	0.58	0.75	0.47	1				
PD Forest	-0.12	0.07	0.43	0.87	-0.88	0.71	0.84	-0.90	0.61	-0.18	0.90	0.75	0.65	0.75	1			
PD Wetland	0.20	-0.21	-0.52	-0.76	0.75	-0.42	-0.73	0.73	-0.21	0.26	-0.84	-0.34	-0.71	-0.57	-0.71	1		
PLADJ Forest	-0.18	-0.24	-0.21	-0.93	0.95	-0.64	-0.91	0.95	-0.50	0.20	-0.80	-0.62	-0.48	-0.56	-0.87	0.61	1	
Contagion	0.20	0.14	-0.40	-0.63	0.64	-0.70	-0.61	0.69	-0.65	0.11	-0.74	-0.77	-0.53	-0.65	-0.88	0.51	0.63	1

*shaded boxes indicate r-values >0.30 or <-0.30

Table 5: Biophysical predictors of TP flux

Regression	**R^2 value**
Log TP flux ~ P accumulation	0.382
Log TP flux ~ Baseflow Index	0.359
Log TP flux ~ P accumulation + Baseflow Index	0.685

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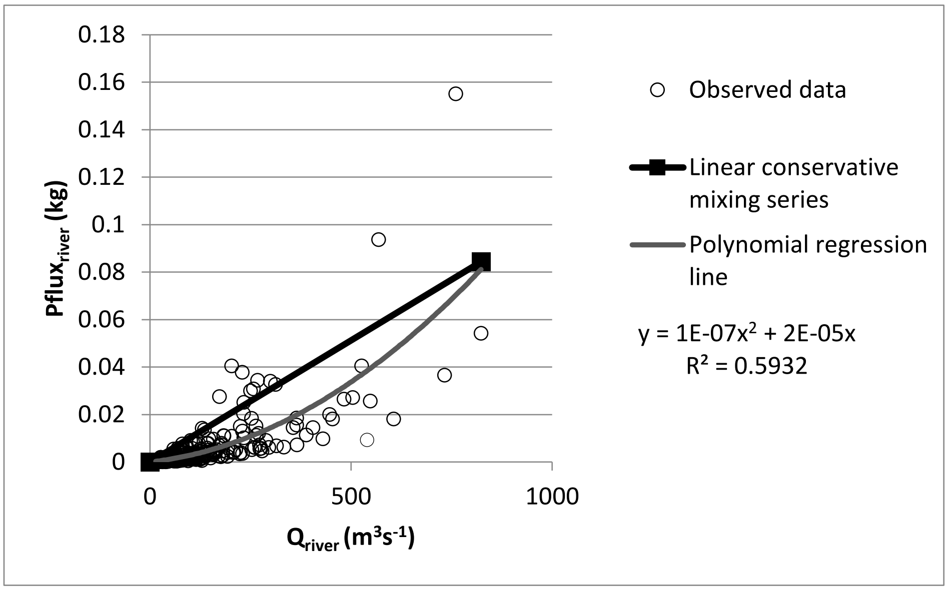
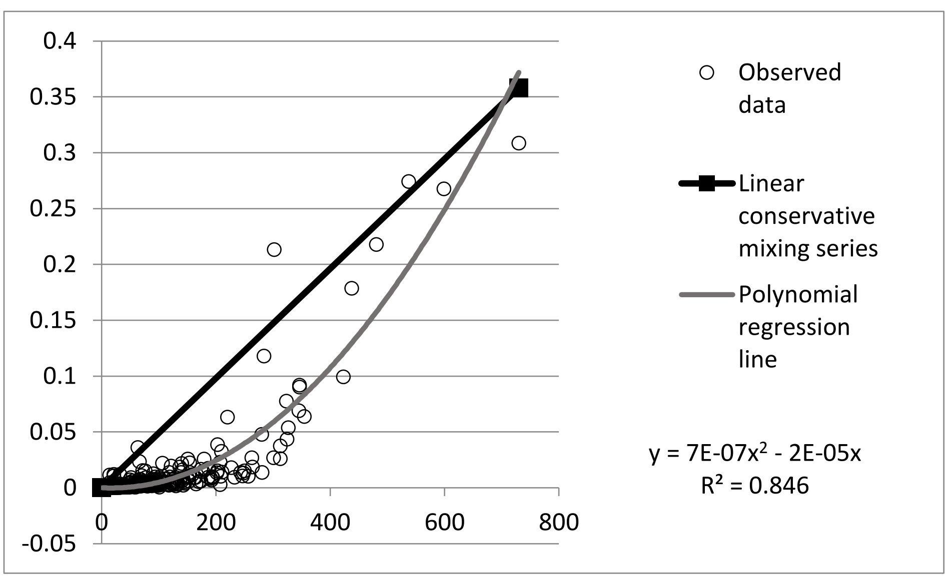
Supplementary Information

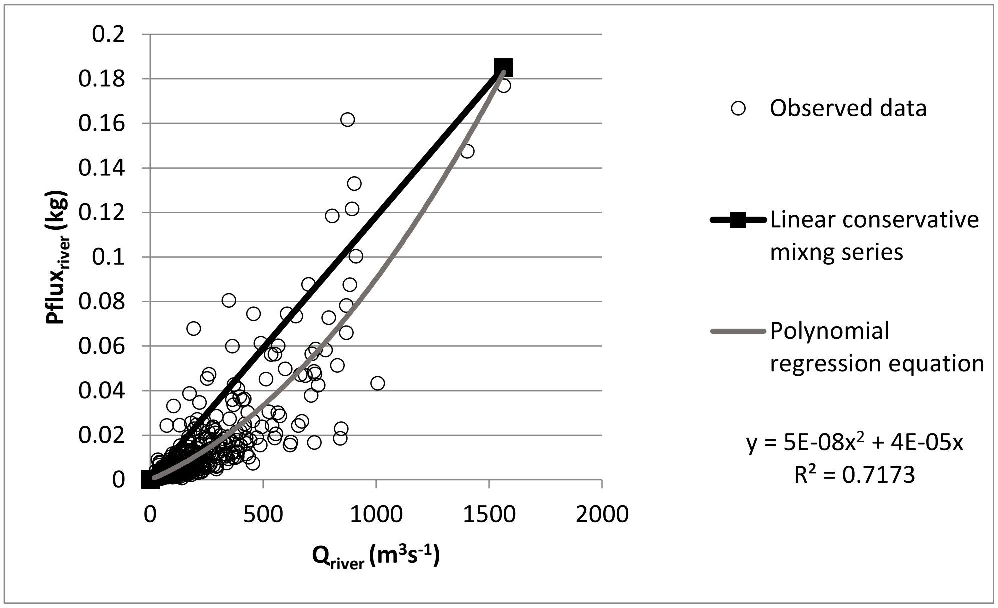
Figure S1. E-EMMA results: Sample plots of P flux ($Pflux_{river}$) and river flow (Q_{river}) for four of the study watersheds between the years 1979 and 2014. These graphs include the corresponding polynomial regression lines representing the relationship between these two factors as well as the corresponding linear conservative mixing series between baseflow and stormwater end-member fluxes.



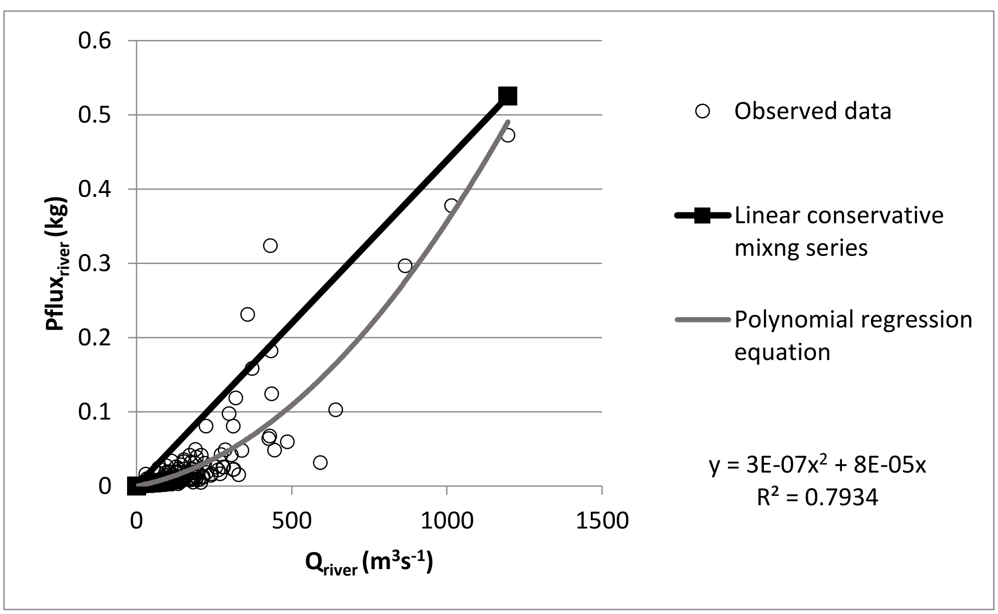
A. Batiscan 1979-2014; estimated P retention 61 percent



B. Becancour 1979-2014; estimated P retention 81 percent



C. Saint-Francois 1979-2014; estimated P retention 44 percent



D. Nicolet 1979-2014; estimated P retention 65 percent

Synthesis, Future Directions, and Contributions to Knowledge

Synthesis

The aim of this thesis was to explore the relationship between legacy P accumulation in agricultural watersheds, water quality, and watershed characteristics that impact the retention and transport of P. In Chapter 1, I reviewed the literature relevant to human-induced changes to P cycling and the research presented in Chapter 2. First, I discussed the global issue of global P pollution in fresh water and coastal ecosystems, covering both the causes and the impacts (Rabalais et al., 2009; Elser and Bennett, 2011). This chapter included a review of the ways in which humans have altered the global P cycle, and the implications of these alterations for the vulnerability of global water systems (Smil, 2000). Next, I considered the literature surrounding P modeling on the watershed scale and how certain models work to quantify long term soil P accumulation in historically agricultural watersheds (Russell et al., 2008; Goyette et al., 2016). This section discusses the issue of legacy P in watersheds and the phenomenon of long-term P retention (Jarvie et al., 2013; Sharpley et al., 2013) and then presents the idea of buffering capacity in watersheds, in which certain watersheds retain historic P longer than others; I explore the literature to determine which watershed characteristics (be they geochemical, hydrological, landscape, or socio-ecological) other studies have associated with the transport of P from agricultural soils to surface waters (Burt, 2001; Doody et al., 2016). I then discuss watershed management to integrate the idea of buffering capacity with a greater understanding of holistic watershed management that brings together multiple goals for long-term watershed sustainability (Flotemersch et al., 2015; Doody et al., 2016).

In Chapter 2, I expanded on these themes by conducting an analysis of 16 agricultural watersheds in Quebec, Canada. In this study, I examined the relationship between long-term P accumulation and thirty years of water quality to determine what watershed characteristics impact the relationship between legacy P and water quality and determine the relative vulnerability of watersheds to long-term P pressure. Two methods were used to investigate the capacity of each watershed to retain P inputs, the buffering index (BI), novel to this study, as well as the Extended End-Member Mixing Analysis (E-EMMA) (Jarvie et al., 2011). The BI measurement was used to determine watersheds' long-term ability to retain P in watershed ecosystems; whereas the E-EMMA calculation was used to determine watersheds' short-term ability to trap P as it was moving through the landscape with flowing water. The results from these two methods gave us a unique look at the long- and short- term dynamics of P retention.

My findings showed that, counterintuitively, riverine P flux values can decrease even as watersheds continue to accumulate terrestrial P stores. Even as watersheds had consistently positive P budgets, water quality indicators increased in many of the watersheds throughout the study period. I contend that this is partly due to specific improvements to P management in QC during this time period that resulted in dramatic short-term improvements in P effluent and run-off (Montpetit and Coleman, 1999; Mailhot et al., 2002; Boutin, 2005; van Bochove et al., 2012). I believe that this is also due to the phenomenon of watershed buffering, which allows watersheds to retain P inputs for decades or centuries and can create a significant delay between initial P accumulation and water quality impacts (Powers et al., 2016). I conclude that this delay represents both a long-term risk to water systems due to eventual P transport as well as an opportunity for potential soil P utilization and drawdown (Rowe et al., 2016).

I also conclude that multiple methods are measurements are needed to get a complete picture of watershed vulnerability. A watershed's unique buffering capacity is a product of diverse landscape qualities and is a dynamic property through space and time. A watershed's long-term vulnerability to P loading to surface waters from legacy P accumulation may differ from its short-term vulnerability to the transport of P from flashy weather events. A greater knowledge of this dynamic watershed property can help land managers to make long- and short-term decisions that prevent unexpected and undesirable changes in fresh water and coastal ecosystems.

Future Directions

There is a great need to further explore the complex factors that determine the vulnerability of watersheds to P pressure and connect these factors to potential management strategies to protect rivers and waterways. Building on the concept of buffering capacity, one concept that could be further explored is that of thresholds and tipping points in watersheds' buffering capacity. That is, using long-term data, is it possible to find out whether or not there is a pressure point at which a watershed's buffering capacity precipitously diminishes and the relationship between P accumulation and riverine P flux changes in a watershed? This question assumes that a watershed's buffering capacity is dynamic through time and changes in watersheds as P pressure mounts. Answering this question could potentially aid in regional landscape management and give an even greater insight into watershed vulnerability to P pressure – how it is determined and how it changes through time. An exploration of this concept would also help to predict and prevent ecological surprises and their negative impacts (Gordon et al., 2008).

Another concept that is important to consider is how social systems and institutions impact the vulnerability and resilience of watersheds to long-term P pressure. For example, how do watershed organizations, local governance systems, farmer-support coalitions, and other community or government initiatives impact the dynamic of farm and landscape planning for watershed resilience to nutrient pressure? How do these different social networks work to potentially create information links and feedback loops between stakeholders and practitioners, and how can their presence affect innovation in farming systems or create mechanisms for the social learning needed for positive transformations in watershed management (Pahl-Wostl et al., 2007; Berthet et al., 2016). Features of human systems are some of the most powerful factors driving change and pressure in watersheds, and it would therefore be useful to understand how social factors integrate with physical factors to get a more comprehensive understanding of the complex socio-ecological system within a watershed.

While it is important to understand the nuanced ways in which people affect water systems, it is also important to understand how impacted water systems affect people. While this study increases our understanding of what makes a watershed vulnerable, we could use a greater understanding on how this watershed vulnerability is distributed among different human populations – that is, when we say that a watershed is 'vulnerable', which stakeholders are included in that vulnerability and to what degree? How is vulnerability spread out among the community? Answers to these questions would provide a richer understanding into the definition of watershed vulnerability, address the diversity of human populations within socio-ecological systems, as well as address potential environmental justice concerns within the system (Barnett et al., 2008; De Chazal et al., 2008). This increased understanding may provide new avenues for mitigation and improved management.

Contributions to Knowledge

While there is a rich literature on the processes of P retention and transport in watersheds, there are few studies that specifically examine the relationships between long-term P accumulation, landscape characteristics, and watershed vulnerability. This is mostly because long-term datasets are uncommon and resource-intensive to create. This thesis provides both a spatial and temporal perspective on the relationship between P accumulation and water quality, as well as a novel interpretation of watershed vulnerability to legacy P pressure. It provides a novel way to conceptualize and measure watershed buffering capacity through the “buffering index” which could potentially be used in other case studies.

Lastly, this thesis is a contribution to complex systems science, which aims to confront and analyse complex problems in the environment. This study contributes a step forward in understanding the resilience of watershed ecosystems to anthropogenic P pressure across multiple scales and including myriad factors. While studies that confront complex concepts, such as this one, rarely contribute unequivocal findings, they push forward a science which aims to embrace complexity in socio-ecological systems.

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