Phosphorus-sediment interactions and their implications for watershed scale phosphorus dynamics in the Le Sueur River Basin

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Abstract

Phosphorus is a leading pollutant of global surface waters, and sediment is a known driver of phosphorus loading to downstream receiving waters. This master's thesis investigates sources and dynamics of phosphorus in the Le Sueur River basin in southern Minnesota, a highly agricultural watershed whose glacial history has rendered it vulnerable to massive erosion, and which contributes disproportionately to downstream sediment and phosphorus loading. We develop a mass balance for sediment-derived phosphorus, incorporating sediment-total and dissolved phosphorus into a robust sediment budget describing sources and sinks of sediment to this system. This budget explores the extent to which agricultural top soil and upland ditch-banks, and eroding near channel features such as bluffs, stream banks, and ravines, can be implicated for phosphorus loading to this basin. Further, we explore the extent to which in-stream processing alters the fate, bioavailability, and persistence of phosphorus in this system via the incorporation of sorption experimental data into this budget. Our results show that fine (silt and clay sized) source sediment can only account for at most 24% of the total phosphorus exported from the Le Sueur River.

These results suggest that sediment and phosphorus sources are largely decoupled, and that if we managed 100% of fine sediment erosion we would only reduce phosphorus loading by 24% or less. Sorption tests were used to examine the role of fine sediment as a source or sink for phosphorus. Results of these tests demonstrate that agricultural sediments donate phosphorus, while near channel sediments bind phosphorus from the water column. Incorporation of these results into our budget indicates that 2-24% of total phosphorus may be in particulate form as a result of in-stream equilibrium processes between sediment and dissolved orthophosphate in the water column. Sorption of dissolved phosphorus by sediment may depress dissolved phosphorus load by as much as 31%. These results point to the importance of understanding dissolved phosphorus source and dynamics, and to the management of both sediment and dissolved phosphorus source being critical to addressing excess phosphorus in this basin.

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Introduction

Anthropogenic eutrophication (nutrient enrichment) is the leading cause of surface water impairment worldwide (Bennett, et al., 2001). Eutrophication has serious effects on aquatic ecosystems including disruption of natural biogeochemical cycling and significant loss of biodiversity (CENR, 2003). Sediment-bound phosphorus is a well-known driver of nutrient enrichment in freshwater ecosystems across the globe (Correll, 1998), and thus, erosion control is often assumed to be an effective strategy for control of phosphorus transport. However, while management strategies have been developed to control erosive loss of phosphorus to surface waters, results of these practices have been slow to manifest as water quality improvements. This is due in part to the accumulation of phosphorus near and within fluvial systems and its subsequent remobilization, which occurs on timescales of years to centuries (Sharpley et al., 2013). Furthermore, soils in many agricultural landscapes have become saturated with phosphorus, resulting in higher potential for runoff of dissolved-phosphorus over the land surface and through subsurface drainage (Liu et al., 2014; Minnesota Pollution Control Agency (MPCA) et al., 2014). Due to the vital role of phosphorus in crop productivity and the widespread deleterious effects of excess phosphorus on surface waters, it is essential that we understand the role of both sediment-bound and dissolved phosphorus sources in driving watershed scale phosphorus dynamics.

Excess phosphorus loading to surface waters is a widespread concern in the highly agricultural midwestern United States. In this setting, glacial history has created uniquely erosive channels, and changing agricultural practices have created an overlay of pressures on these systems. Carving through otherwise relatively planar landscapes, post-glacial channels often make substantial base-level adjustment as they approach deep receiving waters which were carved away by glaciers (Gran et al., 2009). The resulting incision can leave high banks of glacial sediment vulnerable to continuing erosion. In settings such as the Minnesota River Basin, the planar uplands are largely in agricultural land use, while the lower valley is deeply incised. This creates a setting where major inputs of phosphorus occur across the broad, flat uplands, and significant inputs of glacial sediment occur in the incised portion of the channel. Incised tributaries have little connected floodplain area, and as a result, there is little chance of deposition and processing of sediment and excess nutrients. Instead, export to downstream environments dominates. This introduction of sediment may itself serve as a source of phosphorus but is also important because equilibrium processes between sediment and dissolved phosphorus in the water column may influence phosphorus form (dissolved versus particulate) and subsequent bioavailability and retention in the environment.

Phosphorus form is highly important to bioavailability, and frequently is subject to change based upon ambient geochemical conditions. In aquatic environments, phosphorus can be broadly divided into dissolved and particulate forms, each of which are comprised of organic and inorganic forms (Records et al., 2016 and references therein). Inorganic dissolved phosphorus, frequently referred to as soluble reactive phosphorus (SRP) or dissolved-orthophosphate (DOP), is the most readily bioavailable form, and the form that is primarily attributed to driving algal blooms. This bioavailable, inorganic dissolved-P (henceforth referred to as DOP) moves in and out of the dissolved pool via uptake and release by biotic (algal and microbial) and abiotic (sediment equilibrium, precipitation, dissolution) mechanisms (Records et al., 2016; Withers & Jarvie, 2008). Dissolved organic phosphorus is generally considered to be less bioavailable (Dodd & Sharpley, 2015).

The reactions which govern the transformation of phosphorus (P) from one form (dissolved or particulate) to another are dependent upon sediment mineralogy and aqueous conditions including dissolved-P concentration, pH, and redox potential (Eh). Dissolved-P may be removed from solution by sorption, precipitation, occlusion, or incorporation into biomass; and depending upon the mineral association, aqueous conditions, and stability, may be released back to solution. Phosphorus may also alternate between sorbed and desorbed form (cycle or spiral downstream) under specific pH and redox conditions.

Dissolved P may be removed from the water column and incorporated into particulate form via adsorption to mineral or organic matter surfaces or precipitation within a mineral structure. Once attached, P may become physically buried or "occluded" within the mineral due to aggregation. The stability of sediment bound P varies based on several factors including mineral association, pH, and redox potential. Phosphorus binds readily to metal oxyhydroxides; so readily, in fact, that the sorptive capacity of freshwaters has in some cases been related to concentrations of ferric oxyhydroxide and hydroxide [$Fe(OH)_3$], calcium carbonate ($CaCO_3$) and aluminum hydroxide [$Al(OH)_3$] (Kopáček et al., 2005).

While P that has been adsorbed to Fe hydroxides or precipitated as part of an Fe(III)-phosphate mineral may be released back to the water column via reductive dissolution under anoxic conditions (Withers & Jarvie, 2008), complexes formed with Al hydroxide and aluminosilicate minerals tend to be more stable and are generally not subject to transformation under reducing conditions (Hutchinson, 2003). Co-precipitation of P with calcium carbonate as the mineral apatite also produces scarcely available P fraction (Reynolds & Davies, 2001) that requires mineral dissolution to return P to the water column. Furthermore, bonds between P and sediment vary in their strength in accordance with their degree of weathering. Poorly crystalline forms of iron and aluminum oxides have been shown to have greater capacity for sorption due to increased surface area, however, the bonds formed are weaker and more vulnerable to being broken (Records et al., 2016 and references therein). Temperature has also been shown to have positive correlation to P release from bound form (Duan & Kaushal, 2013). These myriad factors affecting the capacity of sediment to bind and release phosphorus lead to complex dynamics in riverine settings, where inputs of sediment from erosional hotspots bearing distinct initial phosphorus concentrations and capacity for binding phosphorus combine and interact with dissolved phosphorus in the water column.

Geologic Setting, Land-Use Change, and Anthropogenic Pressures

The Minnesota River Valley was formed over the course of multiple drainage events of glacial Lake Agassiz between 11,500 and 8,200 radiocarbon years before present (Clayton & Moran, 1982; Matsch, 1983). Occupying the valley initially carved by glacial River Warren, the Minnesota River drains much of southern Minnesota (43,400 km^2) joining the Mississippi River in the Minneapolis-St. Paul metro area. Glacial River Warren formed as meltwater held by glacial Lake Agassiz episodically released, carving through glacial till and saprolite, locally exposing bedrock and generating relief of 40 – 70 meters across the basin (Gran et al., 2011). As a result of this rapid and deep incision, tributaries to the Minnesota River have made dramatic base level adjustment as they approach the Minnesota River, incising up to 70 m and generating "knick zones", or zones of incision through otherwise planar landscapes. Incision in these tributaries is ongoing, with the points of propagation progressively migrating upstream, leaving behind bluffs comprised of glacial till, alluvial, and glaciolacustrine sediments that are highly vulnerable to erosion (Gran et al., 2009).

The evolutionary history of this basin lends itself to extensive erosion, and the naturally high background erosion rate is overlain and exacerbated by anthropogenic pressure. Today, the Minnesota River is the primary source of sediment to the upper Mississippi River in Minnesota, supplying as much as 90% of the load received by Lake Pepin, a naturally impounded section of the Mississippi River located approximately 80 km southeast of the Twin Cities in Minnesota (Engstrom et al. 2009). Analysis of sediment cores from Lake Pepin has revealed a tenfold increase in sedimentation rates and a fifteen-fold increase in P loading to Lake Pepin since the onset of agriculture in Minnesota (Engstrom et al., 2009). The Le Sueur River contributes disproportionately to Minnesota River Basin sediment loads – supplying as much as 30% of the sediment carried by the Minnesota River but comprising only 7% of the drainage area (Belmont et al., 2011; MPCA, 2017). Approximately 87% of the available acreage within of the Le Sueur River Basin is in agricultural land use, with corn and soy rotation accounting for 93% of the acres in cropland (MPCA et al., 2012). In order to maintain soil conditions that can support the extensive row crop agriculture, tile drainage has been installed broadly across the basin. This intensive land use is understood to contribute to the alteration of hydrology and to increases in export of sediment from the Le Sueur River and other tributaries to the Minnesota River Basin (Schottler et al., 2013).

The disproportionate influence of the Minnesota River upon downstream sediment loading has provoked strong interest in uncovering the sources and drivers of sediment export in this setting. Fallout radionuclide signatures were used to differentiate upland from near-channel erosion on Lake Pepin sediment cores. These analyses demonstrated a shift in sediment source over this time, from historical dominance of natural streambank erosion, to a predominance of upland topsoil erosion with the onset of agriculture (enriched radionuclide signature), and more recently, a shift back to streambank erosion (Belmont et al., 2011). The shift back to streambank erosion co-occurs with major changes in basin hydrology which have been linked to the conversion to row-crop agriculture, the widespread institution of tile drainage, and ongoing climate change (Schottler et al., 2013). A sediment budget developed for the Le Sueur has corroborated this, indicating that 70% of the suspended sediment load in the Le Sueur basin was derived from near-channel erosion (Gran et al., 2011), a common occurrence in the highly agricultural landscape of the Midwestern United States (Gellis et al., 2016b).

Phosphorus fate and transport are inextricably linked to sediment. The Le Sueur River basin experiences high phosphorus inputs, coupled with substantial upland topsoil loss and even greater erosion of sediment from near-channel glacial and alluvial features. To effectively mitigate phosphorus pollution in this context, detailed information about feedbacks between hydrology, sediment transport and delivery, and phosphorus flux is needed. This study examines these relationships in the highly agricultural Le Sueur River Basin, where geologic history sets the stage for massive streambank erosion and human activity alters hydrology and increases nutrient loads. Here we use historical data to evaluate trends in phosphorus behavior and construct a budget for sediment-derived phosphorus to examine sources of particulate and dissolved phosphorus loads in this basin. We incorporate the results of sorption experiments to build our understanding of the role of sediment from distinct source areas in driving transformations of P between dissolved and particulate form along its transport path.

Chapter 1

Mass balance for sediment-derived phosphorus reveals sediment as a modulator of phosphorus fate and persistence rather than as its primary source

Summary

Reduction of excess phosphorus and sediment delivery to ecosystems is a critical management target around the globe. In the upper midwestern United States, where agricultural land use is intensive, interactions between sediment and phosphorus may have important influence over the fate, transport, and persistence of phosphorus at a watershed scale. Watersheds where glacial history has resulted in deeply incised river networks, such as the Le Sueur River basin in Minnesota, USA, are geologically primed for high erosion rates and sediment delivery. In addition to being faced with excess sediment, nutrient inputs from agriculture produce phosphorus loads in the Le Sueur River that are among the highest in the state of Minnesota. Due to significant interactions between sediment and phosphorus, clear understanding of sources, sinks, transformations, and mechanisms for export and retention of phosphorus and sediment are needed in order to mitigate excess phosphorus loading to downstream waters in these settings. We build upon a robust sediment budget which draws from multiple lines of evidence to constrain sources of sediment to the Le Sueur River basin, developing a mass balance for sediment-derived phosphorus. This sediment-derived phosphorus budget allows us to explore sources and loading rates from the landscape. Further, we apply sorptive capacity data to this budget to constrain the portion of total phosphorus load that is formed via instream transformations. This mass balance reveals that, despite the very high sediment loads that affect this basin and the naturally high phosphorus concentration of these glacial sediments, only 24% of the total phosphorus load measured at the outlet of this watershed can be attributed directly to source sediment, with 23% in particulate form and less than 1% in dissolved form. Dissolved orthophosphate comprises 37% of the measured average annual total phosphorus load at the Le Sueur watershed outlet. Incorporation of previous study findings into this mass balance suggest that the true dissolved phosphorus inputs to the river may be masked by sorption of dissolved phosphorus to sediment, thereby reducing the fraction of total phosphorus that we observe as dissolved load by as much as 31%. These findings highlight the need for better understanding of dissolved phosphorus source and transport mechanisms as well as the dynamics of phosphorus as it moves between particulate (bound) and dissolved (readily bioavailable) forms.

Key Words: phosphorus budget, sediment, fluvial geomorphology, watershed management, agricultural landscapes

Introduction

The primary objective of this research is to examine the role of sediment in governing phosphorus dynamics in the post-glacial Le Sueur River Basin, located in southern Minnesota, USA (Figure 1). We investigate the extent to which the dissolved and particulate phosphorus loads moving through the Le Sueur can be attributed directly to the dominant sources of sediment in the basin; namely, agricultural upland soil (top soil and upland ditch-bank sediment), glacial till bluffs, alluvial streambanks, and ravines. This is accomplished via analysis of historical data describing spatial patterns and relationships between flow and concentration of total, dissolved, and particulate phosphorus as well as total suspended solids (TSS). Furthermore, we explore sediment-derived phosphorus sources, storage and processing, and export by connecting sediment-phosphorus chemistry to an existing fine-sediment budget. We develop a mass balance for sediment-derived phosphorus, building upon this sediment budget and incorporating data describing total and dissolved phosphorus associated with sediment from distinct erosional sources in the Le Sueur River basin including eroding alluvial streambanks, high glacial till bluffs, and ravines, as well as upland agricultural soil erosion. The results of this analysis allow us to partition the observed total phosphorus load into its respective sources.

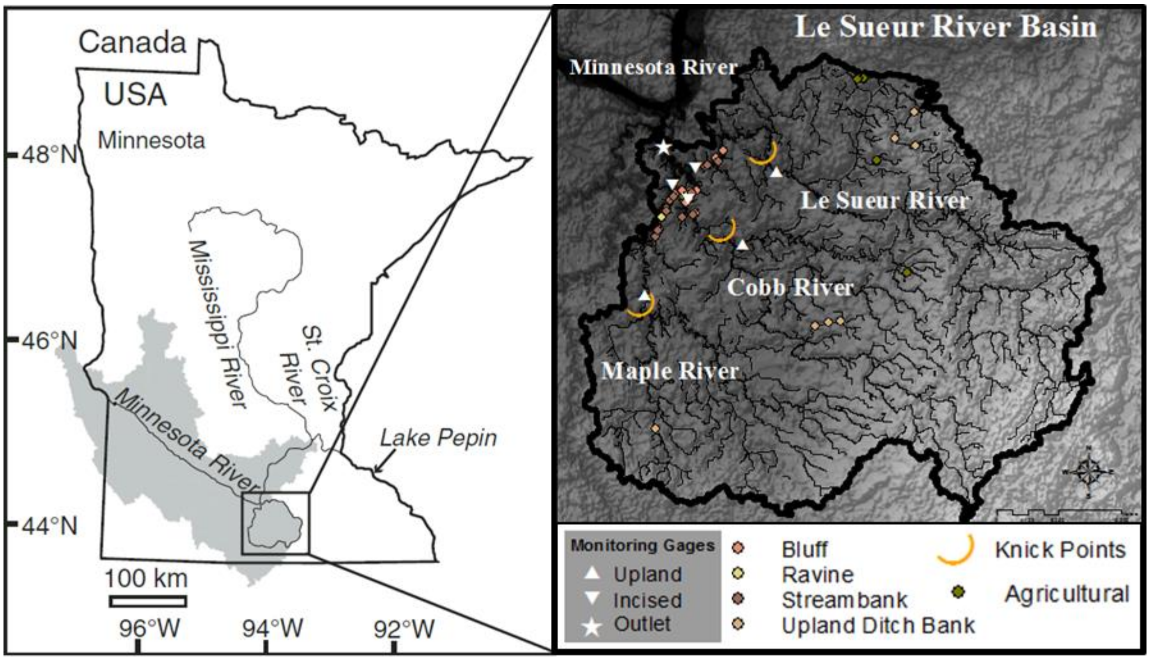


Figure 1. Location map showing sediment sampling locations, gages, and knick points. Modified from Gran *et al.* 2009. Location of the Le Sueur River within the Minnesota River Basin, inset map showing source sediment sample collection locations, gages maintained by Minnesota Pollution Control Agency, Minnesota Department of Natural Resources, and U.S. Geological Survey which serve as collection points for water quality samples, and knickpoints which indicate a transition from upland to incised zone on the river network.

Incorporating total phosphorus and water-extractable phosphorus (a proxy for dissolved orthophosphate associated with sediment) into the fine-sediment budget allows us to constrain the extent to which sediment is responsible for driving phosphorus loading as well as the role of sediment in governing the form and subsequent bioavailability of phosphorus moving through this basin. This mass balance addresses a critical gap in our understanding of how diverse sediment sources may contribute to phosphorus export and retention in the context of highly agricultural streams of the upper midwestern United States.

Sediment is a known source of phosphorus to surface waters (Correll, 1998; Fox et al., 2016; Jarvie et al., 2005; McDowell & Sharpley, 2001; Miller et al., 2014; Pant & Reddy, 2001; Records et al., 2016; Sekely et al., 2002; Sharpley et al., 2013; Withers & Jarvie, 2008), and thus it is frequently implicated for phosphorus delivery to aquatic ecosystems. However, in heavily eroding glacial landscapes such as the Le Sueur River Basin, the primary source and driver of phosphorus dynamics may not be the same as the primary source of sediment. Much of the sediment supply in these settings is derived from glacial till bluffs and streambank alluvial material which are not enriched in readily bioavailable phosphorus, while in other settings eroding streambanks may be comprised of agricultural sediments rich in easily mobilized phosphorus. In settings such as the Le Sueur basin, where agriculture results in high inputs of phosphorus and streambanks contribute sediment with a high capacity for binding phosphorus, there is a strong potential for the development of "legacy" stores of particulate phosphorus in downstream receiving waters. In watersheds that contribute disproportionately to phosphorus and sediment loading and where the primary sources of sediment and phosphorus differ, the development of distinct management actions may be needed to address these interrelated but distinct forms of pollution.

Methods

The process of exploring the dynamics of phosphorus and sediment in this basin was twofold, beginning with 1) analysis of historical monitoring data to explore spatial and flow-related trends in phosphorus form and loading, and 2) using this and previous work on sediment mass balance to construct a sediment-derived phosphorus budget for the basin.

Gaging Network

Both of these efforts used data from a network of gages on the Le Sueur River and its tributaries, the Maple and Cobb Rivers, which was designed to capture conditions above and below the incised zone of each of these rivers (Figure 1, Table 1). Three upland gages, located at or near the knick point on the Le Sueur and each of its two tributaries, capture the drainage of the Le Sueur, Maple and Cobb uplands above their respective incised zones. These upland gages are located at the Le Sueur River at St. Clair, the Maple River at Sterling, and on the Little Cobb River near Beauford. Incised zone gages on the Le Sueur, Maple, and Cobb capture integrated signals of the uplands and incised zone of each of these rivers individually. Incised zone gages include the Le Sueur River at County Road 8, the Maple River at County Road 35, and on the Big Cobb River near Good Thunder. The incised zone gage on the Le Sueur at County Road 8 falls above the confluence with the Maple and Cobb Rivers and thus captures the signal of the uplands and incised zone of the Le Sueur specifically. Lastly, a gage at the watershed outlet of the Le Sueur, which falls below the confluences with the Maple and Cobb Rivers, integrates the signal of the entire watershed. Where results of budget analyses from this network of gages are presented, only the Le Sueur River itself is represented, where the "Upland" and "Incised Zone" gages are on the Le Sueur itself (not integrating the three upland gages or incised zone gages) and the "Outlet" refers to results from the gage location which integrates the signal of the entire watershed.

Table 1. Gage Locations in the Le Sueur River Basin.

MPCA /USGS ID	**Location**	**Gage Name**	**Latitude**	**Longitude**	**Drainage Area km^2**
32077001/ 5320500	Outlet	Le Sueur River nr Rapidan, MN66	44.111085	-94.04163	2875
32076001/ NA	Incised Zone	Le Sueur River nr Rapidan, CR8	44.08476	-93.988667	1157
32079001/ NA	Uplands	Le Sueur River at St. Clair, CSAH28	44.08312	-93.854737	914
32072001/ 5320480	Incised Zone	Maple River nr Rapidan, CR35	44.065368	-94.026162	877
32062001/ 5320450	Uplands	Maple River nr Sterling Center, CR18	43.93498	-94.070748	790
32071001/ 5320330	Incised Zone	Big Cobb River nr Beauford, CR16	44.04725	-94.000611	784
32069001/ 05320270	Uplands	Little Cobb River nr Beauford, MN	43.996667	-93.908333	209

*MPCA refers to Minnesota Pollution Control Agency, USGS refers to U.S. Geological Survey

Analysis of Spatial Trends in Phosphorus Concentration and Export

Due to the inverted geomorphic character of the post-glacial Le Sueur basin (i.e., flat uplands and incised lower valley), we expected that processes that drive export of particulate and dissolved phosphorus would differ spatially, with high inputs of dissolved phosphorus leaching from farm fields in the uplands and high inputs of mineral-associated particulate phosphorus added in the incised zone. We explored the spatial distribution of phosphorus fractionation using historical data from the network of gages described above.

Data from the previously described gaging network, maintained by U.S. Geological Survey (USGS), the Minnesota Pollution Control Agency (MPCA), and their partner agencies were used to explore spatial trends in phosphorus export and to relate this export to flow and sediment flux. Stream discharge was monitored continuously at this network of gages. River water samples for total suspended solids (TSS), total phosphorus (TP), and dissolved orthophosphate (DOP) were collected year-round by the MPCA and the Water Resources Center of Mankato at the Le Sueur watershed outlet and seasonally (during open-water months) at upstream and tributary sites. Sampling targeted storm and snowmelt events but also included monitoring of low flow periods to cover the entire range of flow conditions (MPCA, 2016). River water samples for TP were digested and analyzed using colorimetric methods (MPCA, 2012). Samples for dissolved phosphorus (DOP, soluble reactive phosphorus) were filtered at 0.45 μm and analyzed using the same colorimetric method (MPCA, 2012).

This correction factor (the average percent of TP comprised by dissolved organic P) was found using water samples collected from a sampling network within the Le Sueur River Basin that was designed and maintained by staff from the University of Minnesota. See Appendix A for details regarding water sampling, Table A1 for a list of events, and Figure A1 for water sample collection locations (both from Dolph et al. (2017)). Average percent dissolved organic P from these water samples was found by subtracting soluble reactive phosphorus concentration (equivalent to DOP) from total dissolved phosphorus concentration (achieved via persulfate digestion of a filtered sample) and dividing by TP concentration. The average percent dissolved organic phosphorus correction factor was found to be 17%, with the exclusion of a strongly outlying sampling date which had very high percent dissolved organic phosphorus (Figure A2). This correction factor was then applied where,

$$\mathbf{PP = (TP - DOP) - (TP * 0.17)}. \quad (1)$$

Flow-matched concentration data from the MPCA were used to look at trends in concentration of TP, DOP, PP and TSS and relationships between concentration and discharge. These data in turn were used to calculate instantaneous loads for TP, DOP, PP and TSS, where the closest flow measurement to the time of sample collection was matched to the corresponding concentration data. Instantaneous yields were then found and were used in analyzing spatial trends in export of these constituents.

Annual loads and were computed using a data set comprised of a mix of measured and modeled concentration and load estimates from load estimation conducted by the MPCA. These modeled results were developed by the MPCA using the load estimation program FLUX, which generates daily concentration and load estimates based on point measurements of concentration and continuous flow monitoring, and aggregates these results to annual scale (MPCA, 2016). Instantaneous loads (and yields) were used to look at spatial variation in export. Annual loads were used in the budget for sediment-derived phosphorus.

Sediment-Derived Phosphorus Budget Approach

To further explore the magnitude of phosphorus loading from distinct sources and the role of sediment in driving fractionation between dissolved and particulate form, we developed a budget for sediment-derived phosphorus using an existing fine-sediment budget (Gran et al., 2011; Belmont et al., 2011; Bevis, 2015) as a framework. Sediment budgets use multiple lines of evidence to describe sediment sources, sinks, and export using a mass balance approach (Gellis et al., 2016a).

The mass balance for fine sediment in the Le Sueur River Basin examines the primary erosional sources in the basin, taking the form:

$$\mathbf{Qs = Bl + Ba + R + U - Fp - La,} \qquad (2)$$

where Qs is suspended load of silt and clay, which is equal to the sum of source terms including Bluffs (Bl), Streambanks (Ba), Ravines (R), and Uplands (U); minus sediment sinks including Floodplains (Fp) and Lakes (La) (Bevis, 2015). This budget focuses on fine (silt and clay sized) sediment, which comprises the bulk of measured TSS. Methods including photogrammetry, geochemical fingerprinting, and models of channel migration were used to constrain contributions of sediment from each of these sources to the upper basin and within the incised zone, and at the watershed outlet (Gran et al., 2011).

The sediment budget mass balance described by Equation 2 is used to find a "Predicted" average annual TSS load at each of seven gage locations. In this thesis, results of "Predicted" loads of TSS, TP, DOP, and PP are presented for three of these seven gages; namely, for the upland and incised zone gages on the Le Sueur River (not including the Maple or Cobb River's upland or incised zone loads), and for the Le Sueur watershed outlet, which integrates the signal of the entire watershed, including loads from the Maple and Cobb Rivers. Once the "Predicted" average annual load is found for each of these gages, "Predicted" load is then compared to "Observed" load, which in turn is the average annual load computed by the MPCA (MPCA, 2016).

This sediment budget forms the base of our budget for sediment-derived phosphorus, and therefore, results of analyses of sediment-derived TP, DOP, and PP are identically structured, and herein are presented for upland, incised zone, and outlet locations as described above for the sediment budget. Our analyses for sediment-derived TP, PP, and DOP apply sediment-P chemistry to the predicted loads of sediment from each source in the sediment budget, and subsequently compare "Predicted" TP, PP, and DOP to "Observed" loads measured by the MPCA at each of the gage locations described above. This analysis allowed us to determine the likely proportion of our total TP, PP, and DOP loads that were derived from sediment specifically.

Sediment Phosphorus Chemical Analyses

To link this sediment budget to its corresponding phosphorus chemistry and assess sediment-derived phosphorus, the sediment sources described by the sediment budget were sampled across the basin representing each of the tributaries and its unique soils and glacial and alluvial sediment characteristics (Figure 1). Agricultural upland soils were sampled to capture the greatest variability in phosphorus concentration by sampling in different crop types (corn and soy), soil types, and topographic positions (summit, middle, and toe of slopes). These samples were collected by clearing any vegetation or decaying organic material from the surface, and collecting soil from an area with a diameter of approximately 10 cm to a depth of approximately 10-15 cm. Near channel sediments were collected from bluffs, streambanks, ravines and upland ditch-banks by targeting erosional surfaces for fresh material. For each of these features, the surface ~1 cm of material was first removed and then a sample was collected by scraping the surface of the features to a depth of ~5 cm along a representative profile. Bluff features were comprised of mostly glacial till with beds of alluvium and/or a cap of approximately 2-3 meters of alluvial material. These samples were collected at approximately 10 m above the wetted channel (or greater) and were collected from erosional surfaces. Samples were collected from both till and alluvial strata.

Streambanks, as defined in this and previous (Bevis, 2015; Gran et al., 2011) studies in the Le Sueur basin are features which are 2-4 m high and have much more frequent contact with the channel than bluffs. In the incised zone, these features are comprised predominantly of recently deposited alluvium overlying glacial till which is only sometimes present at the surface. Streambank samples were also collected to represent both till and alluvial strata. In the uplands of the Le Sueur, while streambanks along the mainstem contain some alluvium, a majority of the stream network is comprised of small tributaries and zero- and first-order channels and agricultural ditches that carve through agricultural fields of the uplands of the Le Sueur, Maple, and Cobb. Therefore, in this study, we refer to streams in the uplands of the Le Sueur and its tributaries as “upland ditch-banks”, meaning man-made features and zero- to first-order tributaries that occur in the headwaters of the basin. Upland ditch-banks were sampled with the same methods as streambanks occurring in the incised zone. Vegetation was cleared, the top ~1cm was removed to provide a fresh surface, and material was scraped from the surface to a depth of ~5 cm along a profile. Where an eroding surface was present, it was sampled. Where no active erosion was visible, vegetation was cleared from a steep section of the bank and a sample was collected. These profiles varied in length based on the available surface and were up to 1.5 m in length.

Ravines in the Le Sueur basin consist of head-cuts off the channel into the surrounding landscape which, depending on location, may be comprised of upland topsoil, glacial till, and/or alluvium. Sub-samples from all strata present were collected at each ravine location.

Sample collection from all of these features was accomplished using plastic trowels to avoid interference of metals. Trowels were cleaned between collection with deionized water and were acid washed between sampling events. Following collection, all sediments were stored at 4°C until preservation by drying, which in turn was done within 2-3 weeks of collection. All sediment samples were dried at 60 °C, disaggregated and wet sieved to less than 63 μm, and then disaggregated again and homogenized prior to analysis of TP and DOP. Wet sieving was conducted using non-metallic sieves (polycarbonate frame and polyester or nylon mesh), also in an effort to reduce interference of metals in analysis of elemental concentrations that were later preformed on the sieved sediment.

Total phosphorus analyses were conducted by the University of Minnesota's Research Analytical Lab. These analyses were carried out using nitric acid assisted microwave digestion and analysis of the digest via inductively coupled plasma optical emission spectrometry. Elemental concentrations of iron, aluminum, and calcium were also obtained from this analysis.

Phosphorus which was loosely bound to sediment and would immediately enter solution upon introduction to the water column was represented using water extraction of DOP from source sediments. A 0.25 g subsample of dried sieved sediment was added to a 50-mL centrifuge tube and shaken with 50 mL of deionized water for one hour. The tubes were then centrifuged, and the supernatant was filtered and analyzed for soluble reactive phosphorus using the ascorbic acid method, as detailed in Janke et al. (2014).

Sediment chemical and physical properties that relate to phosphorus concentration were also evaluated in order to understand differences between source sediment types. These analyses included grain size, organic matter percent via loss on ignition (LOI), and pH. Grain size was analyzed via laser diffraction by the Jelinski lab at University of Minnesota. Sediments that were sieved to <63 μm were sub-sampled using a volumetric scoop (approximately equivalent to 0.5 g of sediment) and were added to 30 mL bottles with deionized water and sodium hexametaphosphate (a dispersant) and sodium hypochlorite (to remove organic matter). Samples were shaken overnight to encourage dispersal. Previous work by the Jelinski lab comparing hydrometer analysis to laser diffraction by a particle size analyzer has found that the clay-silt break is equivalent to 8 µm measured by the particle size analyzer (Jelinski, 2017), which is consistent with other studies (Konert and Vandenberghe, 1997).

Organic matter LOI analysis and pH measurement were conducted by the Research Analytical Lab at the University of Minnesota. Measurement of pH was taken on a 1 to 1 volumetric ratio of sediment to water (Research Analytical Lab, 2018a). Organic matter analysis was conducted by ashing a dried sediment sample (dried 2 hours at 105°C and ashed two hours at 360°C) and finding the change in mass following combustion (Research Analytical Lab, 2018b).

Construction of the Sediment-Derived Phosphorus Budget

In order to apply the results of these TP and DOP analyses to the sediment budget, results of detailed analysis of distinct strata within each source sediment category had to be integrated into a single concentration value. This was accomplished by finding weighted average concentrations of TP and DOP for each source sediment type for application to the sediment budget categories (upland, bluff, streambank, and ravine). Field observations (by Bevis, 2015, and this study) of the proportions of distinct strata comprising these features were used to inform weighting factors. Upland sediment was weighted as 100% agricultural topsoil, meaning it was represented using an average of all agricultural topsoil concentrations; while ravine sediment TP and DOP concentrations were weighted as 40% upland agricultural soil, 30% till, and 30% alluvial, meaning the average concentrations from each of those features was combined into a single value using these proportions which describe the typical distribution of strata in ravines across the Le Sueur River Basin. Bluff sediment was weighted as 85% till and 15% alluvial. Streambanks differed in how they were represented at each gage location, because upland ditch-banks were comprised largely of topsoil while incised zone streambanks are characterized by alluvium with smaller proportions of glacial till. Thus, for upland gage locations, streambanks were considered to be 100% upland ditch-bank, while for lower incised reaches streambank sediment was weighted as 85% alluvial and 15% till.

These weighted average phosphorus concentrations for each source sediment category were applied to the mass balance sediment budget by multiplying concentration of TP and water-extracted DOP associated with a given sediment source (mg/kg) by sediment load (Mg/yr) from that source as follows,

Sed-TP load (g/yr) = Sed Load (Mg/yr) * Sed-TP conc (mg/kg) (3)

Sed-DOP load (g/yr) = Sed Load (Mg/yr) * Sed-DOP conc (mg/kg), (4)

where “Sed” refers to sediment and “conc” refers to concentration. Using sediment budget structure and Equations 3 and 4, sediment-derived TP and DOP loads were found for each source (uplands, streambanks, ravines, and bluffs) at each gage location. Storage of TP and DOP in lakes and floodplains was also accounted for. For lakes, storage was found using the mass of sediment found by the sediment budget to be trapped in lakes (Bevis, 2015; Gran et al., 2011) using the upland sediment TP and DOP concentration, and for floodplains where the load is scaled based on the proportions of sediment known to be passing the gage at that point. In example,

$$\mathbf{TP_{FP\ storage} = (Load_U * \%\ Total\ Load_U) + (Load_B * \%\ Total\ Load_B) + (Load_S * \%\ Total\ Load_S) + (Load_R * \%\ Total\ Load_R),} \quad (5)$$

where U refers to upland, B refers to bluff, S refers to streambank, and R refers to ravines. For each gage location, a predicted load was found by summing the source sediment TP or DOP load from each of these distinct sources.

As described above, these analyses follow the structure of the sediment budget and results are presented accordingly. Once the sediment-TP and DOP concentrations (in mg/kg) had been multiplied by sediment load to give sediment-derived phosphorus load, these estimates were then compared to “Observed” phosphorus loads from the network of gages on the Le Sueur and its tributaries. Due to variability in years monitored for the gages in the network, we used load observations from the Le Sueur watershed outlet, which had complete records from 2009-2012, to estimate “Observed” loads for four gages that did not have records for 2009. This was accomplished by dividing the average load over the years monitored at the gage with shorter record by a scaling factor of the average load at the watershed outlet as follows,

$$\mathbf{Site\ A_{Avg\ Load\ 2009\text{-}2012} = (Site\ A_{Avg\ load\ 2010\text{-}2012}) / (Site\ B_{Avg\ Load\ 2010\text{-}2012} / Site\ B_{Avg\ Load\ 2009\text{-}2012})} \quad (6)$$

where Site A is the site with an incomplete record for which we are approximating average load for the full 2009-2012 record, and Site B is the watershed outlet where data are available for the entire 2009-2012 period. Loads were estimated for 2009 for the incised zone gage on the Le Sueur River at County Road 8 and for gages on the Maple and Cobb Rivers (tributaries to the Le Sueur) (see Appendix Table A2 for loads availability). The period 2009-2012 was chosen over 2010-2012, which had complete records, because average annual loads over this period (2009-2012) more closely resemble long term averages for the watershed outlet, which has records spanning from 2007-2015. This time period likely resembles the long-term average because 2009-2012 encompasses a broader range of hydrologic conditions including wet years, dry years, and average years (Table A1).

Results

Seasonal and Spatial Variability in Phosphorus Concentration and Export

Data collected from the gaging network were used to explore trends in phosphorus export, and to relate this export to flow and sediment flux. Plots of concentration of dissolved and particulate phosphorus as a function of stream discharge at the watershed outlet of the Le Sueur River reveal that both fractions of the TP load increase with increasing discharge (Figure 2). Total suspended solids concentration, which is often used as a proxy for suspended sediment concentration, also showed positive correlation to discharge within the Le Sueur Basin. Increase in concentration with discharge can be thought of as a “concentrating” relationship, where, rather than diluting, stormflows concentrate or increase the concentration of the pollutant. These concentrating relationships indicate that the highest instantaneous export of phosphorus occurs when flow is greatest (Figure 2).

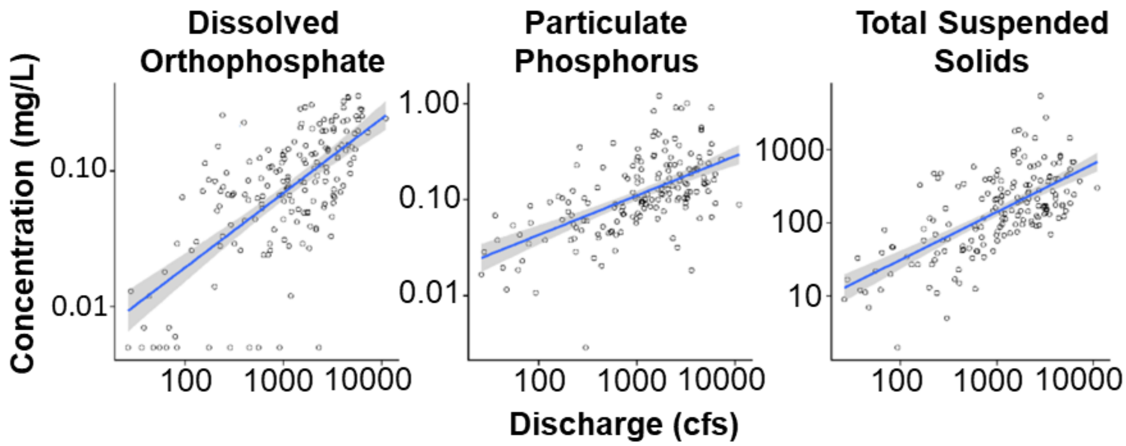


Figure 2. Daily concentration versus discharge for dissolved orthophosphate (DOP), total suspended solids (TSS), and particulate phosphorus. Positive correlations were observed for all constituents, indicating concentrating relationships. Equations for these relationships and R squared values are as follows. Dissolved Orthophosphate: log(y)=0.55log(x)-2.81, R^2=0.45; Particulate Phosphorus: log(y)=0.41log(x)-2.19, R^2=0.34; Total Suspended Solids: log(y)0.64log(x)+0.19, R^2=0.44.

In order to examine spatial variability in phosphorus and sediment export, instantaneous yield at the upper gage was plotted against the lower for each gage pair (Figure 3). Because this network of gages was designed to capture above and below incised zone conditions, it allows us to investigate variability in export along the geomorphic gradient from uplands to incised valley. Results of this analysis for the Maple River, a tributary of the Le Sueur with a longer monitoring record than was available for the upper Le Sueur itself, demonstrate a skew in dissolved phosphorus yield toward the upper part of the basin (Figure 3). This trend was also observed in the Le

Sueur, but due to the smaller amount of data, only the results from the Maple are shown here.

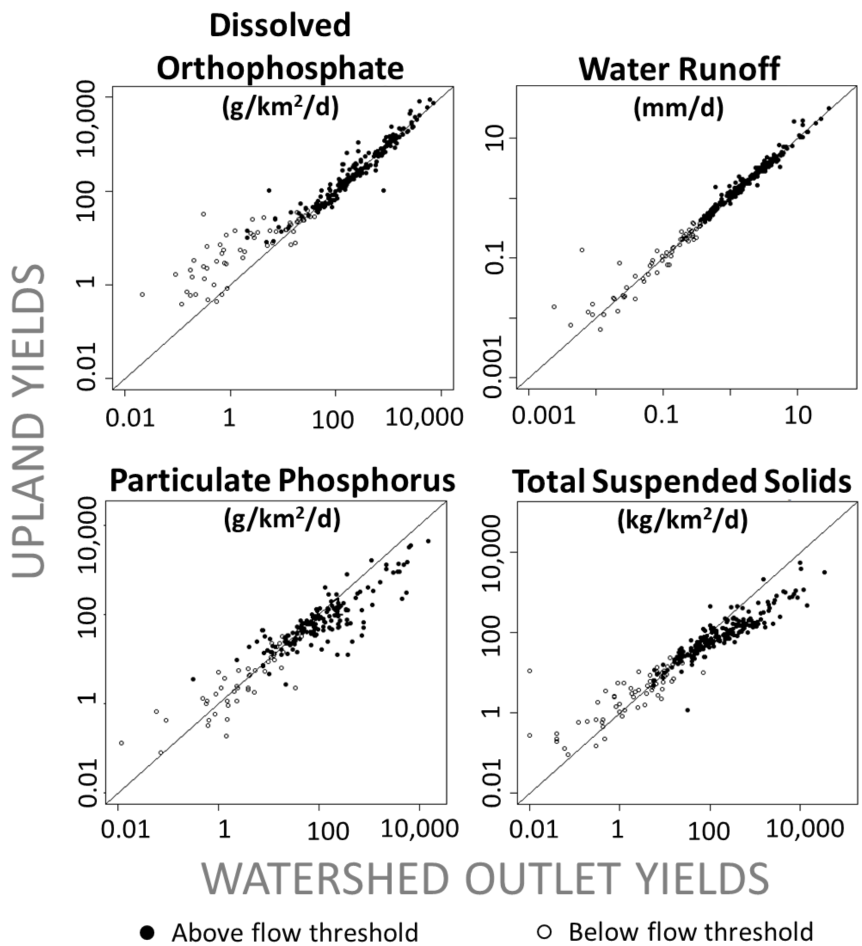


Figure 3. Dissolved orthophosphate, runoff, particulate phosphorus, and total suspended solids yield at the upper gage (above knick point) and lower gage (below knick point) on the Maple River, a tributary to the Le Sueur River. Filled circles correspond to above a threshold flow level of 3.6 m^3/s identified by Cho (2017a). Above this flow threshold the erosion of near channel sources increases dramatically.

Particulate phosphorus also shows a shift as yield increases (Figure 3). Low particulate phosphorus yields skew toward the uplands, while high yields are skewed toward the knick zone. The same relationship is observed in TSS yields at the upper and lower gage. In both cases these increases correspond to the crossing of a flow threshold of 3.6 m^3/s, which was identified by Cho (2017a) as the point at which near channel features such as bluffs, streambanks, and ravines begin eroding rapidly.

Sediment Budget Findings

Near channel sources of sediment, which were demonstrated by Cho (2017a) to become important at high flows in the Le Sueur River, dominate the sediment budget for the basin. Our modified version of the sediment budget developed by Gran et al. (2011) and Bevis (2015) found that as much as 83% of the silt and clay sized suspended sediment exiting the watershed at the watershed outlet gage at Minnesota highway 66 between 2009 and 2012 was derived from near channel sources including bluffs, streambanks, and ravines (Figure 4), with most sediment inputs derived within the incised zone. Sediment load more than doubles from the uplands to the incised zone gages at Le Sueur at County Road 8 and increases more than 7-fold between the uplands and watershed outlet (Figure 5). The sediment budget results also reveal spatial heterogeneity in sediment source on the Le Sueur River mainstem. In the upper Le Sueur above the incised zone, as much of 56% of sediment passing the stream gage is derived from upland (predominantly agricultural) sources. However, at the incised zone gage on the Le Sueur above the confluence with the Maple and Cobb Rivers, the predominant sediment source switches to near channel, with only 38% derived from uplands and the other 62% coming from a mix of bluff, streambank and ravine sources, with a majority of that coming from bluff erosion. At the watershed outlet, where the Maple and Cobb River tributaries are included and the signal of the whole watershed is integrated, only 17% of the total sediment contribution is attributable to upland sources, with 44% of the fine-sediment load derived from bluff erosion alone.

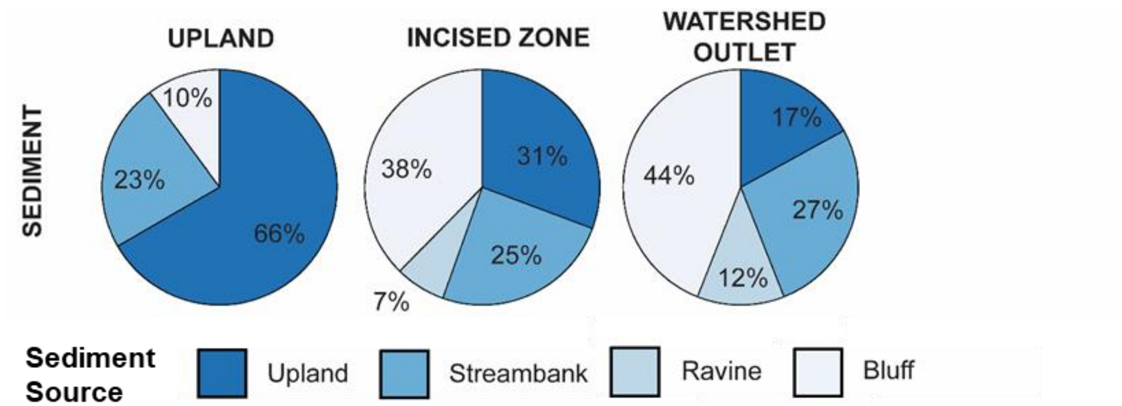


Figure 4. Apportionment of average annual loads of sediment to its sources at distinct geomorphic locations along the Le Sueur River including in uplands at the St. Clair gage, within the incised zone at County Road 8 (above the Maple and Cobb confluences), and at the watershed outlet, where the signal of tributaries is integrated.

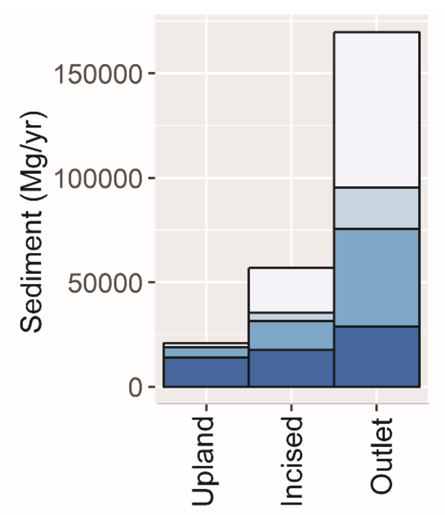


Figure 5. Average annual sediment loads (Bevis, 2015; Gran et al., 2011) from distinct sediment sources to gage locations in the Le Sueur River uplands (at St. Clair), incised zone (at County Road 8) and at the watershed outlet, where the signal of the entire watershed (including the Maple and Cobb Rivers) is integrated. These data represent inputs and do not account for removal by lakes and flood plains. Developed using data corresponding to the monitoring period 2009-2012. Bluff sediment totals include bluffs comprised of glacial till, alluvium and bedrock, but exclude vegetated bluffs.

The influence of sediment source loading upon phosphorus fate and transport were explored via the incorporation of total- and dissolved-phosphorus into the sediment budget, generating a mass balance for sediment-derived phosphorus.

Sediment-Phosphorus Analysis Results

Results of analyses of total- and water extractable- phosphorus reveal differences in phosphorus concentration of sediments from distinct source areas which represent differing depositional histories (alluvial and glacial) (Table 2).

Table 2. Detailed average total (TP) and water extractable (DOP) phosphorus results by sediment source type and strata for samples collected from the Le Sueur River Basin, 2016.

Sediment Type	Sieved size	TP mg/kg	n	DOP mg/kg	n
Bluff - Till	<63um	596	10	3	11
Bluff - Alluvium	<63um	834	5	20	3
Stream Bank - Alluvium	<63um	324	9	5	11
Stream Bank - Till	<63um	542	6	6	4
Upland Ditch-Bank	<63um	693	6	34	7
Agricultural top soil	<63um	659	16	32	16
Ravine (all)	<63um	215	5	18	4
Ravine upland	<63um	304	2	51	1
Ravine till	<63um	150	1	6	1
Ravine alluvium	<63um	159	2	8	2
Channel Bed Sediment - Incised Zone	<2mm	286	5	N/A	N/A
Channel Bed Sediment - Upland	<63um	780	6	32	6
Suspended Sediment - Upland	<63um	1317	5	76	5
Suspended Sediment - Outlet	<63um	877	5	46	5

As discussed in the methods section, to integrate source sediment P concentration data with the sediment budget, weighted average P concentrations were assessed for five broad source sediment categories. Averages were weighted based on approximations of typical proportions of each feature comprised of a given strata (see methods section) to give a single weighted average concentration for each of the source sediment categories described by the sediment budget (Table 3.) These weighted average sediment-P concentrations were developed for application in the sediment-derived phosphorus budget.

Table 3. Weighted average total phosphorus and water-extractable dissolved orthophosphate results by sediment source category, developed for application in the sediment-derived phosphorus budget.

Source Sediment Category	TP (mg/L)	n	DOP (mg/L)	n
Agricultural Upland Soil	659	16	32	16
Ravine Sediment	215	5	25	4
Bluff Sediment	632	15	6	14
Streambank Sediment - Upland	693	6	34	7
Streambank Sediment - Incised Zone	356	15	5	15

Incised zone streambank and ravine sediments were found to be relatively depleted in TP (mean total-P concentrations of 356 and 215 mg/kg, respectively) when compared with bluff (632 mg/kg) and agricultural sediments (659 mg/kg). Upland ditch-banks (which comprise the bulk of streambanks in the uplands of the Le Sueur and its tributaries and therefore were used to represent them) on the other hand, exhibit elevated

TP (693 mg/kg) when compared with streambanks in the incised-zone. In fact, upland ditch-banks show higher average total and water-extractable phosphorus than agricultural soils. Upland ditch-bank sediments have the highest extractable DOP of any of the sediment sources (average of 34 mg/kg), though very similar to upland agricultural soils (32 mg/kg).

Examination of the variability in TP and water extractable DOP concentrations among samples within each source category suggests that bluff till and streambank alluvium both fall within a tight range, while bluff alluvium, agricultural topsoil, upland ditch-banks, and suspended sediments exhibit greater variability (Figure 6). Bluff alluvial samples exhibited high median and outlying TP concentrations, and though median water extractable DOP concentration was low, variability in DOP was also high, overlapping the lower quartile of agricultural sediment concentrations. Streambank till, which underlies streambank alluvial deposits and is in closer contact with the channel, exhibited the highest outliers and a relatively large spread in TP concentrations, but the water extractable portion of this TP was consistently very low. Upland ditch-bank samples exhibited high TP and had median water extractable DOP concentrations that were higher than any other sediment type other than suspended sediment collected at the upland gage (Figure 6).

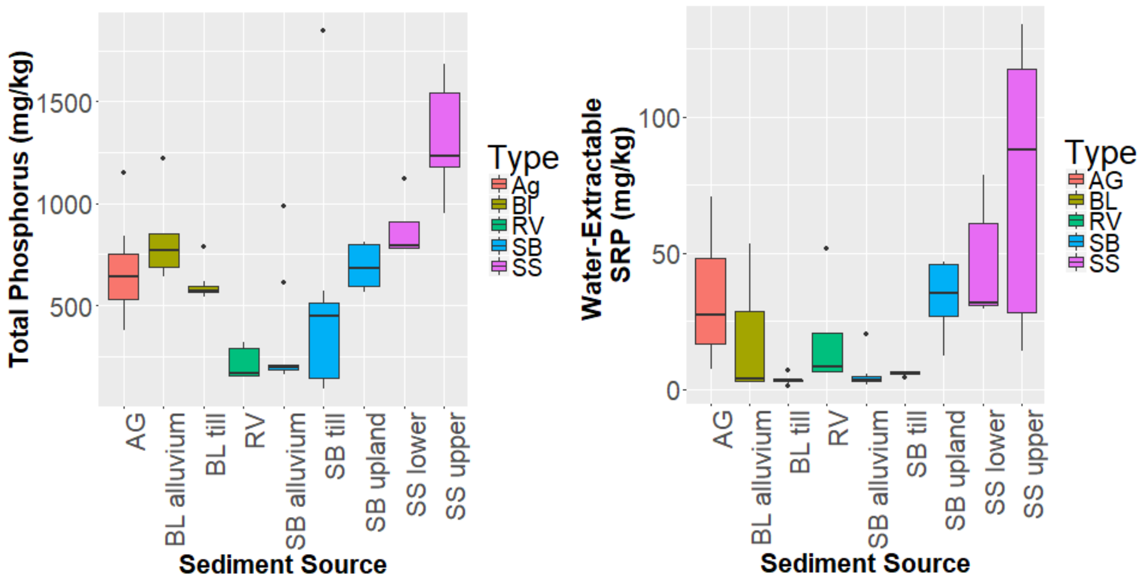


Figure 6. Sediment-derived total phosphorus and water-extractable soluble reactive phosphorus (SRP, or, dissolved orthophosphate) from agricultural topsoil (AG), bluff (BL), channel (CH), ravine (RV), and streambank (SB) sources and suspended sediment (SS). SB upland refers to upland ditch-banks. SS lower and upper refer to suspended sediments from the watershed outlet and the upland gage on the Le Sueur respectively.

In addition to exhibiting variability in TP and DOP, sediments from upland agricultural sources differ from near channel sediments in their mineralogy, and subsequently in their concentrations of iron, aluminum, and calcium (Figure A3 A-C), and their organic content, pH, and percent clay, silt, and very fine sand (Figure A3 D-H). Agricultural top-soils have high organic content as well as high iron and aluminum and low calcium concentrations compared to bluff till sediments. All these characteristics affect phosphorus form and availability.

Suspended sediment collected at the upland and watershed outlet gage on the Le Sueur River represents a mix of sediment from these sources with distinct proportions that vary with landscape position. One might expect that the concentrations of TP and DOP associated with suspended sediment collected from a specific location could be predicted based on the average proportions of sediment and associated phosphorus contributed by the distinct sources (delineated by the budget for each of the gages). However, TP and DOP for suspended sediment collected at the upland gage on the Le Sueur and the watershed outlet of the Le Sueur, which integrates the signal of the whole watershed including the tributaries the Maple and Cobb, differ from predictions based upon the source sediment from which it is derived. Using the proportion of sediment from each erosional source and the average TP and DOP measured on each of these sediments, weighted averages for suspended sediment TP and DOP for the upper and lower gage were estimated. These estimates give average TP concentrations of 664 and 604 mg/kg, and average DOP estimates of 30 and 20 mg/kg for the uplands and watershed outlet respectively (Table 4). Comparison of these estimates to measured average TP and DOP of fine (63 µm) suspended sediments collected from gages in the uplands and at the watershed outlet show consistently higher concentrations (Table 2). Fine suspended sediment had average TP of 1317 mg/kg at the upland gage and 877 mg/kg at the lower gage on average, and water extractable DOP of 76 mg/kg and 46 mg/kg on average at the upland and watershed outlet gages respectively. These concentrations are higher than was found for any of the source sediments, and higher than a weighted average that would represent the mix of source sediments comprising suspended sediment at a given location. This may have implications for the role of fine suspended sediment as a sink for phosphorus while in transport in the Le Sueur basin.

Table 4. Suspended sediment total and dissolved phosphorus estimated using proportions of sediment from distinct sources at the uplands gage location and at the watershed outlet.

	UPLANDS			WATERSHED OUTLET		
Sediment Source Category	**% Sediment from Source Category**	**Weighted Average TP (mg/kg)**	**Weighted Average DOP (mg/kg)**	**% Sediment from Source Category**	**Weighted Average TP (mg/kg)**	**Weighted Average DOP (mg/kg)**
Agricultural Upland Soil	66%	438	21	17%	112	5
Ravine	0%	0	0	12%	25	3
Bluff	10%	66	1	44%	276	3
Streambank - Upland or incised	23%	161	8	27%	190	9
Sum - estimate of background Sediment-P associated with Suspended Sediment	100%	664	30	100%	604	20

Application of Sediment Phosphorus to the Sediment Budget

The application of these source sediment phosphorus concentrations to the sediment budget reveals the relative contribution of total and dissolved phosphorus from each of these sediment sources to the river and its spatial heterogeneity (Figures 7 and 8, Table 3). Predicted concentrations of sediment-derived phosphorus at given gage locations were found by summing inputs from upland agricultural fields, bluffs, streambanks, and ravines, and subtracting sediment removed through trapping by sinks in lakes and floodplains. These predictions were then compared to observed loads from the network of gages on the Le Sueur River (Table 5).

Dividing predicted load by observed load, we find that only 24% of TP, <2% of DOP, and 37% of PP are attributable to fine sediment introductions to the channel at the watershed scale (Table 5). This also shows that a larger proportion of TP at the lower gage and watershed outlet than at the upper gages may be derived from sediment, while a larger proportion of DOP comes from upland sediments than from lower reaches of the system (Table 5).

Table 5. Results of "Predicted" sediment-derived phosphorus load (g/yr), 2009-2012 compared to "Observed" loads.

		TOTAL PHOSPHORUS TP (kg/yr) - Le Sueur River			DISSOLVED ORTHOPHOSPHATE DOP (kg/yr) - Le Sueur River			PARTICULATE PHOSPHORUS PP (kg/yr) - Le Sueur River		
	Location	Uplands	Incised Zone	Watershed Outlet	Uplands	Incised Zone	Watershed Outlet	Uplands	Incised Zone	Watershed Outlet
inputs	Upland	9,181	11,580	18,994	442	557	914	8,739	11,022	18,080
inputs	Ravine	0	826	4,294	0	96	497	0	731	3,797
inputs	Bluff	1,379	13,595	46,909	13	124	429	1,367	13,471	46,480
inputs	Streambank	3,373	6,619	20,060	166	212	535	3,206	6,406	19,525
storage	Lake	1,822	3,704	7,152	88	178	344	1,734	3,525	6,807
storage	Flood Plain	1,919	1,919	14,187	86	86	293	1,834	1,834	13,893
out	**Predicted g/yr**	10,192	26,997	68,919	448	726	1,737	9,744	26,271	67,181
	Observed g/yr	56,843	82,351	290,719	26,977	27,747	108,122	20,203	40,604	133,175
	Pred/Obs	**18%**	**33%**	**24%**	**1.7%**	**2.6%**	**1.6%**	**48%**	**65%**	**50%**

Within this context of the proportion of TP, DOP, and PP load derived from sediment, we can examine the extent to which the sediment-derived portion of load is driven by distinct sources (Figures 7 and 8). Sediment-derived TP and PP are nearly identical in their apportionment (exactly identical at the upland gages), and also nearly match the apportionment for sediment itself that was presented in Figure 4. At the upland gages, a majority of the sediment-derived TP and PP comes from upland sources, while at the outlet this is overwhelmed by sediment-derived TP and PP from near channel sources including bluffs, streambanks and ravines, with over 50% of sediment-derived TP and PP coming from bluffs alone. At the upper gage, above the incised zone in agricultural uplands, agricultural topsoil erosion supplies 66% of the TP load, while 24% is derived from erosion of ditch network and first order streambanks. At the watershed outlet, near channel erosion of bluffs, streambanks, and ravines overwhelms the budget (in agreement with the sediment budget underlying this analysis), comprising 79% of measured sediment-phosphorus load, with 52% of the total load coming from bluff erosion alone. Relative to the sediment budget, agricultural upland erosion comprises a larger portion of the sediment-derived TP budget (22% as opposed to 17%) (Figure 7).

Sediment-derived DOP, which comprises only a tiny fraction of the total DOP load (<2% as shown in Table 5 and Figure 7), retains a stronger upland source signal throughout the watershed, with 38% coming from uplands at the watershed outlet despite the massive influx of sediment in the incised zone. This is likely attributable to the low DOP associated with bluff sediment and high DOP associated with upland sediment.

Examining the loads of TP, PP, and DOP derived from distinct sediment sources at the upland, incised and watershed outlet gages on the Le Sueur reveals the extent to which PP drives the TP loading from sediment, and also shows how distinct sources dominate at these unique geomorphic positions along the stream network (Figure 8). For

TP and PP, bluff sediment contributions increase nearly 10-fold between the uplands and incised zone, and triple from the incised zone gage on the Le Sueur at County Road 8 above the Maple and Cobb confluences and the watershed outlet. The watershed outlet shows a greater than four-fold increase in total, particulate, and dissolved phosphorus load compared to the upland gage on the Le Sueur (Figure 8).

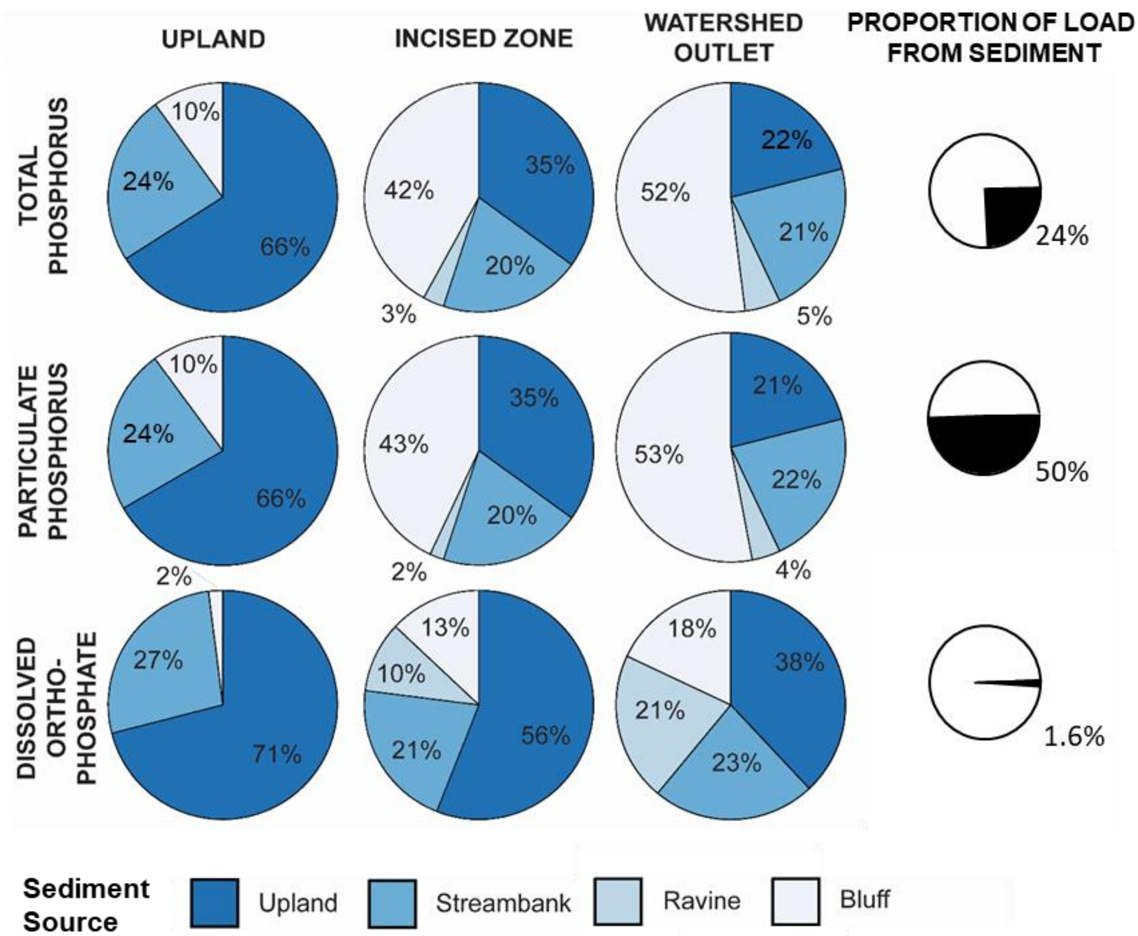


Figure 7. Apportionment of average annual loads of sediment-derived total phosphorus (TP), particulate phosphorus (PP) and dissolved orthophosphate (DOP) to their sediment sources at distinct geomorphic locations along the Le Sueur River including in uplands at the St. Clair gage, within the incised zone at County Road 8, and at the watershed outlet, where the signal of the Maple and Cobb River tributaries is integrated. Apportionment shown corresponds to the sediment-derived fraction of total load for each of these constituents, which is shown at the right.

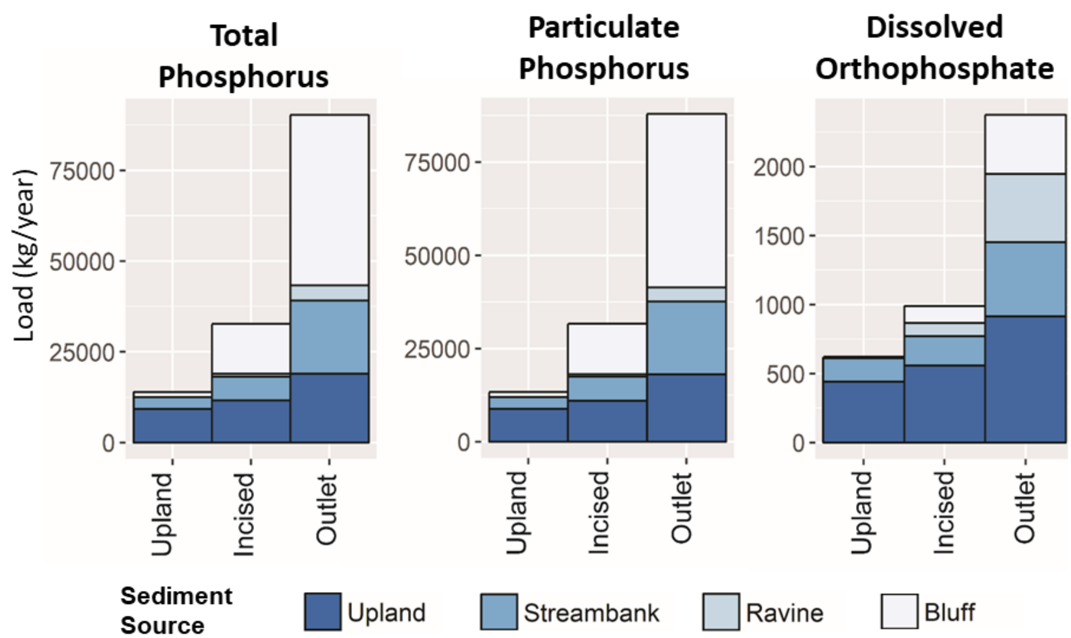


Figure 8. Average annual input of sediment-derived TP, DOP, and PP from distinct sediment sources to gage locations in the Le Sueur River uplands (at St. Clair), incised zone (at County Road 8) and at the watershed outlet. These data represent inputs and do not account for removal by lakes and flood plains. Data correspond to the monitoring period 2009-2012.

While this apportionment provides valuable information about the relative contribution of sediment sources to TP loading, it does not address the larger question of how much of the TP moving through the Le Sueur Basin is derived from sediment as a source. To examine this question, estimates of sediment-derived phosphorus must be compared to observed TP loads from the network of gages along the Le Sueur and its tributaries.

Combining results of load estimates from the gage network with mass balance results helps to constrain contributions from distinct pools. Load estimates from the gage network show that dissolved orthophosphate comprised an average of 36% of the TP load measured at the watershed outlet during the study period (2009-2012). When our predicted average dissolved organic phosphorus is added to this, we see that dissolved phosphorus comprises 54% of total, while particulate phosphorus accounted for the other 46% (Figure 9). Partitioning this further by multiplying the proportions of observed dissolved and particulate-P load accounted for by sediment (1.6% of dissolved and 50% of PP at the watershed outlet, Table 5) by the proportions of the total-P load observed at the watershed outlet (54% dissolved and 46% particulate) reveals that 23% of the total-P budget is comprised of source sediment-derived PP, while another 23% of the total budget is in particulate form but non-source sediment-derived. Only approximately 2% of the DOP at the watershed outlet was attributable to source sediment, and when applied to the 37% of the observed TP at the watershed outlet that is comprised of DOP (i.e. 0.37 * 0.02 – this excludes dissolved organic P because our water extractions were analyzed for the reactive fraction, DOP), this translates to 1% of the TP budget coming from sediment-derived DOP (Figure 9). That leaves 36% of the total budget that is comprised of DOP coming from some form of direct runoff or leakage in dissolved form.

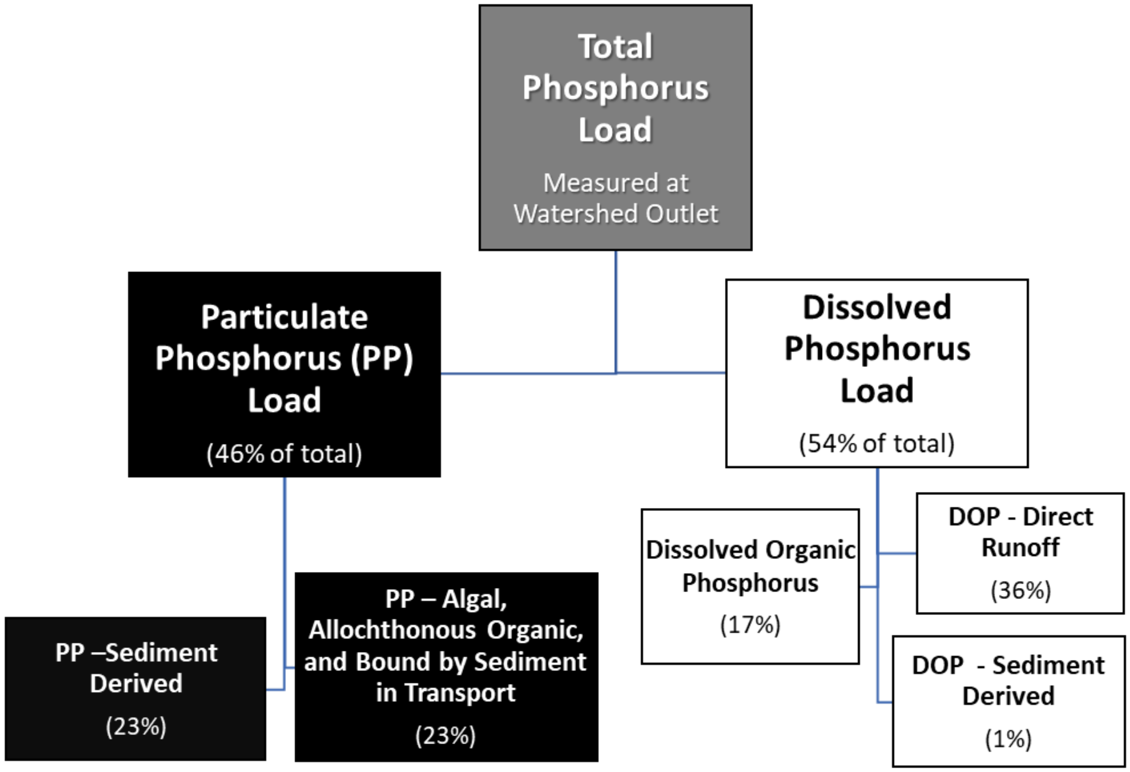


Figure 9. Flow chart showing apportionment of TP load into distinct pools, approximated using load monitoring data from the network of gages on the Le Sueur and its tributaries and results of mass balance for sediment-derived phosphorus. This mass balance reveals that only 24% of TP measured at the watershed outlet can be attributed directly to source-sediment.

Discussion

While it may be expected that sediment would serve as the primary source of phosphorus in such a heavily eroding and highly agricultural river basin, results of our mass balance for sediment-derived phosphorus demonstrate that sediment serves as a modulator of phosphorus dynamics, but not as its primary source. This decoupling of phosphorus and sediment source not only suggests that continued evaluation of phosphorus source maybe necessary, but also points to the importance of mechanisms other than erosion to the introduction of phosphorus, such as runoff of dissolved and non-sediment allochthonous particulate phosphorus.   Historical trends in phosphorus and sediment export and the details of this budget for sediment-derived phosphorus can assist in further constraining the role of sediment. These analyses can also assist in pointing toward mechanisms other than erosion which contribute to phosphorus loading in the Le Sueur. These findings are important to consider in the development of management strategies to address excess phosphorus in the Le Sueur River basin.

Trends in Phosphorus and Sediment

Analysis of historical data reveals important relationships between flow and concentration and export of phosphorus and sediment over time. Plots of concentration versus discharge showed positive linear correlation between flow and DOP, PP and TSS (used to represent suspended sediment). These positive correlations implicate storm flow for delivery of high loads of each of these constituents. Sediment is widely understood to be mobilized by high flow events, and these results indicate that sediment and phosphorus have similar behavior with respect to flow. This is unsurprising in the case of PP, due to its strong association with sediment (though PP may also be non-mineral such as that which is derived from particulate organic matter, algae, and microbial cells), but was less expected in the case of DOP.

Relationships between yields at the upland and watershed outlet gages on the Maple River help elucidate where in the basin processes that drive export are greatest for DOP, PP, and TSS (Figure 3). Particulate phosphorus and TSS display a similar relationship, with low yields skewed toward the uplands and high yields skewed toward the incised zone. This correspondence between PP and TSS is likely due to the strong relationship between sediment and particulate phosphorus. The shift from upper to lower basin skew observed in both particulate phosphorus and TSS correspond to a change in flow regime that drives a shift in sediment export in the incised zone. Previous work by Cho (2017a) and Cho et al. (2017) has indicated that at a stream discharge threshold of 3.6 m^3/s, sediment loading in the incised zone of the Maple River increases dramatically, changing from one power function to another (Cho, 2017a). This flow threshold is understood to mark the initiation of erosion of streambank and bluff sediments (Cho, 2017a).

Dissolved orthophosphate, on the other hand, skews toward the uplands across the range of yields suggesting that upland release of dissolved phosphorus dominates watershed-wide export. There are several potential causes for this which warrant further exploration. First, DOP source may be greater in the upland reaches of the watershed. Not only are the uplands highly agricultural, but the upper part of this basin is characterized by extensive artificial drainage, which has been demonstrated by the Discovery Farms monitoring program to serve as a conduit for dissolved phosphorus transport (Discovery Farms, 2018). The uplands are also where floodplain connectivity is greatest (though still low relative to less incised settings). Floodplains are hotspots for nutrient processing, and subsequently, when inundated, can become sites of export (Noe et al., 2013). However, elevated DOP source may not be the only reason for this skew toward the uplands, rather it may also reflect the depression of DOP load via sorption by bluff and streambank sediment introduced in the incised zone, which could convert DOP to particulate form. Further exploration of the results of the budget for sediment-derived phosphorus can help constrain dissolved and particulate phosphorus load and the sources of each.

Sediment-derived Phosphorus Budget implications

Sediments from distinct source areas in this basin were demonstrated to have differing TP and water extractable DOP characteristics. Agricultural top soils and upland ditch-bank sediments had high TP and the highest extractable DOP of any of the source sediments. Upland ditch-bank samples have higher mean TP and DOP than agricultural soils, suggesting that upland ditch networks may be accumulating high concentrations of sediment-derived phosphorus. Bluff till and alluvium (which were sampled at least 10 m above the water's surface and have little contact with the channel) have high naturally occurring TP, but consistently low extractable DOP. Previous studies have shown that, while bluff till material is high in TP, as much as 73% of that phosphorus on average is bound to calcium (Grundtner, 2013) and would not become bioavailable without dissolution of the mineral structures. Streambank alluvium and till, which are in more frequent contact with river water than bluff features, were found by our analyses to be depleted in both TP and DOP. This may be a result of preferential removal of finer sediment particles which tend to store more phosphorus, as evidenced by the lower median percent clay and silt associated with these sediments (Figure A3 F and G). These sediments were also depleted in iron, aluminum, and calcium relative to bluff sediment (Figure A3 A, B, and C), likely due to preferential removal during interaction with the active channel. For all sediment types, linear models examining analysis of variance in TP between sediment source groups shows statistically significant difference ($F = 5.514$, $p = 3.659e^{-7}$). These differences in TP concentration are likely resultant of differences in chemical and physical properties of these sediments. Adding iron and aluminum to this linear model shows that these variables are strongly explanatory for TP concentrations ($p = 5.669e^{-12}$ for source sediment category, $p = 1.410e^{-8}$ for iron, and $p = 1.336e^{-5}$ for aluminum).

Suspended sediment, which is comprised of a mix of these sediment sources, has much higher total and dissolved-P than would be predicted by a weighted average of the sources contributing to its composition (Table 4). Instead, fine suspended sediment average TP concentrations (1,197 mg/kg P for the upper and lower gage combined) are twice as high as the highest source concentration, and average water extractable DOP concentrations (61 mg/kg extractable-P for the upper and lower gage combined) are nearly twice that of the highest extractable concentrations from source sediment. This is likely a result of interactions with the water column and the sorption of DOP by suspended sediment during transport, and of the inclusion of organic (algal, microbial) phosphorus as part of TSS, which could be broken down via the sieving and drying of these sediments, causing them to be measured as both TP and DOP associated with our suspended sediment samples. Higher TP and DOP in suspended sediment at the upland gage than at the watershed outlet gage is expected due to the predominance of higher phosphorus concentration sediment (agricultural topsoil and upland ditch-bank sediment) in that part of the system. However, in both the case of the upper and lower basin, fine suspended sediment bears a higher TP and DOP signature than can be accounted for by simply considering TP and DOP associated with the mix of sediments known to comprise average annual loads at these gage locations. Examining the potential of each of the source sediment types contributing to suspended sediment to bind phosphorus in transport can help elucidate potential causes for the discrepancy between observed and predicted suspended sediment phosphorus concentrations.

Sediments from upland agricultural sources differ from near channel sediments in their mineralogy, texture, and organic content as well as their background phosphorus form and concentration. These characteristics affect the capacity of sediment to bind and release dissolved, bioavailable phosphorus. The sediment budget development for this basin (modified from Belmont et al., 2011, Gran et al., 2011; Bevis, 2015) demonstrated that near channel sediment is the dominant source in the lower, incised portion of the Le Sueur River and its tributaries, while agricultural topsoil erosion dominates in the uplands. This muting of the upland sediment signal is owed to the massive influx of near channel sediment occurring in the incised zone of the Le Sueur, and to the high near channel sediment loads coming from the Maple and Cobb Rivers which enter the Le Sueur upstream of the watershed outlet. Agricultural top-soils have high organic content as well as high iron and aluminum concentrations and low calcium concentrations compared to bluff till sediments (Figure A3 D, A, B, and C respectively). Iron-bound phosphorus is widely understood to be more exchangeable than that which is bound to aluminum oxides or oxyhydroxides or bound in mineral structures with calcium carbonates. This speaks to the facility with which phosphorus associated with agricultural sediments may be converted to dissolved, bioavailable form when compared to materials from near channel sources. Bluff till and alluvium are higher in calcium (Figure A3 C), which can precipitate with phosphorus to form more stable mineral structures that are less exchangeable with the water column. Thus, the spatially heterogeneous distribution of these sediment additions is likely to have implications for phosphorus fate and transport in this system, with upland sediment donating phosphorus and incised zone sediment binding some of that dissolved load and contributing to the accumulation of particulate phosphorus in the channel corridor and downstream receiving waters.

Using the results of our budget analysis in conjunction with average annual observed loads from 2009-2012, we are able to parse apart important sources of the TP budget for the Le Sueur River Basin. Using observed loads of TP and DOP from the MPCA, we found the average annual PP of load by difference, and corrected this estimate based on the average percent of PP known to be composed of dissolved organic P for this basin. This reveals that on an average annual basis, TP load is 37% DOP, 17% dissolved organic P, and 46% PP (Figure 10A). Our budget analysis for sediment-derived phosphorus demonstrated that only 24% of TP could be explained by fresh inputs of fine sediment from distinct erosional source areas, with 23% of this in particulate form and 1% in dissolved form (Figure 10B). This leaves 23% of the TP budget that is particulate form but not associated with source sediment. This missing load could include a combination of algal-P, PP from allochthonous/terrestrial organic material or coarse particles >63 μm in size, and PP that is formed in the channel corridor as a result of sorption of dissolved form-P onto sediment, which in turn may depress the dissolved-P signal at a watershed scale. Incorporation of estimates of algal phosphorus load (Dolph, 2017a) into the budget suggested that 4% of TP could be algal (Figure 10C), leaving 19% of the budget as some combination of allochthonous organic PP or PP formed via sorption. Further, application of results of sorptive capacity estimates reported by Grundtner (2013) for sediments from this basin suggested that, if all sediments bound the maximum possible phosphorus in mg/kg of sediment, 24% of the TP observed at the watershed outlet could be explained by sorption of DOP to sediment during transport (Figure 10D). This estimate is larger than the 19% of the budget that we estimated would encompass PP formed via sorption, likely because this is a high-end estimate of the sorbed fraction of the budget (Figure 10D).

This analysis suggests that the true magnitude of dissolved phosphorus inputs may be masked by sorption to sediment. Without sorption and uptake of dissolved phosphorus, we estimate that DOP load could be as much as 24% higher, comprising 61% of average annual load rather than the 37% observed at the basin outlet. Our estimated corrected DOP load of 61% of TP is similar to values observed in other agricultural watersheds that lack extensive post-glacial incision and that have much lower sediment yields (Boardman, 2016, Peterson et al., 2017). Summing all the sources of dissolved-P (the 37% of the average annual budget that is measured as DOP, plus average dissolved organic P (17%), plus the portion that may be bound to sediment and dissolved organic P (24%)), we find that as much as 78% of TP exported from the basin may have entered the stream network as dissolved-P. If we divide the percent sorbed (24%) by this potential total dissolved-P (78%), we find that sorption may mask the total dissolved-P load by as much as 31%. Dissolved organic P is not included in our estimates of sorbed concentration because the sorption tests discussed measured DOP, the reactive portion, rather than total dissolved P, which would have allowed us to find the organic portion by difference.

While sorption clearly plays an important role in governing P phase at the scale of the Le Sueur watershed's total phosphorus budget, this scenario of all sediments reaching their full sorptive capacity may be unlikely due to ambient DOP conditions that are far below the concentrations that drive sediment to bind a maximal amount of phosphorus.

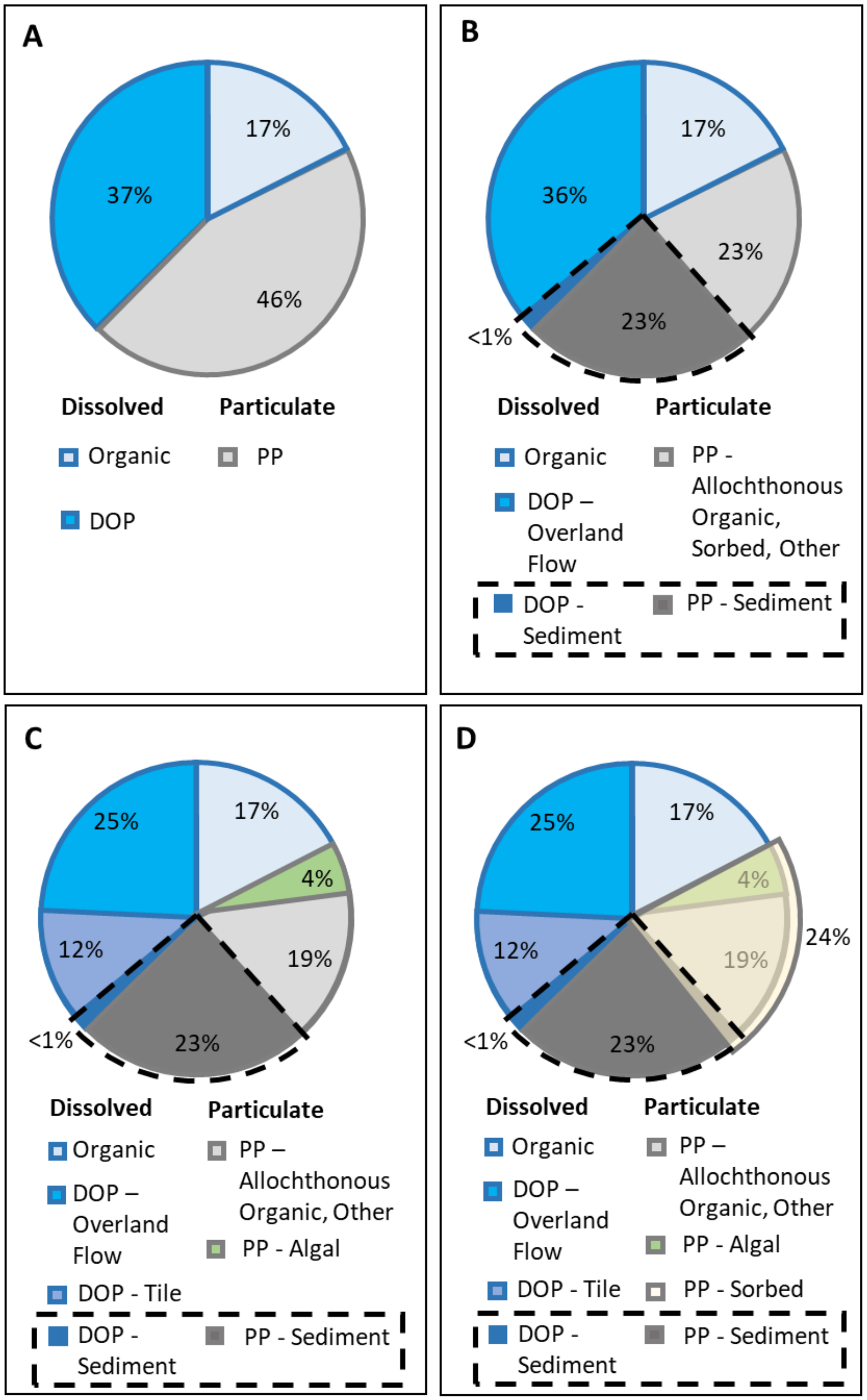


Figure 10. Estimated TP budget apportionment for the Le Sueur watershed outlet, partitioned into forms and export processes. Figure incorporates results from this study as well as from previous work (Grundtner, 2013; Wall et al., 2017), and unpublished data (Dolph, 2017a; Dolph, 2017b; Wall, 2017). “PP” refers to particulate phosphorus and “DOP” to dissolved orthophosphate. Portion of load derived from sediment is indicated with dashed lines.

Our budget for sediment-derived phosphorus also demonstrated that only approximately 2% of the DOP at the watershed outlet could be attributed to source sediment, or 1% of the TP budget. That leaves 36% of the total budget that is comprised of DOP that is coming from direct runoff from the landscape such as may be flushed by storm events or delivered through drainage tiles, or from leaking sources such as highly saturated sediment in upland ditch networks. An even larger percent of dissolved P may be moving through these pathways if organic P were considered, but we are unable to parse apart the dissolved organic portion of the budget because it was not measured. Using estimates of drain tile density for this basin (Wall et al., 2017) and estimates of tile nutrient flux from Discovery Farms Minnesota locations within the Le Sueur watershed (Wall, 2017), we estimate that as much as 18% of the TP at the watershed outlet may be tile derived, 12% as DOP (Figure 10D) and 6% as PP. If we correct this PP for the portion of TP load expected to be in dissolved organic form, we find that this is 3% particulate and 3% dissolved organic P. These results highlight the importance of dissolved phosphorus source and transformation along the transport path, and the strong role of sediment in driving bioavailability. This points not only to the importance of investigating dissolved-P sources, but also to mechanisms for movement between dissolved and particulate pools and the influence of these processes on basin-wide phosphorus behavior.

Previous work by Boardman (2016) has demonstrated that proportions of dissolved to particulate phosphorus vary widely across Minnesota watersheds, with the Le Sueur River among the lowest with respect to its ratio of DOP to PP. While correcting PP for dissolved organic P changes observed PP from 61% of the TP budget to 46%, PP is still a critical component of this budget. Multiple regression of landscape variables against PP and DOP suggested that PP was most strongly related to TSS export, which in turn was correlated to bluff and streambank erosion, while DOP was most strongly related to fertilizer inputs in Minnesota watersheds (Boardman, 2016). Streambank and other near channel sediments have been demonstrated in many environments to be high in phosphorus (>250 mg/kg, as discussed in Fox, et al. 2016 and references therein). While streambank and other near-channel source sediment erosion is a clear contributor to phosphorus loading, the potential of that phosphorus to become bioavailable may vary based upon the evolutionary history of the features being eroded. Phosphorus additions to upland agricultural soils has resulted in P concentrations 2-10 times higher than in natural mineral soils occurring in forested environments (Fox, et al. 2016 and references therein). The potential impacts of introduction of sediment-P from fields to streams versus streambank erosion to river systems (in particular the potential of that P becoming bioavailable during transport in the river corridor) also varies not only with initial concentration of TP but also with the amount of P bound to different minerals. McDowell and Sharpley showed that while streambank sediments in their study catchment in an agricultural part of Pennsylvania had higher TP, bed sediments released more DOP to the water column. This higher release of P was attributed to higher concentrations of extractable iron to which that phosphorus may bind and be released under anoxic conditions (McDowell & Sharpley, 2001). Streambank erosion can serve as an important source of phosphorus to watersheds and therefore be a critical target for management, however, the role of streambanks as a source also varies widely among watersheds, contributing anywhere from 6-93% of TP load (Fox et al., 2016 and references therein). Therefore, it is critical that watersheds be evaluated on a case by case basis for their primary sources of TP and DOP and the driving mechanisms for movement of DOP in and out of particulate pools.

Implications for Management

Sediment and phosphorus loads from the Minnesota River Basin are some of the highest in the state of Minnesota, and results of our mass balance for sediment-derived phosphorus suggest that, while phosphorus fate is strongly affected by sediment, sediment does not serve as the primary source of phosphorus. This has important implications for management because it suggests that even if we were able to address 100% of erosion, we could only reduce TP loads by at most 24%. This decoupling of phosphorus and sediment source may be attributable to heightened runoff of dissolved phosphorus due to saturation of soils in agricultural settings, especially ditches where phosphorus-rich sediment accumulates. Tile drainage, which is extensive in this basin, may also serve as a conduit for elevated introduction of phosphorus in both dissolved and particulate form. Furthermore, if the signal of dissolved phosphorus loss is in fact muted by sorption to sediment as this budget suggests, then reducing erosion may only serve to alter the form of phosphorus in transport, resulting in higher dissolved, bioavailable phosphorus loads. Therefore, management strategies that reduce dissolved phosphorus source will be as important as those that reduce erosion if phosphorus reductions are to be achieved. Further, more information about the role of sediment as source or sink for phosphorus under typical ambient stream DOP conditions is needed to understand the extent to which adsorption and desorption may drive stream concentrations of dissolved versus particulate phosphorus and subsequent bioavailability.

Despite the importance of dissolved phosphorus source management, managing sediment source can still offer important benefits with respect to phosphorus reduction. Near-channel sediment may play multiple roles in influencing phosphorus behavior in this basin, acting as a source of TP and a sink for dissolved phosphorus which may subsequently be stored in the channel corridor and beyond. Agricultural sediment and upland ditch-bank and streambank sediments have order-of-magnitude higher extractable-P, which would become part of the dissolved, bioavailable-P pool immediately upon delivery of this sediment to the channel corridor and would also be likely to be leached from these soils from their position in the landscape. Thus, agricultural top soil is also still an important management target due to its disproportionate contribution to stream concentrations of bioavailable DOP.

Accordingly, management must consider spatial heterogeneity of dominant sediment source and corresponding phosphorus content. Previous investigation of sediment routing through the basin has revealed that not just erosion but delivery of eroded sediment to streams varies widely based on the geomorphic setting within the basin. This understanding informed the development of a water and sediment routing model that seeks to determine best placement for management practices across the landscape for reduction of sediment loss from the basin. This model has demonstrated that a mix of approaches tailored to the varying geomorphology can provide the most effective and affordable reductions in sediment. In particular, this modeling effort suggests that water storage in upland settings may greatly reduce sediment loading to the Le Sueur by both trapping sediment along its transport path and by retaining water in the landscape to reduce peak flows which initiate bluff erosion, the primary source of sediment to this system (Cho, 2017a, Cho et al., 2017). Practices that promote water retention in uplands, such as wetland restoration, not only decrease peak flows, but also serve to trap sediment, process and store nutrients, and provide habitat for waterfowl and other biota (Cho, 2017a; Wall et al., 2014). However, accumulation of phosphorus-enriched sediment in these settings may result in water storage areas transitioning from phosphorus traps to sources of dissolved phosphorus load over time requiring additional consideration in their construction and management to reduce this risk. Furthermore, sediment routing can delay the downstream movement of P, further decoupling best management practices from their intended water quality improvement time scale. Incorporating data describing sediment phosphorus concentrations and dynamics of phosphorus as it moves between dissolved and particulate form into such models will vastly improve our ability to manage for multiple benefits.

A holistic view of the Le Sueur Basin and other post-glacial watersheds of the Upper Midwestern United States must consider the distinct geomorphology and corresponding sediment geochemistry of these rivers and their implications for best management. By tailoring management to geomorphic context and targeting water retention in the uplands of such environments, we may be able to reduce both erosion and phosphorus flux, and work toward slowing the accumulation of particulate "legacy" phosphorus in channels and in downstream receiving waters.

Conclusion

Though the role of sediment as a source of phosphorus to watersheds is widely accepted, results of our analysis suggest that only 24% of TP measured at the outlet of the highly agricultural Le Sueur watershed could be attributed to source sediment. Results of our budget analysis suggest that, while sediment plays a strong role in driving phosphorus bioavailability and persistence in the environment, it is not the primary source in this basin. Dissolved phosphorus not only comprises a large portion of loads that cannot be attributed to source sediment, but the true magnitude of dissolved load may be masked due to sorption processes between DOP and fresh mineral sediments from bluffs and streambanks.   Further investigation is needed to explore the role of sorption processes in driving phosphorus export and retention from fluvial networks, particularly in geomorphic settings such as the post-glacial Le Sueur River Basin, where large contributions of fine-grained glacial till sediment may serve to bind dissolved phosphorus in transport, thus generating potential for development of legacy phosphorus in the fluvial network and in downstream receiving waters.

Incorporation of results of sediment-phosphorus mass balance into models for placement of management practices for reduction of erosion and sediment transport will greatly aid our understanding of how to manage watersheds for reduction of both erosive loss of sediment and phosphorus. However, modeling of phosphorus transport and management practice effectiveness cannot be complete without constraining the sources, sinks and transformations of dissolved phosphorus. Greater understanding of the movement of dissolved phosphorus between soluble and bound form via equilibrium exchange with sediment and movement in and out of the biological pool is needed at the scale of large river basins to guide management of dissolved and particulate phosphorus. Better understanding of dissolved P will help guide the development of management practices to prevent the development of legacy stores of high phosphorus sediment in fluvial networks and receiving waters, which will in turn make whole network reductions in phosphorus more attainable.

Chapter 2

In-stream sediment-phosphorus equilibrium processes and their implications for basin-scale phosphorus dynamics in the agricultural Le Sueur River Basin

Summary

Equilibrium (sorption) processes are important in regulating phosphorus form, bioavailability, and persistence in stream environments. This study examined the sorptive behavior of sediment sources entering the Le Sueur River from bank and bluff erosion using laboratory experiments designed to mimic field channel conditions. These analyses used native river water and a ratio of sediment to solution representative of high TSS concentrations in the Le Sueur River, and tested sediment from primary erosion sources including agricultural upland fields, upland ditch-banks, alluvial streambanks, and glacial till bluffs. Sorption was tested across a range of stream-relevant DOP spiking concentrations, in contrast to tests that determine sorptive capacity by spiking sediments to orders of magnitude higher phosphate concentrations than those that occur in the stream environments discussed in chapter one. Weighting factors were applied to our sorption data to find the average sorbed concentration associated with bed sediment, TSS in suspension under average daily DOP concentrations, and as TSS under event conditions corresponding to daily export loads >1% of average annual TSS load. Results of these analyses suggest that agricultural top soils and upland ditch-bank sediments are sources of DOP upon entering channels, while bluff tills and streambank alluvial

sediments are sinks for dissolved phosphorus. When we incorporated these weighted, stream-relevant sorbed phosphorus concentrations into the sediment-phosphorus budget described in chapter one, we observed that particulate phosphorus formed via sorption accounted for only 2% of average annual TP load measured at the outlet of the Le Sueur River. This estimate of the proportion of total load that may be influenced by sorption is much smaller than estimates derived using published values of sorptive capacity (Grundtner, 2013), which suggested sorbed particulate phosphorus could comprise as much as 24% of TP (detailed in chapter one). We expect that the true proportion of particulate load comprised by sediment bound phosphorus that forms via sorption in the river corridor falls between these two end members. The use of sorptive capacity represents an upper bound because typical stream dissolved orthophosphate conditions are too low to drive sediment to its sorptive capacity and our experimental results represent a lower bound because they only characterize what occurs in the first 24 hours of interaction between sediment and the water column and did not capture longer-term equilibrium processes. In either case, the net effect of sediment at a watershed scale is to bind phosphate from the water column, depressing the signal of DOP and increasing the mass of bound particulate phosphorus. This sediment-bound particulate phosphorus may settle out and be stored in the river corridor or downstream receiving waters as legacy phosphorus rather than being flushed out of the system in dissolved form. These results point to the importance of managing both dissolved phosphorus and sediment inputs in order to slow eutrophication and the development of legacy phosphorus stores in the channel corridor and downstream receiving waters.

Introduction

Phosphorus (P) in aquatic ecosystems is a primary cause of eutrophication. Sediment, owing to its capacity to transport, bind and release P, is an important modulator of its concentration and bioavailability. Sediment may serve to donate or remove dissolved phosphorus from stream water, forming sediment-bound particulate phosphorus, and may settle out and be stored on timescales ranging from days to centuries (Sharpley et al., 2013). The role of sediment in driving stream phosphorus concentrations has been explored in estuarine (Pant & Reddy, 2001), lake (Stone & Mudroch, 1989; Olila & Reddy, 1993) and riverine (Grundtner et al., 2014; Jalali & Peikam, 2013; James & Larson, 2008; Kerr et al., 2011) settings. River phosphorus and sediment dynamics, in turn, have been investigated with respect to the influences of stream bank sediment (Fox et al., 2016), fluvial suspended sediment (James & Larson, 2008) , and bed sediment (House, 2003) on phosphorus form and bioavailability. These studies and others attest to the complexity of sorption reactions and their importance in regulating stream dissolved phosphorus concentrations.

As previously discussed, the bioavailability and persistence of phosphorus in the environment are both regulated in part by equilibrium processes with sediment. The potential for phosphorus to be removed from the water column and stored in sediment-bound particulate form varies based on sediment geochemistry, stream phosphorus concentrations, and sediment equilibrium phosphorus concentration. Additionally, the potential for this bound, particulate phosphorus to be released back to the water column depends on the type of bond formed. Phosphorus bound to iron oxides and oxyhydroxides and heavily weathered minerals is more likely to be released than that bound to aluminum oxides or precipitated with calcium phosphate minerals (Records et al., 2016 and references therein). Redox conditions, pH, and temperature also affect the likelihood of release (see thesis introduction for additional details).

Sorption experiments are a common laboratory approach to testing the capacity of sediment to bind and release phosphorus over a range of simulated water column DOP conditions. These tests involve spiking sediment at a range of phosphate concentrations and allowing equilibration over a 24-hour period. Following equilibration, the concentration in solution is plotted against sorbed concentration to examine the relationship between stream phosphorus level and sorptive behavior of sediments. Equilibrium phosphorus concentration in solution can be equated with stream conditions when looking at these plots, with the x-axis representing the stream concentration where sediment transitions from desorbing (negative sorbed concentrations) to adsorbing (positive concentrations). This point is referred to as the equilibrium phosphorus concentration at zero sorption. The equilibrium concentration at this point can be likened to the stream concentration above which sediment will bind phosphorus and below which it will desorb phosphorus. This type of data can be incorporated into phosphorus budgets to quantify the role of equilibrium exchange in governing basin wide phosphorus behavior (James & Larson, 2008; Stabel & Geiger, 1985).

This study builds upon a budget describing sediment-derived phosphorus in the Le Sueur River basin (see thesis introduction and chapter one methods for details about this study area and development of the budget). Using this budget, historical data, and sorption experimental results, we explore the most relevant stream dissolved orthophosphate (DOP) conditions corresponding to suspended sediment load in order to describe the most likely sorptive behavior of sediments moving through this basin. The budget describes the extent to which basin total phosphorus (TP) can be attributed to sediment as a source, and partitions TP into its dissolved and particulate fractions and their respective sources. Furthermore, the budget described in chapter one makes a first attempt to differentiate between particulate phosphorus (PP) that is derived from allochthonous sources from that which is formed via adsorption of phosphorus by sediment in the channel corridor. This estimate of particulate load formed via in-stream equilibrium processes uses sorptive capacity of sediment determined in controlled sorption tests by Grundtner (2013) that used a weak molarity calcium chloride solution rather than river water, a ratio of sediment to solution that is much higher than observed TSS concentrations, and which spiked sediments to DOP concentrations an order of magnitude larger than any observed in the Le Sueur river basin. Thus, this estimate represents the maximum sorption that could be achieved if all sediment bound phosphate to its capacity. In this chapter we explore a lower bound estimate of in-stream particulate phosphorus formation, using sorption tests that mimic natural stream conditions, and restricting these results based on average in-stream DOP conditions using monitoring data from the watershed. We apply weighted average sorbed concentration associated with each distinct sediment source to the budget to establish an estimate of the portion of particulate phosphorus formed via in-stream processes under average stream conditions. Results of this analysis offer a broadened understanding of the potential role of sediment in driving in-stream phosphorus dynamics including the depression of stream DOP concentrations and the formation of particulate phosphorus that may settle out and become temporarily stored in the channel corridor and downstream receiving waters, generating “legacy” phosphorus that may be released or resuspended and fuel algal blooms long after its introduction to the stream.

Methods

Sorption experiments

The primary objective of these sorption tests was to isolate equilibrium exchange of phosphorus between sediment and the water column while mimicking natural channel conditions as closely as possible. Tests of sorption of DOP to sediment followed a modified version of Nair et al. (1984), a widely used protocol in studies of phosphorus equilibrium with sediment. This method used filtered (0.45 µm) Le Sueur River water collected in January 2016 under low (~40 µg/L) DOP conditions. In addition to using native river water, the tests used a ratio of sediment to solution that mimics high total suspended solids (TSS) in the basin (500 mg/L or 1:2000), and spiking concentrations that are at environmentally relevant stream conditions in the Le Sueur River (40 (background), 100, 200, 300, 400, 500, 750, 1000 µg/L). Stock solutions used to spike sediments consisted of a mix of river water, 20 g/L chloroform (added to inhibit microbial uptake of P during equilibration) and phosphate added to the previously mentioned spiking levels. Fresh stock solutions were prepared 24 hours at most prior to spiking and were stored at approximately 4° C.

Sorption tests were carried out on samples representing each of the major sediment sources to the Le Sueur River basin, namely, agricultural topsoil, bluff till sediment, streambank alluvial sediment, and upland ditch-bank sediment, as well as on suspended sediments collected from the river at the upper gage (above the zone of incision) and lower gage (at the watershed outlet) (see chapter one for further collection details). These sediments were dried at 60° C, disaggregated, wet sieved to 63 µm, dried at 60° C again and disaggregated a second time. For each sample, 0.02 g of dried sediment was weighed into a series of eight 50-mL centrifuge tubes, and 40 mL of solution was added to each, corresponding to the given treatment. Each series of eight spiking concentrations was run in duplicate or triplicate. Samples were dosed with solution, capped, sealed with electrical tape, and shaken on a rotary shaker at 125 rpm for 24 hours at room temperature. Samples were shaken on their sides to maximize mixing. A set of eight "blank" matrix spikes corresponding to each of the eight stock solutions but containing no sediment, were added at the same volume (40 mL) to individual centrifuge tubes and added to the shaker to equilibrate alongside the sediment samples. Following the 24-hour equilibration, samples were removed, and each solution was filtered to 0.45 µm and analyzed for DOP using the ascorbic acid method (detailed in Janke et al., 2014). Spiking solutions were tested for initial and final DOP concentration.

Additionally, pH was monitored in initial spiking solutions and final equilibrated solutions during six of these final experiments to ensure pH was consistent throughout these tests.

In addition to the suite of tests described above, several adjustments to the method were attempted in order to identify sources of variability observed in the relationship between sorbed-P concentration and equilibrium-P concentration. Matrix effects were explored by comparing results from the tests with Le Sueur River water to those carried out in a weak (0.005 M) calcium chloride solution, chosen for agreement with prior studies in the basin and to minimize interference from calcium in isolating the equilibrium exchange between sediment and solution. A higher range of phosphorus concentrations was also tested, which included spiking concentrations 2,500, 5,000, and 10,000 µg/L P with fewer levels at the environmentally relevant (background – 1,000 µg/L) range. Four ratios of sediment to solution were also tested (1:25, 1:100, 1:200, 1:2000) in order to compare with more standard methods (1:25 (Nair et al., 1984 and many others); 1:100 (Grundtner et al, 2014); 1:200 (ratio used in water extractable-P tests (Kleinman et al., 2005)) to more environmentally relevant ratios (1:2000 (James and Larson, 2008)). See Appendix B for additional details and results.

Data Analysis

Sorption tests are a commonly used experimental technique for determining sediment sorptive capacity (Smax) and equilibrium phosphorus concentration at zero net sorption. In traditional sorption tests, the difference between initial spiking solution concentration and final phosphorus (P) concentration in solution (following equilibration with sediment) is taken as the amount of P sorbed by sediment during the equilibration process. Here we measured initial and final stock solution concentration in blanks and used the final concentration in our blanks as “initial” concentration in these calculations. This was done in order to correct for two potential sources of phosphorus transformation occurring over the course of the tests. The first of these potential transformations is a decrease in DOP in solution due to precipitation of phosphate minerals, such as the calcium-phosphate mineral apatite [$Ca_5(PO_4)_3OH$]. The potential for precipitation of calcium phosphates was suggested by high calcium levels in the Le Sueur River water (Table 6 presents results of elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) and major ion analysis via ion chromatography of Le Sueur river water used in these sorption experiments). The second of these potential transformations is an increase in DOP resulting from microbial cell lysis. Although this water was filtered to 0.45 µm, some microbes are small enough to pass through this filter, and the addition of chloroform to solution may cause their cell walls to rupture, releasing DOP into solution. The use of final concentration in our blanks at the end of equilibration as the “initial” concentration in our calculations of sorbed-P concentration makes the assumption that any change that occurred from start to finish in the solutions themselves was a background effect that should be removed from the measurement to ensure that equilibrium exchange was isolated. This corrected sorbed concentration in µg/L was converted to mg/kg of sediment and plotted against equilibrium-P concentration to examine sorptive capacity.

Table 6. Elemental and major ion chemistry of water used in sorption experiments collected from the Le Sueur River at St. Clair, January 2016.

Analysis	ICP-OES					Ion Chromatography		
Element or Ion	**Al**	**Ca**	**Fe**	**Mg**	**P**	**Cl-**	**NO^{3-} -N**	**SO_4^{2-} -S**
Concentration (mg/L)	<0.006	117.070	<0.001	32.610	0.044	20.9	7.8	10.6

Results of controlled laboratory sorption experiments are frequently evaluated using two common analytical solutions to evaluate sorptive properties of sediment - the Langmuir and Freundlich equations (Grundtner et al., 2014; Guzner, 2017; Hongthanat, 2010; House, 2003; James & Larson, 2008; Pant & Reddy, 2001; Stabel & Geiger, 1985). These equations fit the data described above (sorbed concentration plotted as a function of equilibrium concentration) to a logarithmic distribution, using equations which can be solved to provide sorptive capacity (Smax). Due to the non-logarithmic form of most of our data, these variables could not be obtained for the final tests conducted under environmentally representative conditions.

In lieu of logarithmic data that could be fit to an isotherm, we obtained weighted averages of sorbed concentration for the distinct source sediment categories across an environmentally relevant range of stream DOP and TSS conditions and applied these averages to sediment loads quantified by a sediment budget for the Le Sueur River basin. This provided estimates of percent of TP that may be formed during exchange between the river water and sediment during transport, and the percent of DOP that may be removed from solution via adsorption to sediment in the stream corridor.

Three methods were used to determine the most environmentally relevant stream DOP concentration for application in weighting average sorbed concentration. Each of these methods corresponded to a different compartment of in-channel exchange of P, namely, between 1) the river water and bed sediment, 2) TSS in suspension, and 3) the bulk of TSS exported from the basin. Each of these methods used daily DOP and/or TSS concentration or load data from the Le Sueur watershed outlet to restrict and weight the sorbed concentration data. Daily stream DOP and TSS data, consisting of a mix of measured and modeled observations, were downloaded from the MPCA's website for 2009-2012 (MPCA Data Viewer, 2017). The Le Sueur watershed outlet was used because it integrates the signal of the entire watershed, and because it is the only site in the basin with annual records of flow and corresponding DOP and TSS measurements with which to generate daily estimates for the entire year. Daily DOP data were broken into bins of concentration in 100 µg/L increments (resulting in bins of <100, 101-200, 201-300, 301-400, 401-500, 501-600, 601-700, 701-800, 801-900, 901-1000). Weights were established by binning daily observed stream DOP concentration, finding the frequency of DOP observations in a given bin that would correspond to each of the previously mentioned compartments of in-channel P exchange (bed sediment, TSS in suspension, and TSS exported), and using that frequency as a weighting factor for sorbed concentration.

Weighting factors were applied to sorbed concentrations based on the understanding that equilibrium-P can be equated to stream concentration in these tests. As shown in Figure 11, experimental sorbed concentrations were broken into bins based on their corresponding equilibrium P (which is equivalent to stream DOP), and weights (which in turn were derived from gage data distributions of DOP) were applied to the sorbed concentrations found in each bin. In this conceptual figure the heaviest weight (shown in italics) was applied to observations between the bin 200-300 µg/L equilibrium P (shown in the darkest box), indicating that the bulk of stream DOP observations in this conceptual example were between 200-300 µg/L, while most of the experimental results fall in the lowest equilibrium concentration bin (0-100 µg/L). This weighting scheme gives the greatest weight to those experimental results that correspond most closely to environmental conditions that would characterize a given compartment of in-stream interactions between sediment and DOP.

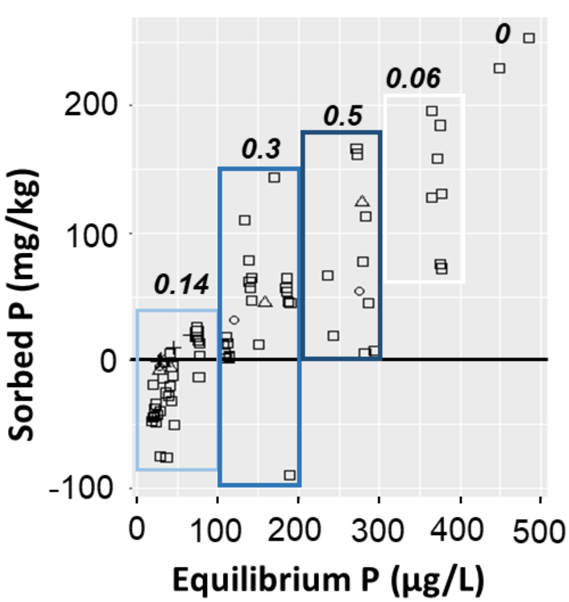


Figure 11. Conceptual diagram showing application of weighting factors (given in italics) to sorption data. Weighting factors were determined in these analyses using the frequency of stream dissolved orthophosphate (DOP) concentration under a given condition. Weights are applied to bins of equilibrium phosphorus (P) concentration (shown in rectangles) based on the understanding that equilibrium P can be equated with stream DOP concentration in interpreting these plots.

For the three evaluations of sediment-P exchange with the water column, the bin receiving the heaviest weight differed as a result of the distinct methods used to restrict the data (Table 7). For exchange of P between the water column and bed sediment, the entire set of MPCA daily DOP concentration observations from the Le Sueur watershed outlet from 2009-2012 (corresponding to the sediment-derived phosphorus budget) were used. This was done assuming that bed sediment is exposed to the water column on all days of the year regardless of flow condition. Thus, the weighted means of sorbed concentration produced are reflective of ambient stream conditions that would affect bed sediment and its equilibrium with the water column.

Table 7. Stream dissolved orthophosphate (DOP) concentration (2009-2012) bins and weighting factors. The strongest weights are given in bold italics for each evaluation.

	Bed Sediment		TSS in suspension		TSS Exported	
Bin - DOP (µg/L)	**n**	**weight**	**n**	**weight**	**n**	**weight**
<100	1221	***0.836***	1217	***0.864***	10	0.152
101-200	164	0.112	156	0.111	21	0.318
201-300	54	0.037	35	0.025	31	***0.470***
301-400	11	0.008			4	0.061
401-500	3	0.002				
501-600	4	0.003				
601-700	1	0.001				
701-800	2	0.001				
801-900	1	0.001				

Interactions between the water column and suspended sediment on an average day, on the other hand, were restricted using the 98th percentile of TSS concentration, which was 500 mg/L (which is also the concentration of sediment used in our sorption tests). This restricted DOP data set was then further restricted to the 98th percentile of DOP concentrations, and weights were established based on the frequency of occurrence of DOP observations within a given bin (Figure 12, Table 7). These weights were in turn applied to sorbed concentration as was done for bed sediments. This produced a dataset of weighted average sorbed concentration reflective of the most common conditions affecting TSS in suspension.

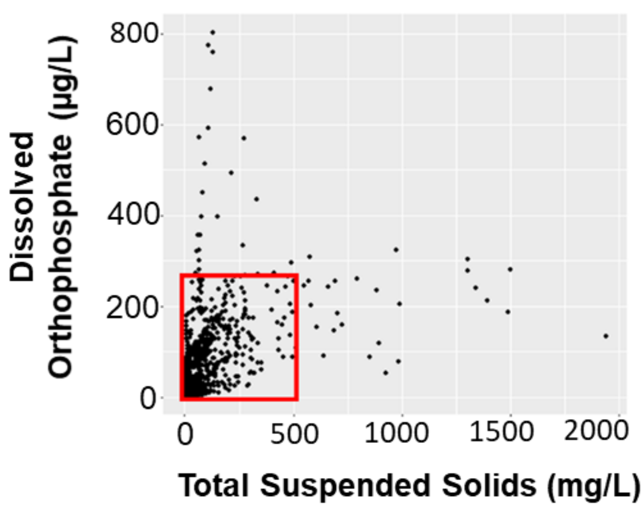


Figure 12. Daily DOP concentration plotted against TSS concentration at the Le Sueur watershed outlet, 2009-2012. The red box indicates where TSS and DOP are each subset to less than the 98th percentile of their concentration.

Lastly, since most of the sediment exported by river systems is exported in a handful of high flow events, those events that export at least 1% of the average annual TSS load were considered. Average annual TSS load was computed for 2009-2012 to correspond to a sediment-phosphorus budget developed for the basin. Days where sediment load comprised at least 1% of the average annual load for the monitoring period 2009-2012 were identified, and the orthophosphate data were restricted to only these days where the bulk of sediment was transported. The timeframe 2009-2012 was used for correspondence to the period of greatest monitoring data availability, for representativeness of long term load trends, and for agreement with the sediment-phosphorus budget detailed in chapter one (see Table A1, associated with chapter 1 for context of average annual loads for monitoring period 2009-2012 versus longer periods of record). These orthophosphate observations were binned and used to establish weighting factors that were in turn applied in a weighted average of sorbed concentration for each sediment type. Weighted mean sorbed concentration from this evaluation was applied to a sediment budget to estimate potential mass of DOP bound by sediment in transport.

Results

Sorption test results

Plots of sorptive properties of soils and sediments from the Le Sueur River basin reveal the challenges of isolating equilibrium exchange in the context of the complex aqueous chemistry of aquatic ecosystems. Sorption tests frequently employ phosphorus spiking concentrations that extend well beyond the levels observed in natural systems. This is done in order to ensure that the relationship between equilibrium phosphorus concentration and sorbed concentration reaches a plateau at the sediment's maximum sorptive capacity. Tests using an agricultural top-soil sediment, Ag-19, run to spiking concentrations as high as 10,000 mg/L (an order of magnitude higher than any observed concentration in the river) using Le Sueur River water and a high sediment to solution ratio (1:100) produces a smooth curve when plotting equilibrium P concentration against sorbed concentration (Figure 13).

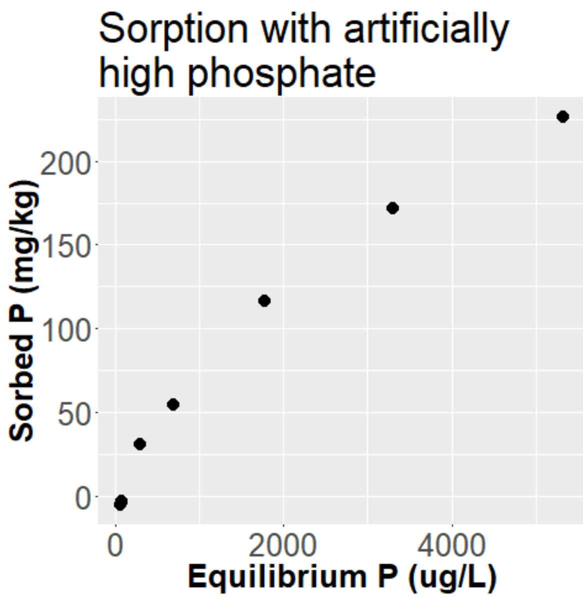


Figure 13. Sorption isotherm for sample Ag-19, spiked 10,000 µg/L phosphate in Le Sueur River water at a 1:100 sediment to solution ratio.

Even though this curve does not strongly plateau, its logarithmic shape lends it to being fit to an isotherm to determine sorptive capacity (see Figure B1, Smax = 418.1 mg/kg, which exceeds the sorbed concentrations observed even when sediments were spiked to 10 mg/L P). This example suggests that stream concentrations more than an order of magnitude higher than those observed in the Le Sueur River would have been needed to achieve Smax for this sediment sample during a 24-hour period.

Results tests which mimic natural conditions, on the other hand, showed substantial variability and were not able to be fit to an determine sorptive capacity. Replicate tests of the same sample (Ag-19) run with higher resolution (more spiking concentrations) within an environmentally relevant range of DOP concentrations and at a ratio of sediment to solution that reflects natural conditions (1:2000, equivalent to 500 mg/L sediment) show substantial variability in the relationship between sorbed and equilibrium P (Figure 14). These results could not be fitted to an isotherm to determine Smax.

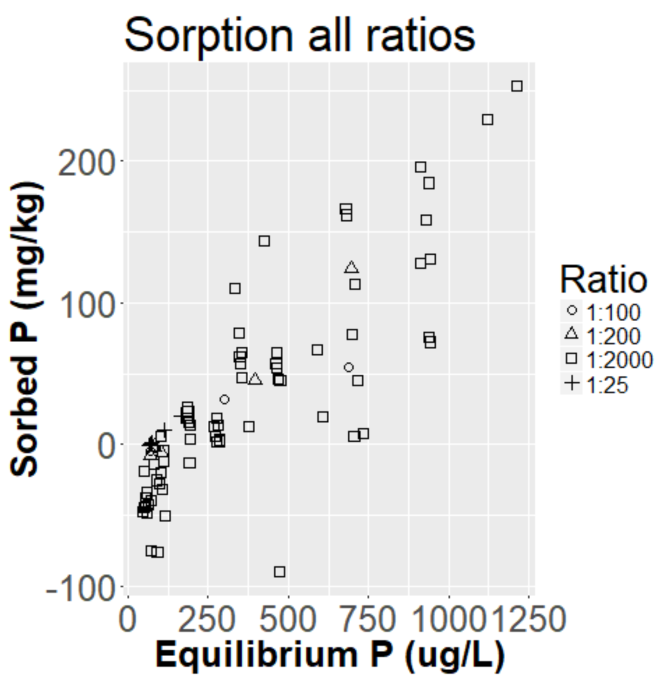


Figure 14. A single agricultural soil (Ag-19) was run at four different ratios of soil to Le Sueur river water, showing variability in the relationship between sorbed and equilibrium P concentrations. This sample was run at the 1:2000 ratio with replication at a range of spiking concentrations because this ratio represents an environmentally relevant TSS concentration (500 mg/L). Other ratios were run without replication and only at a limited number of spiking concentrations

While the results of our sorption tests exhibit variability, a distinct trend in the relationship between sorbed-P concentration and equilibrium-P concentration in solution at the end of the experiments is observed. Results of tests run on the same sample (Ag-19) using the same spiking solutions with four distinct ratios of sediment to solution show a consistent trend crossing the x-axis at an equilibrium phosphorus concentration between 50 and 350 µg/L, releasing phosphorus at concentrations less than equilibrium concentration (below the x-axis) and binding phosphorus above (Figure 14). The greatest variability observed was in the results of tests using an environmentally relevant ratio of sediment to solution (1:2000). This high degree of variability was observed in samples representing all source sediment types that were tested in this environmentally relevant range of P spiking concentrations and with an environmentally relevant ratio of sediment to Le Sueur River water (1:2000, which is equivalent to 500 mg/L). However, even with this high degree of variability within tests run on individual samples, distinct differences in the sorptive behavior of sediment from differing source categories was observed.

Trends in average sorbed concentration across replicate treatments

The distinct sorptive properties of agricultural top-soil, bluff glacial till, stream bank alluvium, and upland ditch-banks were summarized by plotting averages of sorbed- and equilibrium-P concentration across the replicates for each sample; by constructing boxplots to look at differences in distribution of sorbed concentration between source sediment groups; and using one-way ANOVA to determine the statistical significance of differences in mean sorbed concentration between groups.

Plotting averages of sorbed- and equilibrium-P concentrations at each target spiking concentration by sediment type revealed distinct patterns in sorbed concentration based on sediment origin and physicochemical properties (Figure 15). The equilibrium concentration where each sample crosses the x-axis can be thought of as the corresponding stream concentration where the sediment moves from desorbing (negative sorbed concentration) to adsorbing (positive sorbed concentration) phosphorus.

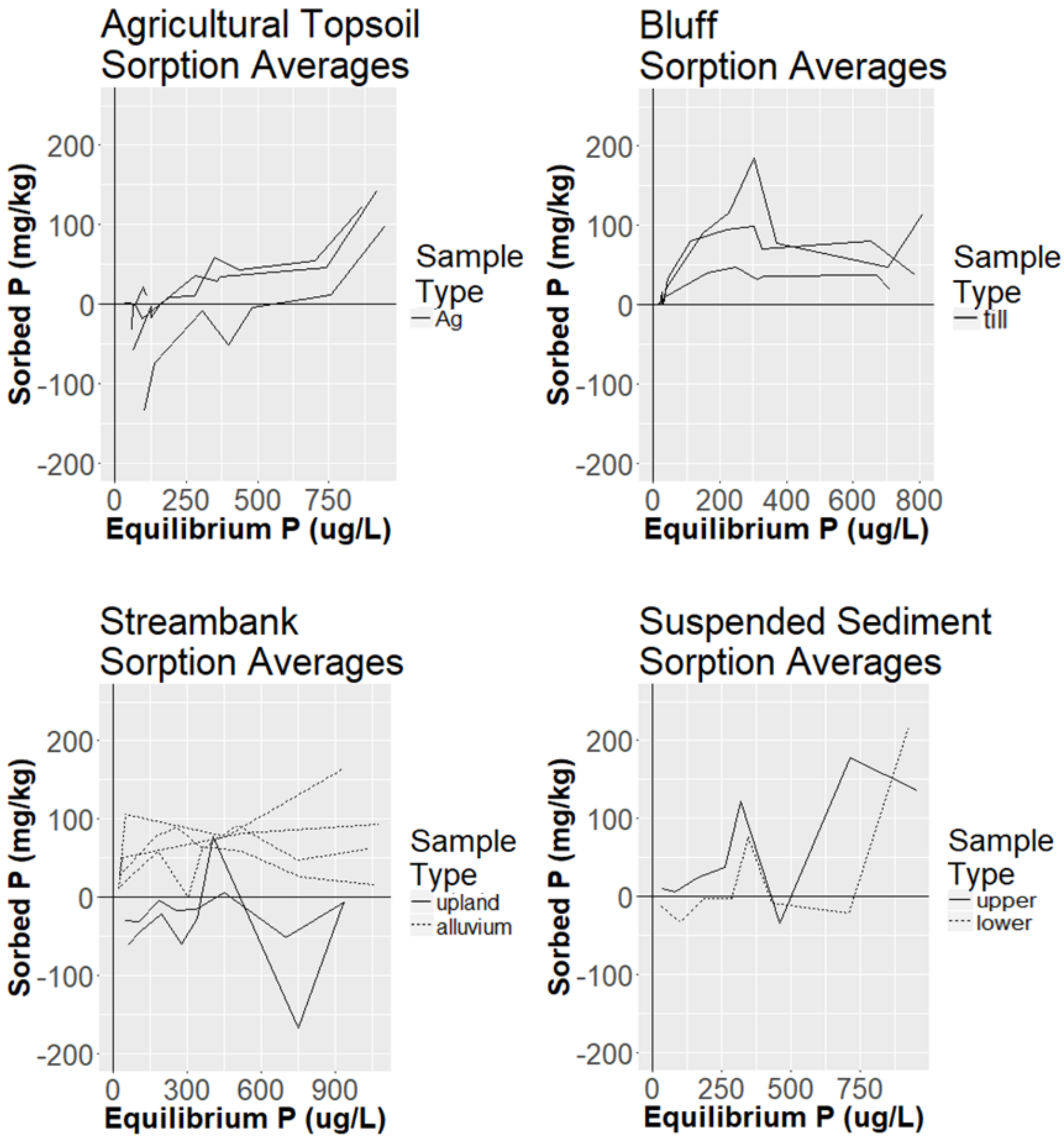


Figure 15. Average sorbed-phosphorus (P) and equilibrium-P by target spiking concentration for individual samples plotted together by sediment source category (agricultural, bluff, streambank, and suspended sediment). Dashed and solid lines indicate differing subtypes within a category (i.e. streambank alluvium versus upland ditch-bank sediment, and suspended sediment from the upper and lower gage on the Le Sueur River).

Agricultural sediments desorbed phosphorus at low stream DOP concentrations and adsorbed at higher concentrations, with a large range of equilibrium-P concentrations (50 - ~550 µg/L) among samples. Bluff till sediment, in contrast, had positive average sorbed concentration at all stream DOP concentrations, indicating that this sediment would bind phosphorus from the water column at all environmentally relevant stream DOP conditions. Similarly, alluvial streambank sediment collected from the incised zone of the river binds phosphorus at all spiking concentrations. However, streambank sediment from organic-rich upland ditch-bank sites desorbed phosphorus across nearly all ambient equilibrium/stream DOP conditions (Figure 15).

Suspended sediments collected at the upper and lower gage on the Le Sueur represent a mixture of these source sediments that have been interacting with the water column during transport. Proportions of sediment from each of these sources varies with position in the watershed, with 66% of suspended sediment coming from agricultural top-soil erosion at the upper gage, and only 17% at the lower gage attributable to uplands sources while the other 83% is derived from near channel sources (see chapter one). However, the sorptive behavior of suspended sediments collected from the upper and lower gage are quite similar. Suspended sediments from both gages bind phosphorus at most equilibrium concentrations but show a decline in sorption at moderate equilibrium concentrations (~500 -750 µg/L) (Figure 15).

These differences between source sediment groups were also summarized using boxplots (Figure 16), which confirm that at environmentally relevant stream DOP concentrations, agricultural topsoil and upland ditch-banks predominantly desorb P while bluff till and alluvium adsorb P. One-way ANOVA revealed these groups to have statistically significant difference in mean sorbed concentration ($F = 36.161$, $p = 2.2*10^{-16}$)

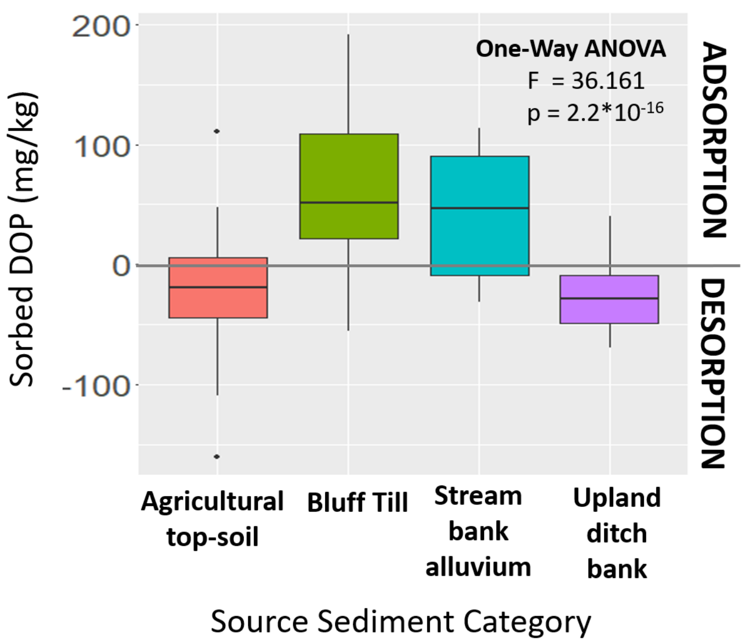


Figure 16. Boxplots showing distribution of sorbed DOP concentration for source sediments from four categories.

Determination of sorptive properties of bed sediment, suspended sediment, and exported suspended sediment

To further explore the potential net effects of sorption and desorption by this mix of sediment upon phosphorus fate and form in the Le Sueur River, sorbed concentration data were summarized according to conditions affecting bed sediment, suspended sediment on an average day, and suspended sediment exported from the basin. As previously described, due to the non-logarithmic nature of our sorption test data, sorptive capacity could not be determined, and instead, weighted averages of sorbed concentration associated with each sediment type were obtained within the most environmentally pertinent range of stream DOP conditions. Weighted averages that reflect the most relevant stream DOP conditions interacting with bed sediment (<100 µg/L), suspended sediment in suspension on an average day (also <100 µg/L), and suspended sediment during major storm events when the bulk of TSS export occurs (100-300 µg/L) (Tables 6 and 7) were determined. Average sorbed P concentrations corresponding to the bulk of TSS export were then multiplied by mass of sediment described by the sediment budget (Gran et al., 2011; Bevis, 2015) to find the potential average annual mass of phosphorus bound by sediment during transport.

First, daily bed sediment exposure to stream DOP was considered using the full range of daily DOP concentrations, binning these concentrations, and using their frequency to generate a weighted average of sorbed-P concentration. Maximum DOP concentration was 803 µg/L. Average sorbed concentration estimates of -42.2 mg/kg for agricultural soils, -34.3 mg/kg for upland ditch-banks, 37.9 mg/kg for alluvial streambank material, and 32.7 mg/kg for glacial till bluff material were found, where positive values indicate adsorption and negative values indicate desorption (Table 8).

Table 8. Weighted average sorbed-phosphorus concentrations.

Target	DOP* max (µg/L)	n DOP* obs	Mean sorbed-P (mg/kg) at this range of stream concentrations					
			Ag	Bl	SB-U	SB-A	SS-U	SS-L
Bed sediment 2009-2012	803	1461	-42.2	32.7	-34.3	37.9	10.3	-17.1
TSS in suspension 2009-2012	266	1408	-43.4	31.9	-34.7	37.7	9.6	-17.7
Exported suspended sediment 2009-2012	333	66	-14.8	68.5	-28.6	47.5	25.9	-1.5

*DOP = dissolved orthophosphate measured at the Le Sueur watershed outlet

Second, suspended sediment interactions with the water column were considered by restricting daily monitoring data first to the 98th percentile of TSS concentrations and second to the 98th percentile of stream DOP concentrations. The plot of DOP concentration against TSS concentration shows that the highest TSS concentrations observed in the Le Sueur (above 500 mg/L) are interacting with lower DOP concentrations (Figure 12). The 98th percentile of DOP concentration in this TSS concentration range (less than 500 mg/L) was 266 mg/L DOP. Obtaining a weighted average of sorbed concentration across the range of DOP concentrations in this data subset (0-266 mg/kg DOP) produced comparable results to those found for bed sediment (Table 8).

Third, the bulk of annual suspended sediment export was examined in order to consider DOP conditions that would interact during most of the sediment export described by the Le Sueur sediment budget. This was accomplished by looking at DOP conditions corresponding to days where >1% of the average annual TSS load from the Le

Sueur watershed outlet was transported. The maximum DOP concentration in this group of high TSS export events was 333 mg/L. Weighting factors for DOP established based upon this restricted data set were applied to the sorption data. These weighted averages show lower magnitude desorption from agricultural top-soils and upland ditch-banks (-14.8 and -28.6 mg/kg sorbed, respectively), and higher magnitude adsorption by bluff and alluvial stream bank materials (68.5 and 47.5 mg/kg sorbed, respectively) (Table 8).

Results of this evaluation provide a range of average conditions affecting sediment that occurs as TSS or stored bed sediment in the channel, and show that agricultural top soils desorb 14.8 to 42.2 mg/kg phosphate on average while bluff till sediment adsorbs 32.7 to 68.5 mg/kg across the range of relevant stream orthophosphate concentrations observed in the Le Sueur. Sediment from streambanks varies based on location within the basin; with upland ditch-banks desorbing 28.6 to 34.7 mg/kg P and incised zone alluvial streambanks adsorbing 37.7 to 47.5 mg/kg on average.

Application of sorbed concentration averages to sediment-phosphorus budget

In order to evaluate the potential net effect of sorption on DOP loads in the Le Sueur River, weighted average sorbed concentrations for each source sediment type (Table 8) were applied to the sediment-phosphorus budget developed for this basin. As described in the methods section, this evaluation used weighted averages obtained across the range of stream DOP conditions where TSS load was >1% of total average annual load. Average sorbed-P concentration for each sediment type was incorporated by multiplying average sorbed-P in mg/kg by sediment mass from each distinct source in Mg/yr, giving results in g/yr, which were then converted to kg/yr (Table 9). These average sorbed-P concentrations, which were weighted based on conditions where the bulk of TSS export occurs, have the highest sorption by bluff and streambank alluvium, and the lowest release of P by agricultural and upland-ditch bank sediments of any of our evaluations of sorption by DOP sediment. Average annual sorbed P loads were found through the same process described in the methods section of chapter 1 for the sediment-derived P budgets. Here, "Predicted" sorbed load is compared to "Observed" load of TP measured at each location in Table 9.

Table 9. Le Sueur River sorbed-phosphorus budget using weighted average sorbed concentration corresponding to events where greater than 1% of average annual TSS export. Negative values indicate desorption, positive values indicate adsorption.

	Average Annual Sorbed Phosphorus Budget (kg/year)		
	Uplands	Incised Zone	Watershed Outlet
Upland	-206	-260	-427
Ravine	0	111	578
Bluff	150	1,474	5,086
Streambank	-139	294	1,433
Lake	-41	-83	-161
Flood plain	-27	-27	1,078
Predicted Sorbed-P	**-128**	**1,729**	**5,754**
Observed TP	56,843	82,351	290,719
Pred/Obs	**-0.2%**	**2.1%**	**2.0%**

These source sediment effects were summed to find the net effect of sorption by sediment on DOP at each gaged location along the river corridor on an average annual basis. The upper gage on the Le Sueur was dominated by desorption (net -128 kg/yr sorbed) while the watershed outlet showed adsorption three orders of magnitude greater (5,754 kg/yr). Comparison of this mass of phosphorus potentially bound by fine suspended sediment to the measured TP loads at the watershed outlet suggests that, on average, 2% of the TP budget may be comprised of particulate phase phosphorus that is formed via adsorption of dissolved P to sediment in the channel network (Table 9, Figure 17B).

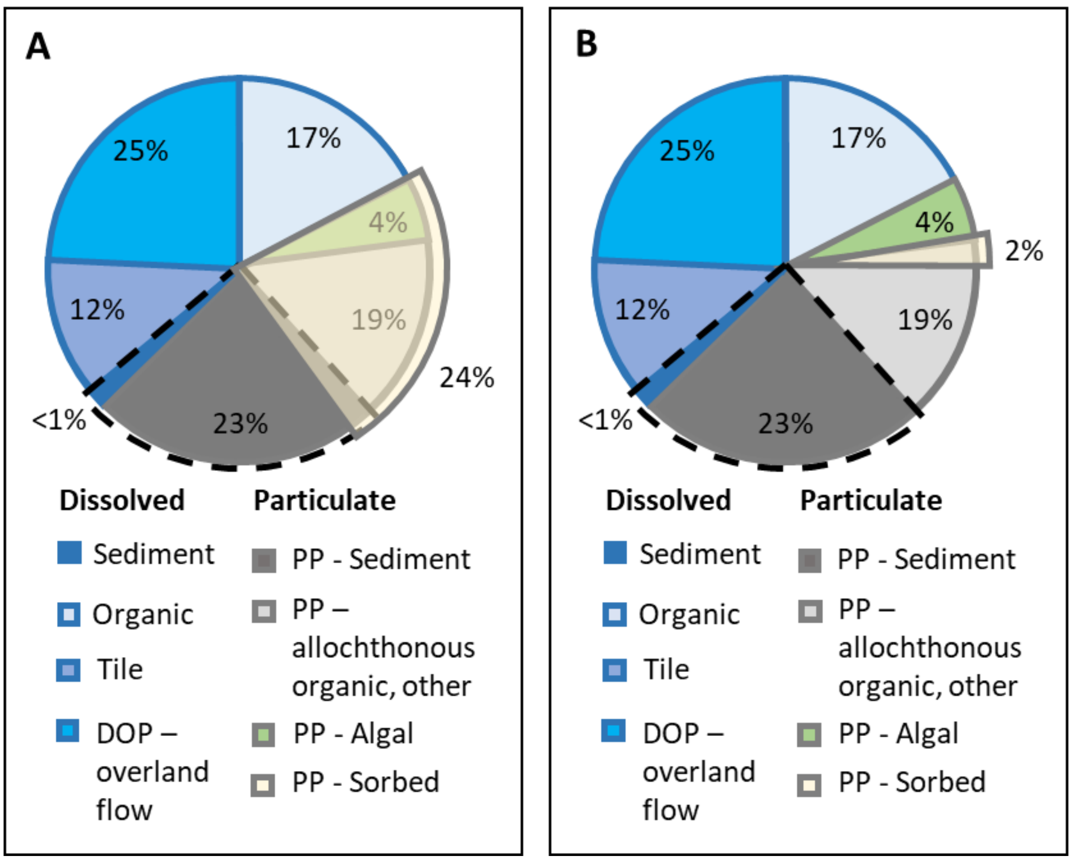


Figure 17. Adjusted TP budget for the Le Sueur watershed outlet. Figure 17A shows apportionment including an estimate of sorbed load using Smax from Grundtner (2013). Figure 17B incorporates results of the application of weighted average sorbed concentration determined as part of this study. Dashed line shows the portion of TP derived from sediment directly.

Discussion

Sorptive effects of sediment of differing origin in storage and in transport

In evaluating basin scale phosphorus dynamics and strategies to mitigate excess phosphorus loss, considering the effects of sediment from all its distinct sources to the channel and their potential for binding and releasing phosphorus to the water column is critically important. Results of sorption tests from the Le Sueur River basin indicate that sediment from distinct sources behaves differently with regard to its capacity to bind and release phosphorus. We contextualize this by examining average sorbed concentrations under differing flow conditions. Differing flow conditions are considered by finding weighted average sorbed concentration for each of these sediments under stream DOP conditions that would be experienced by bed sediment under low flow conditions, by suspended sediment under moderate flow conditions, and suspended sediment under the highest sediment loading events that occur in the basin. The results of these weighted averages suggest that sorptive behavior of sediment is similar whether under low flow conditions affecting bed sediment and under moderate conditions affecting TSS in suspension. However, weighted average sorbed concentration corresponding to events that contribute >1% of average annual TSS load showed that bluff and stream bank sediments bind more phosphorus and agricultural sediments release less phosphorus under these conditions (Table 8).

These results suggest that agricultural and upland sediment will undergo a larger magnitude of phosphorus release when stored as bed sediment (under low flow conditions) or in suspension as TSS under moderate flow conditions than under major storm events where the majority of TSS export occurs. This is due to the higher frequency of higher DOP observations during events where >1% of TSS is exported compared to on an average day, which places greater weight on those observations (highest weighting factors are highlighted in Table 7, and a conceptual example of the weighting method is shown in Figure 11). Under ambient daily conditions, the majority of stream DOP concentrations are <100 µg/L (83% of observations for bed sediment and 86% for TSS in suspension), while during events that contribute >1% of the average annual TSS load, only 15% of observations fall below 100 µg/L, while 47% are between 200 and 300 µg/L. This stronger weighting of higher stream DOP concentrations results in higher sorbed concentrations associated with bluff till and streambank alluvial sediments, and lower magnitude release (less negative sorption) from agricultural top-soils and upland ditch-bank sediments on average.

Phosphorus sorption by suspended sediment and application of sorbed phosphorus concentrations to the sediment phosphorus budget

Condensing the results of these tests into a single value representing the sorptive properties of each sediment type was particularly challenging due to temporal variation in both TSS and orthophosphate concentration, and because the two do not vary linearly, as evidenced by the plot of DOP against TSS concentration (Figure 12). However, restricting the sorption data to the most relevant stream DOP concentrations corresponding to TSS export allows us to obtain a weighted average sorbed concentration that can be reasonably applied to a sediment budget which averages TSS export over time and space.

In the Le Sueur River basin, the net effect of sediment on stream DOP concentration varies with stream size and geomorphology and the associated mix of sediments entering the network. In the uplands, where agricultural top-soil and phosphorus rich streambank sediment together comprise 90% of the sediment inputs (see chapter one), the net contribution of sediment to the TP budget is to donate dissolved phosphorus to the water column (Table 9). This is likely due to the sediments in uplands having a high degree of saturation with P, which has been observed in previous studies (Dodd & Sharpley, 2015) in agricultural settings. However, within the incised zone and at the watershed outlet, this mass balance for sorbed-P is overwhelmed by the higher magnitude of average sorbed-P and greater mass of bluff and streambank sediments.

The high capacity of bluff and streambank sediment for sorption of phosphorus generates a net sorption of DOP by suspended sediment at the watershed scale. This finding corroborates previous work conducted in the Le Sueur River Basin (Grundtner et al., 2014). Additionally, we found that suspended sediments from the upper and lower gage both exhibited sorption of DOP at most spiking concentrations in our sorption tests, supporting the findings of studies of suspended sediment binding capacity conducted in the lower Minnesota River downstream of the Le Sueur (James & Larson, 2008). These findings suggest that sediment plays an important role in partitioning TP into particulate and dissolved form at the scale of the Le Sueur River basin. As suggested in chapter one, some fraction of the DOP introduced to the system in the uplands is likely bound by suspended sediment (which is comprised largely of bluff and streambank materials) in the incised zone of the river, resulting in an increase in PP and a depression of the DOP load observed at the outlet compared to the amount input in the headwaters.

Incorporating our weighted average sorbed-P concentrations into the budget suggests that the portion of this budget comprised by sorbed-P formed via instream processes is of smaller magnitude than was indicated by the incorporation of sorptive capacity (from Grundtner, 2013). These results suggest that only 2% of TP is accounted for by sorption on average, providing a lower bound to compare against the 24% estimated using sorptive capacity of sediment as determined by Grundtner (2013). This lower sorption value leaves a larger proportion of particulate phosphorus which must be accounted for by sources other than mineral bound, algal, and sorbed particulate phosphorus (Figure 17). Additionally, if we replace the 24% estimated sorbed P with 2% in the summation of total dissolved P (measured DOP plus dissolved organic P plus sorbed P) we find that dissolved P may comprise as much as 56% of total P; and if we divide that sorbed-P by the estimate of total dissolved P (0.02/0.56), we find that the input of dissolved P to the stream corridor may be masked by sorption at the basin outlet by 4% rather than 31%. Furthermore, the role of stored bed sediments as a net source of DOP to the water column in upland settings (see the negative “Predicted” sorbed-P load for uplands presented in Table 9) is completely missed when sorptive capacity of sediments is applied to the budget in place of weighted average sorbed concentration (budget for sorbed-P using sorptive capacity presented in Table B1). These two approximations of the portion of TP formed via instream processes serve as end members – with the application of sorptive capacity presenting a maximum (24%), and the application of average sorbed concentration weighted to environmentally relevant conditions presenting a minimum (2%) of TP in particulate form formed via instream equilibrium processes.

The effects of sorption processes are reflected in phosphorus partitioning between dissolved and particulate phosphorus across the basin. Using data from the network of gages on the Le Sueur River, we plotted particulate and dissolved load as proportions of TP load, averaged within bins of percent exceedance of TSS load to reflect event scale (Figure 18, Dolph, 2017c). This plot shows a shift along the geomorphic gradient from uplands to incised zone to outlet. More than half the TP load is in dissolved form in the uplands of the watershed, while particulate form dominates (during storm events) in the incised zone and at the watershed outlet. This signal is observed across event scales at the network of gages (Figure 18).

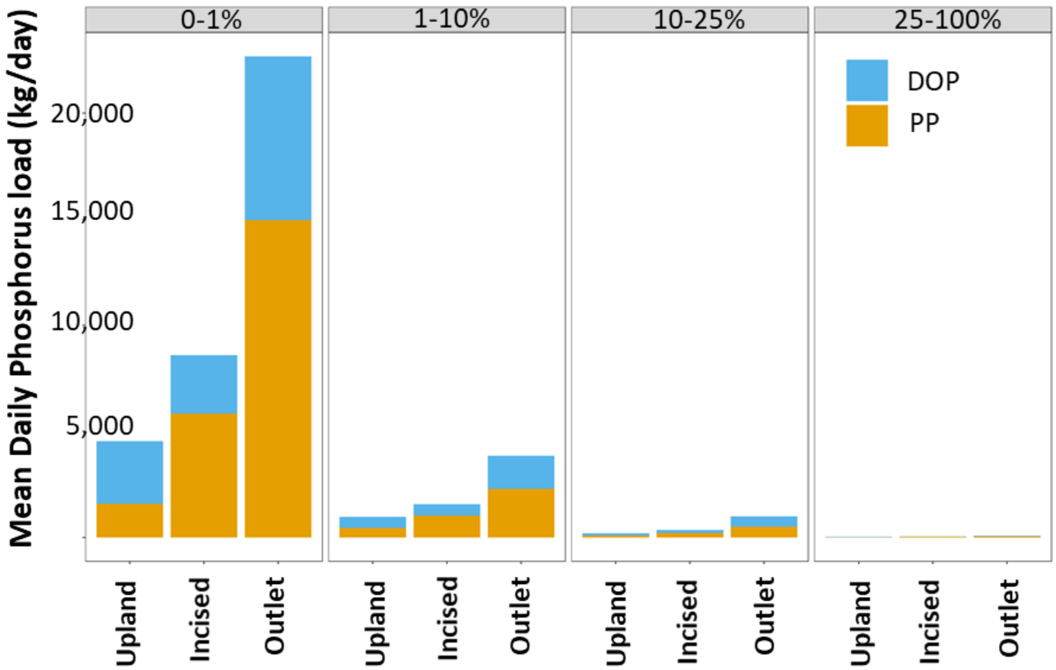


Figure 18. Plots from Dolph (2017c) showing partitioning of total phosphorus into dissolved (DOP) and particulate (PP) form at the upland gage at St. Clair, incised zone gage at County Rd 8 and watershed outlet ("Outlet") gage on the Le Sueur River across event scales. Events were averaged within bins by percent exceedance of TSS load, shown at the top of the plot.

Furthermore, plots of phosphorus fractions by storm event at a large network of first order tributaries and upland ditch sites in the upper Le Sueur and at the network of gages (Dolph, 2017c) show higher particulate phosphorus at the watershed outlet than in the uplands under all TSS load conditions (Figure 19, Dolph, 2017c); and at several load conditions, show concurrent decrease in soluble reactive phosphorus (SRP, equivalent to DOP) and dissolved unreactive phosphorus (DUP) concentrations, which can be likened to dissolved organic P concentration.

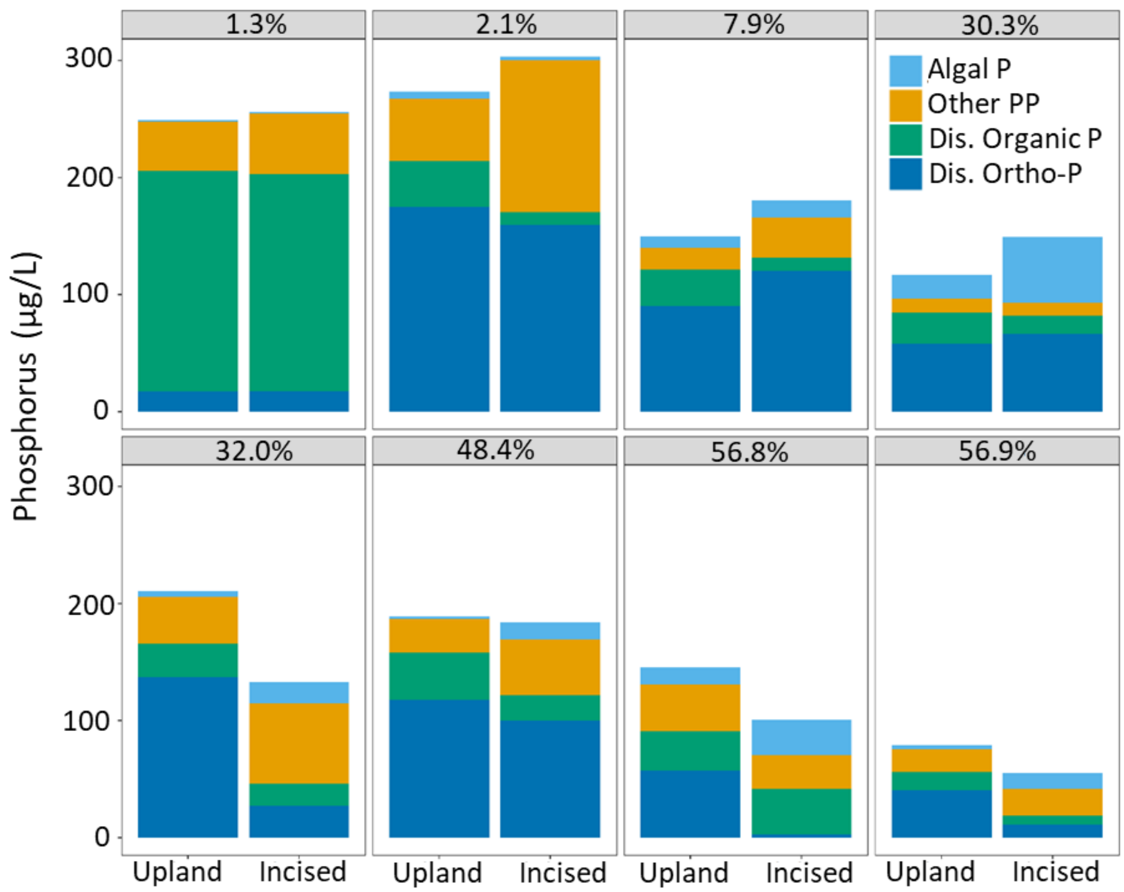


Figure 19. Fractions of phosphorus measured at a network of upland and incised zone locations across the Le Sueur River Basin including the Maple and Cobb sub-watersheds (see Figure A1 for map) during events representing a range of flow and subsequent total suspended solids (TSS) load conditions (from Dolph, 2017c). Each paneled plot represents a single sampling event, with the percent exceedance of TSS load associated with each sampled event shown at the top of each plot. “Dis.” Indicates dissolved, “PP” indicates particulate P.

Conversion of dissolved phosphorus to particulate form is also suggested by plots of dissolved and particulate phosphorus and TSS yield at gages on the upper and lower Maple River, a tributary to the Le Sueur (Figure 3, chapter one). The Maple River is ideal for examining these relationships due to the very small increase in drainage area occurring between the gages. This allows for examination of transformations occurring along this incised section of the stream, where large masses of freshly eroded bluff till and streambank alluvial sediment are contributed to the channel. This plot shows a slight skew in dissolved phosphorus yield toward the uplands. As discussed in chapter one, this may be a result of both the saturation of upland soils and the leaking of DOP from this part of the basin as well as the depression of the DOP signal in the incised zone due to sorption. Particulate phosphorus and TSS, on the other hand, both show a shift from upper basin to lower basin skew with the crossing of a flow threshold that has been described by Cho (2017a). This flow threshold corresponds to the initiation of bluff erosion in the incised zone of the Le Sueur. Combining these observations with results of sorption tests on these materials, we see that it is likely that dissolved phosphorus introduced in the headwaters is being sorbed by bluff and streambank materials in the incised zone, depressing the dissolved phosphorus signal at watershed scale.

This formation of particulate, sediment-bound phosphorus has high potential to cause persistence of phosphorus in the river network, as sediments settle out and enter storage in the river corridor and downstream receiving waters with high bound phosphorus concentrations. Legacy phosphorus such as this can trigger algal blooms into the future as resuspension and release reintroduce the phosphorus to the water column (Sharpley et al., 2013). Using estimates of average annual fine-sediment mass storage (Cho, 2017b) we approximated maximum and average annual mass of stored phosphorus associated with fine sediment in storage. This was accomplished by first weighting sorptive capacity and average sorbed concentration respectively for each of the gage locations based on the fraction of sediment from distinct sources that would be likely to comprise bed sediment within channel reaches in the drainage to the upper Le Sueur (Le Sueur only, not including Maple and Cobb) and Le Sueur watershed outlet (cumulative for the whole basin). We then multiplied these weighted concentrations by the mass of sediment at each location. Stored sediment mass was evaluated for all reaches of channel with flow accumulation >100 m^2 and Strahler stream order of 4 or greater (Cho, 2018b). Total reach length evaluated by Cho was 622 km in the upper Le Sueur and 1,984 km at the Le Sueur watershed outlet for the entire basin cumulatively (Cho, 2018b).

From this analysis, we estimate that bed sediment may bind and store a maximum of 7,305 kg of phosphorus per year in upland reaches of the Le Sueur and approximately 12,731 kg/yr cumulatively at the watershed outlet. In contrast, using average bed sediment sorbed concentration, we find that sediments in the upland reaches of the Le Sueur could be donating as much as 536 kg/yr phosphorus to the water column, at the watershed outlet, the cumulative effect of bed sediment is to bind 430 kg/yr of phosphorus from the water column, or approximately 0.15% of the 290,719 kg/yr TP exported from the basin at this location (Table 10). This suggests that the net effect of sediment in the Le Sueur is to bind dissolved-P from water column.

Table 10. Estimates of in-channel sediment storage and associated phosphorus (P).

Location	Reach Length (km)	Fine Sediment In storage (Mg/yr)	Max Stored P (kg/yr)	Average Stored P (kg/yr)
Le Sueur Uplands	622	19,117	7,305	-536
Le Sueur Watershed Outlet	1,984	23,866	12,731	430

Validity of equilibrium experiment application to environmental systems

Perhaps the clearest message in the variability observed in the data set produced by these sorption experiments is that mimicking natural environmental conditions in sorption tests may limit the ability to isolate equilibrium exchange. Potential sources of variability that were explored during these tests include the solution matrix ionic chemistry; the sediment to solution ratio (which mimics the concentration of sediment suspended in suspension); and the mass of sediment used, which affects the ability to draw a representative sub-sample for each replicate treatment.

We observed high variability in the relationship between sorbed and equilibrium concentration across a wide range of ratios of sediment to solution and volume of solution tested (see Appendix B for figures and greater detail). Despite the attempt to isolate equilibrium exchange through the design of these tests, additional reactions affecting the measured concentration of DOP are likely to occur in waters with complex ionic chemistry. We tested for precipitation of phosphate minerals that may occur when Le Sueur River water is spiked across a range of phosphate concentrations, by measuring total dissolved phosphorus (TDP) on filtered (0.45 µm) and unfiltered replicates of stock solutions following 24-hour shaking and equilibration. This test showed that filtered replicates had lower TDP concentrations across the environmentally relevant range of spiking concentrations, and that there was a slight increase in amount precipitated (observed as the difference between filtered and unfiltered TDP concentration) with increasing spiking concentration (Figure B5). While it is clear that precipitation was occurring, there are additional reactions that these tests were unable to isolate, including complexation. Under complex ionic chemistry such as that which occurs in river systems, to really understand the mechanisms governing TP fate and dynamics, a mass balance at every spiking concentration is needed, where

Total-P = [sorbed-P] + [precipitated-P] + [complexed-P] + [free-P]. (7)

This is important because other chemical reactions in settings such as the Le Sueur River may also play a strong role in governing phosphorus distribution and bioavailability. Future testing should include greater resolution and replication of multiple matrices (a simple, weak calcium chloride solution compared to river water) to determine if in fact the complex ionic chemistry of the matrix drives this variability.

Conclusion

Sediment is a known to play a key role in regulating stream DOP conditions, and our results suggest that equilibrium processes between sediment and DOP in the water column may comprise anywhere from 2-24% of the TP budget for the Le Sueur River Basin. Application of average sorbed phosphorus concentration associated with agricultural top soil, bluff till, streambank alluvium, and upland ditch-bank sediments to the sediment budget showed that the net effect of sediment on water column phosphate concentrations varies along a geomorphic gradient, with upland sediment donating phosphorus and incised zone sediment binding phosphorus from the water column. The net effect of sediment at the scale of the entire watershed, even under conservative estimates, is removal of DOP from solution and conversion to particulate form. Sediment in storage also varies along a geomorphic gradient, with upland bed sediment likely donating substantial amounts of DOP to the water column and incised zone bed sediments binding even larger masses of DOP. This represents a significant accumulation of legacy phosphorus in this river system which may be remobilized and could serve to drive algal blooms well into the future. These equilibrium processes have important implications for management and suggest that improved understanding of dissolved phosphorus source and dynamics is needed to prevent the development of legacy phosphorus and future algal blooms in this and other heavily eroding agricultural river systems.

Conclusions – Chapters 1 and 2

Phosphorus is a critically important target for management in surface waters around the globe, and the management of phosphorus is particularly complicated due to its affinity for sediment and its potential to accumulate in river networks and receiving waters, generating "legacy" stores that may remobilize and cause eutrophic conditions far into the future. This study presented the findings of a three-part effort to better understand phosphorus cycling in the highly agricultural Le Sueur River Basin in southern Minnesota. This effort included 1) the exploration of trends in phosphorus from the development of a mass balance for sediment-derived phosphorus and the exploration of in-channel exchange of phosphorus between sediment and the water column, and its role in driving phosphorus behavior at the scale of the watershed. These efforts found that:

- Both dissolved and particulate-P are mobilized by stormflows in the Le Sueur River, with increasing concentration as discharge increases.
- Sediment is not the primary source of P in the Le Sueur River basin. Only a small proportion of the total loads of TP (24%), PP (50%), and DOP (<2%) exiting the basin at the watershed outlet were sediment-derived on an average annual basis between 2009-2012.
- Near channel (till and alluvial) features are the primary source of sediment and sediment-derived P to the system. These sediments have a strong affinity for binding P and convert it from dissolved to particulate form.
- Upland sediments (agricultural topsoils and upland ditch-bank sediments) are enriched in P and were also shown by our sorption tests to release P under most ambient stream conditions. These sediments are likely a leaking source of dissolved P to the river network.
- Inputs of DOP to the Le Sueur River are likely higher than suggested by measured loads of DOP due to being masked by conversion of DOP to PP via adsorption to sediment.
- Controlling 100% of erosion would only reduce P loss by 24% at most; thus management needs to focus on both dissolved and particulate sources of P in the Le Sueur River Basin.

Bibliography

CENR (2003). An Assessment of Coastal Hypoxia and Eutrophication in U.S. Coastal Waters. *National Science and Technology Council Committee on Environment and Natural Resources*, Washington. Retrieved from http://www.nccos.noaa.gov/publications/hypoxia.pdf.

Belmont, P., Gran, K. B., Schottler, S. P., Wilcock, P. R., Day, S. S., Jennings, C., Lauer, W., Viparelli, E., Willenbring, J.K, Engstrom, D.R., Parker, G. (2011). Large shift in source of fine sediment in the upper Mississippi River. *Environmental Science and Technology*, *45*(20), 8804–8810. https://doi.org/10.1021/es2019109

Bennett, E. M., Carpenter, S. R., & Caraco, N. F. (2001). Human Impact on Erodable Phosphorus and Eutrophication: A Global Perspective. *BioScience*, *51*(3), 227-234. https://doi.org/10.1641/0006-3568(2001)051[0227:HIOEPA]2.0.CO;2

Bevis, M. (2015). Sediment budgets indicate Pleistocene base level fall drives erosion in Minnesota's greater Blue Earth River basin. (Masters Thesis). Retrieved from https://conservancy.umn.edu/handle/11299/170661

Boardman, Evelyn. (2016). Nutrient dynamics in Minnesota watersheds (Masters Thesis). Retrieved from https://conservancy.umn.edu/handle/11299/191194

Cho, Se J.; Wilcock, Peter; Gran, Karen; Belmont, Patrick; Hobbs, Ben; Collaborative for Sediment Source Reduction--Greater Blue Earth River Basin. (2017). Management Option Simulation Model (MOSM) and supporting documents. Retrieved from the University of Minnesota Digital Conservancy, http://hdl.handle.net/11299/191082.

Cho, S. J. (2017a). Development of data-driven, reduced-complexity watershed simulation models to address agricultural non-point source sediment pollution in Southern Minnesota (Doctoral Dissertation). *Johns Hopkins Univeristy*.

Cho, S. J. (2017b). "sediment storage question." Message to Anna Baker. December 5, 2017. Email.

Clayton, L., & Moran, S. R. (1982). Chronology of Lake Wisconsinan Glaciation in Middle North America, *Quaternary Science Reviews*, *1*, 55–82.

Correll, D. L. (1998). The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. *Journal of Environment Quality*, *27*(2), 261-266. https://doi.org/10.2134/jeq1998.00472425002700020004x

Dodd, R. J., & Sharpley, A. N. (2015). Recognizing the role of soil organic phosphorus in soil fertility and water quality. *Resources, Conservation and Recycling*, *105*, 282-293. https://doi.org/10.1016/j.resconrec.2015.10.001

Dolph, C.L., Hansen, A.T., Kemmitt, K.L., Janke, B., Rorer, M., Winikoff, S., Baker, A.C., Boardman, E., Finlay, Jacques, C. (2017). Characterization of streams and rivers in the Minnesota River Basin Critical Observatory: water chemistry and biological field collections, 2013-2016. Retrieved from https://conservancy.umn.edu/handle/11299/189907

Dolph, C. (2017a). "algal P flux - LS Rapidan, MN 66 outlet." Message to Anna Baker. October 9, 2017. Email.

Dolph, C. (2017b). "Fwd RE recent Chla data for Le Sueur River outlet gage." Message to Anna Baker. December 18, 2017. Email.

Dolph, C. (2017c). "more P fractions and TSS." Message to Anna Baker. December 5, 2017. Email.

Dolph, C. L., Hansen, A. T., & Finlay, J. C. (2017). Flow-related dynamics in suspended algal biomass and its contribution to suspended particulate matter in an agricultural river network of the Minnesota River Basin, USA. *Hydrobiologia*, *785*(1), 127–147. https://doi.org/10.1007/s10750-016-2911-7

Duan, S. W., & Kaushal, S. S. (2013). Warming increases carbon and nutrient fluxes from sediments in streams across land use. *Biogeosciences*, *10*(2), 1193–1207. https://doi.org/10.5194/bg-10-1193-2013

Engstrom, D. R., Almendinger, J. E., & Wolin, J. A. (2009). Historical changes in sediment and phosphorus loading to the upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin. *Journal of Paleolimnology*, *41*(4), 563–588. https://doi.org/10.1007/s10933-008-9292-5

Fox, G. A., Purvis, R. A., & Penn, C. J. (2016). Streambanks: A net source of sediment and phosphorus to streams and rivers. *Journal of Environmental Management*, *181*, 602–614. https://doi.org/10.1016/j.jenvman.2016.06.071

Gellis, A. C., Fitzpatrick, F., & Schubauer-Berigan, J. (2016a). A Manual to Identify Sources of Fluvial Sediment, *U.S. Environmental Protection Agency*, Washington, DC, EPA/600/R-16/210, 2016.

Gellis, A. C., Fuller, C. C., & Van Metre, P. C. (2016b). Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States. *Journal of Environmental Management*, *194*, 73–85. https://doi.org/10.1016/j.jenvman.2016.06.018

Gran, K. B., Belmont, P., Day, S. S., Jennings, C., Johnson, A., Perg, L., & Wilcock, P. R. (2009). Geomorphic evolution of the Le Sueur River, Minnesota, USA, and implications for current sediment loading. *The Geological Society of America Special Paper*, *451*(08), 119–130. https://doi.org/10.1130/2009.2451(08).

Gran, K., Belmont, P., Day, S., Jennings, C., Lauer, J. W., Viparelli, E., Wilcock, P., Parker, G. (2011). An Integrated Sediment Budget for the Le Sueur River Basin, (Final Report), 1–128.

Grundtner, A. (2013). Role of Bank Materials As Potential Source and Carrier of Phosphorus (Masters Thesis). Retrieved from https://conservancy.umn.edu/handle/11299/148635.

Grundtner, A., Gupta, S., & Bloom, P. (2014). River Bank Materials as a Source and as Carriers of Phosphorus to Lake Pepin. *Journal of Environment Quality*, *43*(6), 1991. https://doi.org/10.2134/jeq2014.03.0131

Guzner, M. (2017). Water Quality Benefits of a MN Floodwater Storage Impoundment (Masters Thesis). 1-117. Retrieved from https://conservancy.umn.edu/handle/11299/191285

Hongthanat, N. (2010). Phosphorus sorption-desorption of soils and sediments in the Rathbun Lake watershed (Masters Thesis), 1-71. Retrieved from http://lib.dr.iastate.edu/etd/11558

House, W. (2003). Geochemical cycling of phosphorus in rivers. *Applied Geochemistry*, *18*(5), 739–748. https://doi.org/10.1016/S0883-2927(02)00158-0

Hutchinson, K. (2003). Dissolution of Phosphate in a Phosphorus-Enriched Ultisol as Affected by Microbial Reduciton. (Masters Thesis). https://doi.org/10.1007/s13398-014-0173-7.2

Jalali, M., & Peikam, E. N. (2013). Phosphorus sorption-desorption behaviour of river bed sediments in the Abshineh river, Hamedan, Iran, related to their composition. *Environmental Monitoring and Assessment*, *185*(1), 537–552. https://doi.org/10.1007/s10661-012-2573-5

James, W. F., & Larson, C. E. (2008). Phosphorus dynamics and loading in the turbid Minnesota River (USA): controls and recycling potential. *Biogeochemistry*, *90*(1), 75–92. https://doi.org/10.1007/s10533-008-9232-5

Janke, B. D., Finlay, J. C., Hobbie, S. E., Baker, L. A., Sterner, R. W., Nidzgorski, D., Wilson, B. (2014). Contrasting influences of stormflow and baseflow pathways on nitrogen and phosphorus export from an urban watershed, *Biogeochemistry*, *121*(1), 209–228. https://doi.org/10.1007/s10533-013-9926-1

Jarvie, H. P., Jürgens, M. D., Williams, R. J., Neal, C., Davies, J. J. L., Barrett, C., & White, J. (2005). Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: The Hampshire Avon and Herefordshire Wye. *Journal of Hydrology*, *304*(1–4), 51–74. https://doi.org/10.1016/j.jhydrol.2004.10.002

Jelinski, N. (2017). “grain size data”. Message to Anna Baker. November 1, 2017. Email.

Kerr, J. G., Burford, M., Olley, J., & Udy, J. (2011). Phosphorus sorption in soils and sediments : implications for phosphate supply to a subtropical river in southeast Queensland, Australia, *Biogeochemistry*, *102*(1-3), 73–85. https://doi.org/10.1007/s10533-010-9422-9

Kleinman, P. J. A., Wolf, A. M., Sharpley, A. N., Beegle, D. B., & Saporito, L. S. (2005). Survey of Water-Extractable Phosphorus in Livestock Manures, *Soil Science Society of America Journal*, *69*(3) 701–708. https://doi.org/10.2136/sssaj2004.0099

Konert, M., and J. Vandenberghe. 1997. Comparison of laser grain size analysis with pipette and sieve analysis: A solution for the underestimation of the clay fraction. Sedimentology 44:523–535. doi:10.1046/j.1365-3091.1997.d01-38.x

Kopáček, J., Borovec, J., Hejzlar, J., Ulrich, K. U., Norton, S. a., & Amirbahman, A. (2005). Aluminum control of phosphorus sorption by lake sediments. *Environmental Science and Technology*, *39*(22), 8784–8789. https://doi.org/10.1021/es050916b

Liu, K., Elliott, J. A., Lobb, D. A., Flaten, D. N., & Yarotski, J. (2014). Nutrient and Sediment Losses in Snowmelt Runoff from Perennial Forage and Annual Cropland in the Canadian Prairies. *Journal of Environmental Quality*, *43*(5), 1644–1655. https://doi.org/10.2134/jeq2014.01.0040

Matsch, C.L., 1983, River Warren, the southern outlet of Lake Agassiz, *in* Teller, J.T., and Clayton, L., eds., Glacial Lake Agassiz: Geological Association of Canada Special Paper 26, p. 232–244.

McDowell, R. W., & Sharpley, A. N. (2001). Approximating phosphorus release from soils to surface runoff and subsurface drainage. *Journal of Environmental Quality*, *30*(2), 508–520. https://doi.org/10.2134/jeq2001.302508x

Miller, R. B., Fox, G. A., Penn, C. J., Wilson, S., Parnell, A., Purvis, R. A., & Criswell, K. (2014). Estimating sediment and phosphorus loads from streambanks with and without riparian protection. *Agriculture, Ecosystems and Environment*, *189*, 70–81. https://doi.org/10.1016/j.agee.2014.03.016

Minnesota Pollution Control Agency. (2012). Methods and Analytes Requiring Laboratory Certification, *Minnesota Pollution Control Agency*, *p-eao2-09c*, 1–7.

Minnesota Pollution Control Agency. (2014). The Minnesota Nutrient Reduction Strategy. *Minnesota Pollution Control Agency*, *wq-s1-80*. Retrieved from https://www.pca.state.mn.us/sites/default/files/wq-s1-80.pdf

Minnesota Pollution Control Agency. (2016). Watershed Pollutant Load Monitoring Network. *Minnesota Pollution Control Agency*, *wq-cm1-03,* 1–2. Retrieved from https://www.pca.state.mn.us/sites/default/files/wq-cm1-03.pdf

Minnesota Pollution Control Agency. (2017). Watonwan , Blue Earth , and Le Sueur River Watersheds. *Minnesota Pollution Control Agency*, 1-12. Retrieved from https://www.pca.state.mn.us/sites/default/files/watershed-blueearth.pdf

Minnesota Pollution Control Agency, Data Viewer. (2017). Watershed Pollutant Load Monitoring Browser. [Data from database] Retrieved from https://public.tableau.com/profile/mpca.data.services#!/vizhome/WatershedPollutantLoadMonitoringNetworkWPLMNDataViewer/WPLMNBrowser

Minnesota Pollution Control Agency, Spindler, B., Baskfield, P., O'Hara, K., Helwig, D., Hotka, L., Thompson, S., Dingmann, T., Laing, K., Monson, B., Parson, K. (2012). Le Sueur River River Watershed Monitoring and Assessment Report. *Minnesota Pollution Control Agency, wq-ws3-07020011b,* 1-140. Retrieved from https://www.pca.state.mn.us/sites/default/files/wq-ws3-07020011b.pdf

Noe, G. B., Hupp, C. R., & Rybicki, N. B. (2013). Hydrogeomorphology Influences Soil

Nitrogen and Phosphorus Mineralization in Floodplain Wetlands. *Ecosystems*, *16*, 75–94. https://doi.org/10.1007/s10021-012-9597-0

Olila, O., & Reddy, K. (1993). Phosphorus sorption characteristics of sediments in shallow eutrophic lakes of Florida. *Archiv Für Hydrobiologie*. *129*(1), 45-65

Pant, H. K., & Reddy, K. R. (2001). Phosphorus Sorption Characteristics of Estuarine Sediments under Different Redox Conditions, *Journal of Environmental Quality, 30*, 1474–1480.

Peterson, H. M., Baker, L. A., Bruening, D., Nieber, J. L., Ulrich, J. S., & Wilson, B. N. (2017). Agricultural Phosphorus Balance Calculator: A tool for watershed planning. *Journal of Soil and Water Conservation*, *72*(4), 395–404. https://doi.org/10.2489/jswc.72.4.395

Records, R. M., Wohl, E., & Arabi, M. (2016). Earth-Science Reviews Phosphorus in the river corridor. *Earth Science Reviews*, *158*, 65–88. https://doi.org/10.1016/j.earscirev.2016.04.010

Research Analytical Lab, Univeristy of Minnesota. (2018a). *pH.* Retrieved from http://ral.cfans.umn.edu/ph

Research Analytical Lab, Univeristy of Minnesota. (2018b). *Organic Matter.* Retrieved from http://ral.cfans.umn.edu/organic-matter

Research Analytical Lab, Univeristy of Minnesota. (2018c). *Phosphorus-Bray-1 Extractable.* Retrieved from http://ral.cfans.umn.edu/phosphorus-bray-1-extractable-non-calcareous-soils

Research Analytical Lab, Univeristy of Minnesota. (2018d). *Phosphorus-Olsen Bicarbonate Extractable.* Retrieved from http://ral.cfans.umn.edu/phosphorus-olsen-bicarbonate-extractable-calcareous-soils

Research Analytical Lab, Univeristy of Minnesota. (2018e). "*Buffer index method."* Message to Anna Baker. May 29, 2018. Email.

Reynolds, C. S., & Davies, P. S. (2001). Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biological Reviews of the Cambridge Philosophical Society*, *76*(1), 27–64. https://doi.org/10.1111/j.1469-185X.2000.tb00058.x

Schottler, S. P., Ulrich, J., Belmont, P., Moore, R., Lauer, J. W., Engstrom, D. R., & Lauer, J. Wesley; Engstrom, Daniel R.; Almendinger, J. E. (2013). Twentieth century agricultural drainage creates more erosive rivers. *Hydrological Processes*, *28*, 1951–1961. https://doi.org/10.1002/hyp.9738

Sekely, A. C., Mulla, D. J., & Bauer, D. W. (2002). Streambank slumping and its contribution to the phosphorus and suspended sediment loads of the Blue Earth River, Minnesota. *Journal of Soil and Water Conservation*, *57*(5), 243–250.

Sharpley, A., Jarvie, H. P., Buda, A., May, L., Spears, B., & Kleinman, P. (2013). Phosphorus Legacy: Overcoming the Effects of Past Management Practices to

Mitigate Future Water Quality Impairment. *Journal of Environment Quality*, *42*(5), 1308. https://doi.org/10.2134/jeq2013.03.0098

Stabel, H., & Geiger, M. (1985). Phosphorus adsorption to riverine suspended matter. *Water Research*, *19*(11), 1347–1352.

Stone, M., & Mudroch, A. (1989). The Effects of Particle Size , Chemistry and Mineralogy of River Sediments on Phosphate Adsorption. *Environmental Technology Letters*, *10*, 501–510. https://doi.org/10.1080/09593338909384766

Wall, D. (2017). "tile nutrient export." Message to Anna Baker. December 8, 2017. Email.

Wall, D., Gosack, B., & Pearson, T. (2017). River Nutrient and Sediment Loads - why differences across 60 Minnesota watersheds ? (Powerpoint slides)

Withers, P. J. ., & Jarvie, H. P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of The Total Environment*, *400*(1–3), 379–395. https://doi.org/10.1016/j.scitotenv.2008.08.002

Appendix A

This appendix presents supporting information for the sediment-derived phosphorus budget development detailed in both chapter one and two of this thesis.

Water sample collection

Water sampling that supported the development of our method for correcting particulate phosphorus for percent dissolved organic phosphorus, which is also discussed in chapter 2 of this thesis, was carried out at a large network of stream and river sites (n=79; excluding sites located at the immediate outlet of a lake or wetland) sampled between 2013-2016 by research staff from the University of Minnesota (Figure A1), for which all forms of P (total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP, equivalent to DOP), and particulate phosphorus (PP) and chlorophyll (Chla) were measured.

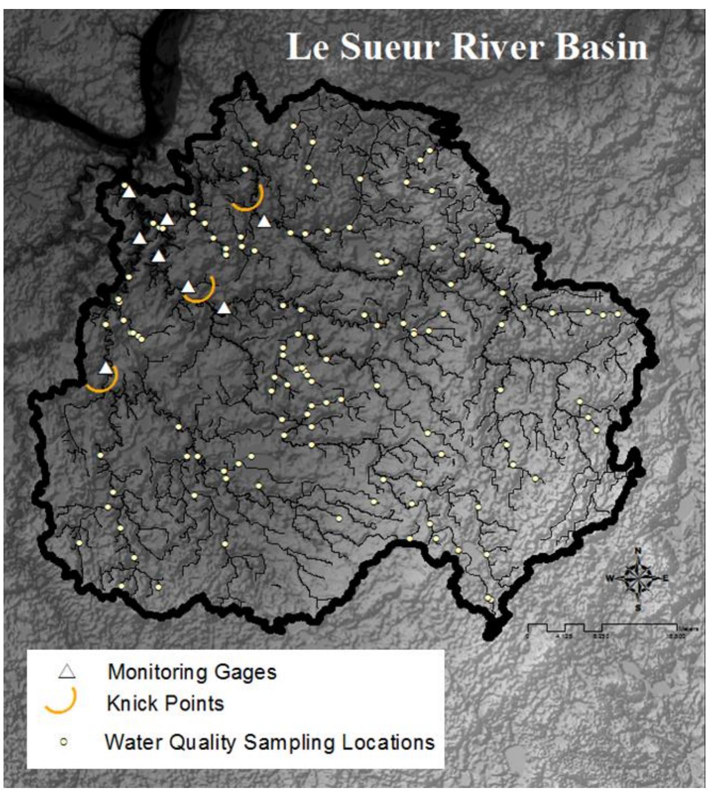


Figure A1. Location map showing water sample collection locations.

This sampling network was designed to capture conditions above and below a zone of incision. Active down-cutting is removing channel bed sediment and incising into the underlying till, thus causing the Le Sueur and its tributaries to incise deeply near their mouths (Gran et al., 2009). The majority of the 79 University of Minnesota sampling sites were located in upland settings above the zone of incision, while a smaller number were located within the zone of incision and at the watershed outlet. Water samples were collected from subsets of these study sites during ten sampling events between 2013 and 2016 (Table A1; total number of samples = 273, (Dolph et al., 2017). Samples were collected on an event basis, where an event may span several days but where flow exceedance probability varied by less than 10% over the course of the event. With each sampling event we sought to collect similar numbers of samples from upland tributary and larger 4th-6th order stream sites. Many of these sites were sampled during multiple events. However, some inconsistencies occurred due to variable site accessibility, the ephemeral nature of some smaller order sites, and variable objectives between sampling events. In collecting these data, we sought to capture a range of flow regimes in order to elucidate relationships between seasonal changes in TSS, water chemistry, and flow. In chapter two these data from Dolph, et al. (2017) are presented to provide context for basin-wide partitioning of phosphorus between dissolved and particulate forms.

Stream discharge and 25-year exceedance probability of streamflow at the Le Sueur River Basin outlet (measured at the gage Le Sueur River nr Rapidan, MN66) were averaged across the date range for each sampling event, as a proxy for flow conditions in the watershed during each sampling event. Twenty-five-year exceedance probabilities were calculated from average daily discharge conditions, 1991-2016. This time period was chosen to represent a long-term record and to encompass our last year of field data collection (2016) (Dolph, 2017c).

Table A1. Water sampling event and location descriptions.

Sampling event	Date range	# sites sampled above knickzone	# sites sampled below knickzone	Streamflow daily average at basin outlet (m^3/s)	Streamflow exceedance probability at basin outlet
1*	06/11/2013-06/12/13	29	4	53.34	13%
2	08/13/2013-08/15/2013	29	3	6.65	57%
3	06/23/2014-06/26/2014	11	3	263.20	0.6%
4	08/03/2014-08/07/2014	14	3	2.64	74%
5**	06/15/2015	48	6	50.12	14%
6	07/13/2015-07/15/2015	18	5	24.57	29%
7	07/29/2015-07/30/2015	10	4	63.56	10%
8	09/01/2015-09/03/2015	48	2	11.19	47%
9	11/03/2015	14	4	7.90	54%
10	09/27/2016	15	3	372.40	0.2%

*No Chla data collected below knickzone
** No TDP data collected below knickzone

Particulate Phosphorus Correction

Particulate phosphorus was corrected as described in the methods section of chapter one of this thesis. Data from seven sampling events (Table A1) were used to determine the average percent of total phosphorus comprised by dissolved organic phosphorus. Figure A2 shows dissolved organic phosphorus during these events plotted by exceedance probability. One event was considered to be an outlier because it had much higher dissolved organic phosphorus and a 0.2% exceedance probability and was therefore excluded.

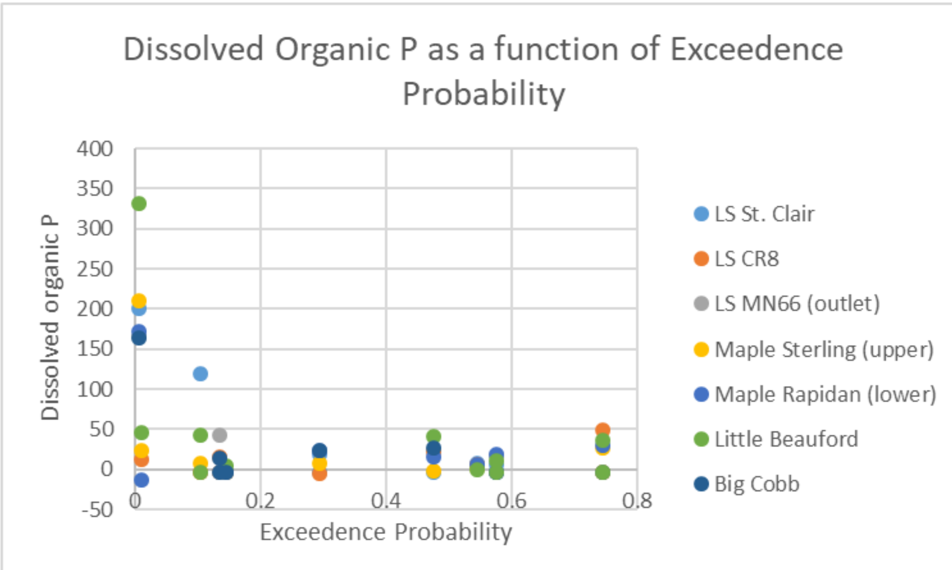


Figure A2. Dissolved organic phosphorus by exceedance probability using water data collected from the Le Sueur River and tributaries by staff from the University of Minnesota.

Study Period

The time period selected for development of the phosphorus budget and for monitoring data that were used to restrict sorption test data to the most representative stream conditions (which were in turn incorporated into this budget) was selected for greatest data availability across monitoring sites within the Le Sueur Basin (Table A2). Though the period 2010-2012 had data available at all sites, examination of long term average load (2007-2015) at the Le Sueur watershed outlet showed that the period 2009-2012 was more representative than 2010-2012 (Table A2).

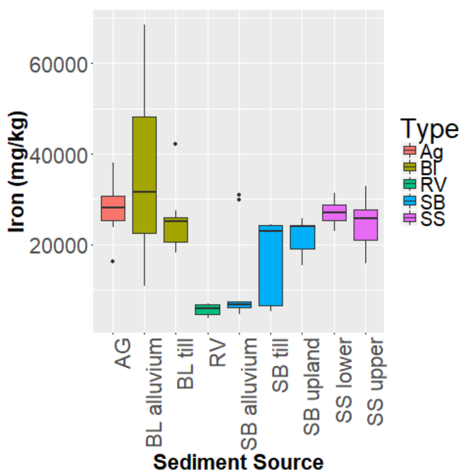
Table A2. Summary of average annual load data for TP, DOP, TSS, and discharge (Q) at the network of gage sites on the Le Sueur River and its tributaries the Maple and Cobb Rivers. Loads from the Little Cobb River is not presented here because phosphorus loads data were scarce (DOP loads were only available for 2011, TP for 2009-2011).

	LS at Rapidan				CR8				LS St. Clair			
	TP (kg/yr)	DOP (kg/yr)	TSS (kg/yr)	Q (acre ft)	TP	DOP (kg/yr)	TSS (kg/yr)	Q	TP	DOP (kg/yr)	TSS (kg/yr)	Q
2007	346886	136621	184,873,721	675,697	N/A	N/A	N/A	N/A	N/A	N/A	38,098,120	185,583
2008	102639	29349	88,495,250	370,481	N/A	N/A	N/A	N/A	N/A	N/A	20,705,160	117,037
2009	83600	27631	37,375,500	203,655	14,665	N/A	13,142,430	53,146	8,498	2,990	3,755,980	41,596
2010	699462	268679	537,463,330	1,220,310	184,397	64,515	127,097,130	350,907	124,483	61,978	44,818,224	297,281
2011	315015	117402	229,657,760	827,269	99,084	32,621	78,012,077	270,436	70,016	32,311	32,747,368	233,736
2012	64800	18775	39,220,210	153,890	22,241	6,761	11,800,470	54,324	16,527	6,725	8,430,592	41,663
2013	278448	105374	168,293,500	578,527	63,775	21,930	34,814,450	178,551	N/A	N/A	N/A	N/A
2014	501669	141812	344,998,400	660,525	228,610	45,466	210,987,310	301,449	N/A	N/A	N/A	N/A
2015	262176	71946	211,544,870	592,854	108,410	23,019	96,368,408	208,191	N/A	N/A	N/A	N/A
Average 2009-2012	290,719	108,122	210,929,200	601,281	80,097		57,513,027	182,203	54,881	26,001	22,438,041	153,569
Average 2010-2012	359,759	134,952	268,780,433	733,823	101,907	34,632	72,303,226	225,222	70,342	33,671	28,665,395	190,893
Average of all data available	294,966	101,954	204,658,060	587,023	103,026	32,385	81,746,039	202,429	54,881	26,001	24,759,241	152,816
	294,966											
Range of available data	2007-2015				2009-2015							

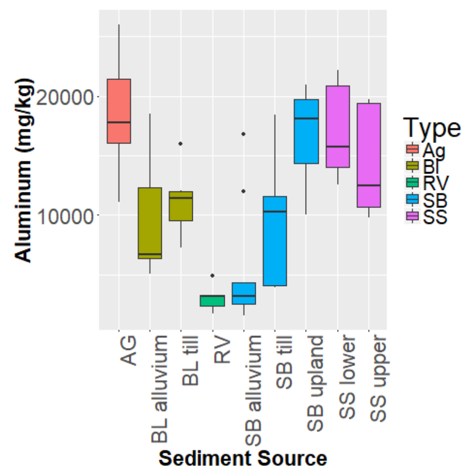
	Maple CR18				Maple at CR35				Big Cobb			
	TP	DOP (kg/yr)	TSS (kg/yr)	Q	TP	DOP (kg/yr)	TSS (kg/yr)	Q	TP	DOP (kg/yr)	TSS (kg/yr)	Q
2007	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2008	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2009	15,619	N/A	3,650,962	46,295	14,952	N/A	4,549,736	42,722	12,485	N/A	5,054,465	33,592
2010	147,028	96,962	19,754,564	328,822	226,753	94,248	187,970,720	349,389	129,282	75,922	47,149,006	286,268
2011	69,484	41,316	12,357,741	194,111	98,717	43,764	53,249,602	211,839	56,571	27,678	21,470,286	191,097
2012	14,005	3,798	3,802,746	35,793	16,594	4,873	7,992,152	38,159	11,033	4,263	4,288,574	34,873
2013	73,668	43,124	18,523,800	169,714	102,377	37,664	68,196,900	180,714	43,511	19,865	13,058,880	131,798
2014	54,648	29,688	14,253,000	130,420	99,472	26,138	72,826,100	139,429	79,992	34,754	40,620,983	153,578
2015	13,537	6,553	4,706,577	62,079	21,254	6,853	16,391,347	71,461	32,254	11,410	14,388,028	98,534
Average 2009-2012	61,534		9,891,503	151,255	89,254		63,440,553	160,527	52,343		19,490,583	136,458
Average 2010-2012	76,839	47,359	11,971,684	186,242	114,021	47,628	83,070,825	199,796	65,629	35,954	24,302,622	170,746
Average of all data available	55,427	36,907	11,007,056	138,176	82,874	35,590	58,739,508	147,673	52,161	28,982	20,861,460	132,820
Range of available data	2009-2015				2009-2015				2009-2015			

Sediment Chemical and Physical Properties

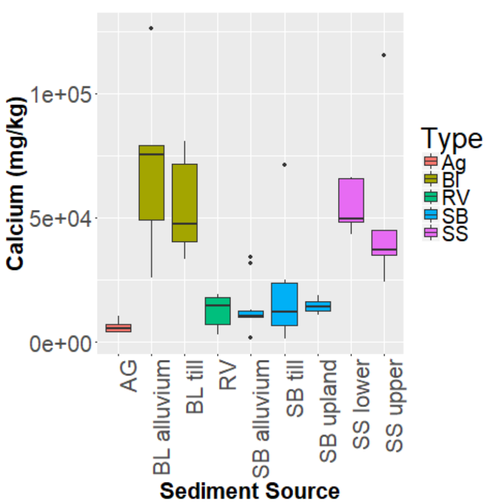
Chemical and physical properties of soils exert influence over the extent to which phosphorus may be bound and released by that sediment, and thus, the variability in chemical parameters (iron, aluminum, and calcium concentration as well as organic matter percent and pH) and physical parameters (percent clay, silt and sand) were evaluated and are presented here in Figure A3. Results of analyses of elemental concentrations, organic content, and percent silt, clay and very fine sand were used to inform linear models relating differences in source sediment group total and dissolved phosphorus to corresponding physicochemical characteristics (Figure A3).



A.



B.



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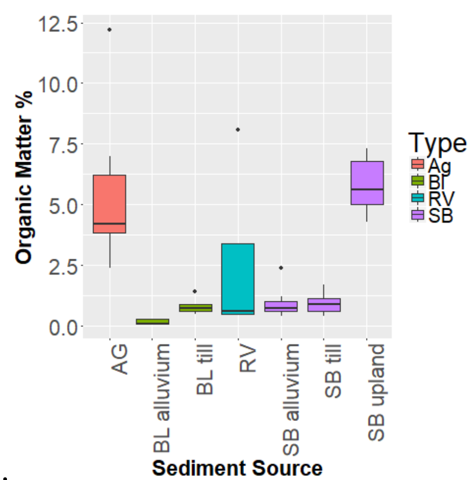

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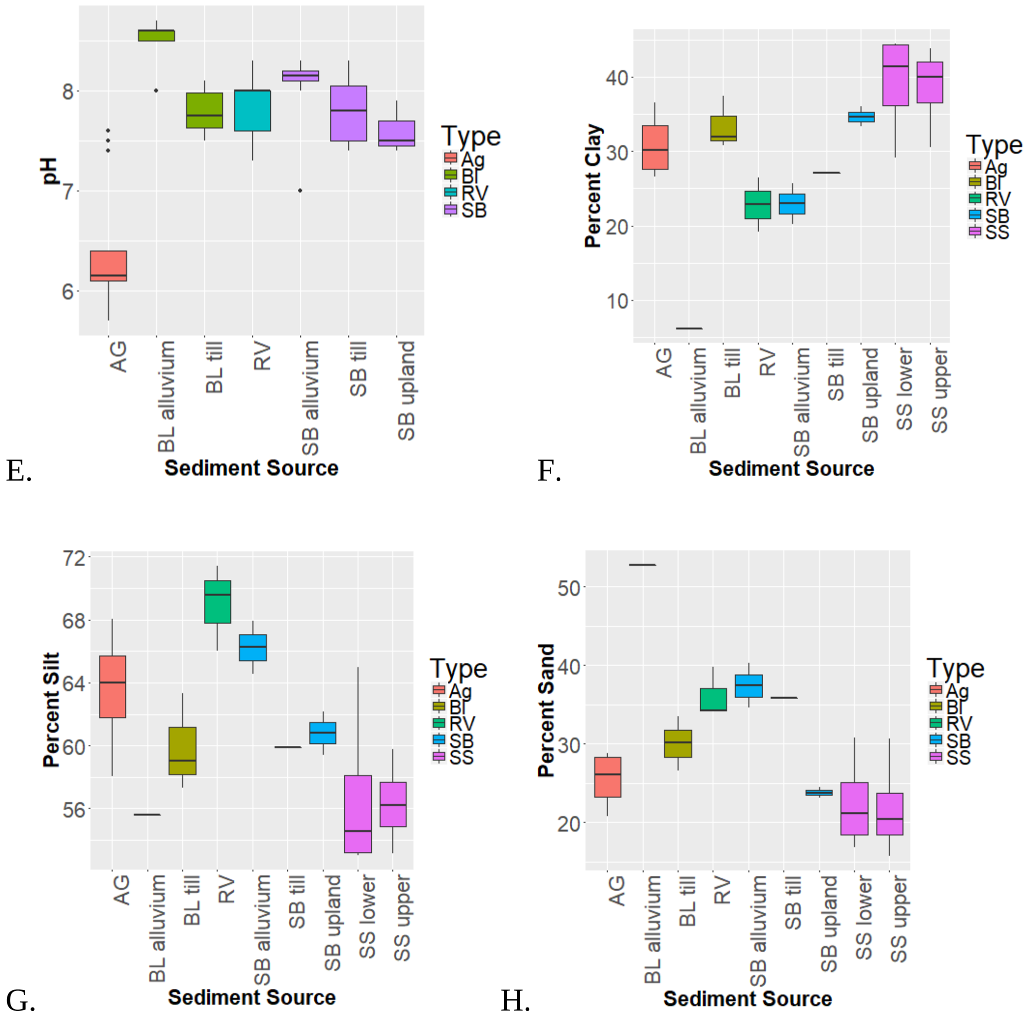


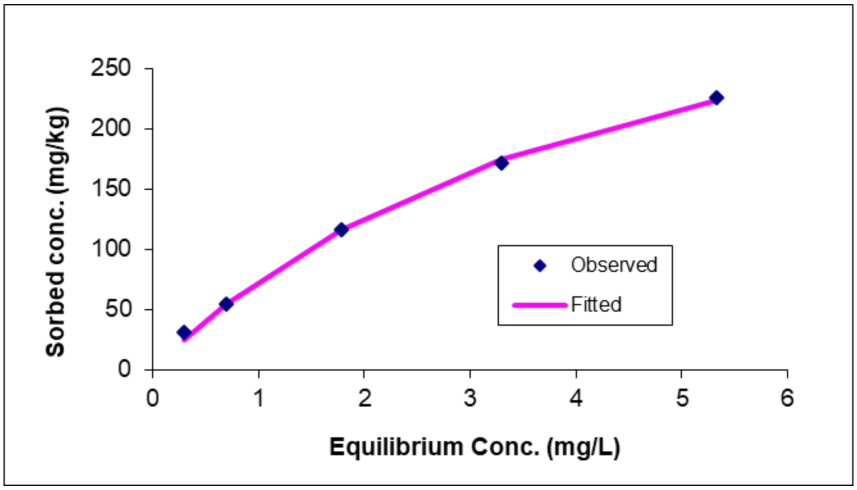
Figure A3. Box plots showing variability in A) iron, B) aluminum, C) calcium, D) organic matter, E) pH, F) percent clay, G) percent silt, H) percent very fine sand.

Appendix B

This appendix provides supplemental material supporting chapter two of this thesis, which describes sorption experiments and their application to a sediment budget to determine the component of TP which is accounted for by particulate phosphorus formed during instream processing.

Exploration of potential sources of variability in sorption test results

In these sorption tests, we attempted to mimic natural stream conditions as closely as possible. While these experiments produced results with high variability within treatments of a single sample, we observed that spiking to artificially high phosphate concentrations produced a curve that was able to be fit, even in the complex matrix of Le Sueur River water (Figure B1).



				Approx 95 % confidence limits	
Parameters	*Initial estimates **	*Fitted Values*	*Standard errors*	*Lower bound*	*Upper bound*
K	0.263	***0.218***	*0.0250*	*0.1385*	*0.2975*
Smax (mg/kg)	380.0	***418.1***	*26.9332*	*332.39*	*503.82*

Figure B1. Curve fit for Ag-19 soil. This treatment was spiked to 10,000 µg/L (10 mg/L), producing a curve that was able to be fitted to the Langmuir isotherm.

However, this test did not evaluate stream relevant concentrations at the high resolution that revealed variability in subsequent tests. To determine causes of variation in these sorption tests we explored the role of solution matrix, sediment to solution ratio, and volume upon variability (described in chapter two methods). A few important trends in solution and experimental treatment behavior were observed that may have contributed to the variability in results of sorbed and equilibrium concentration and the poor reproducibility observed in these experiments.

First, variability in the relationship between sorbed concentration and equilibrium solution concentration was observed in all results run at high resolution in the environmentally relevant range. Sources of this variability were investigated by running samples Ag-19 (agricultural soil 19) and B-12T (bluff-12 till) at different ratios of sediment to solution (1:25, 1:100, 1:200, and 1:2000; Figure B2-A), differing volumes of solution at the same ratio (10, 40, and 400 mL at the environmentally relevant 1:2000 sediment concentration, Figure B2-B), and different solution types (0.005M $CaCl_2$ solution and Le Sueur River water).

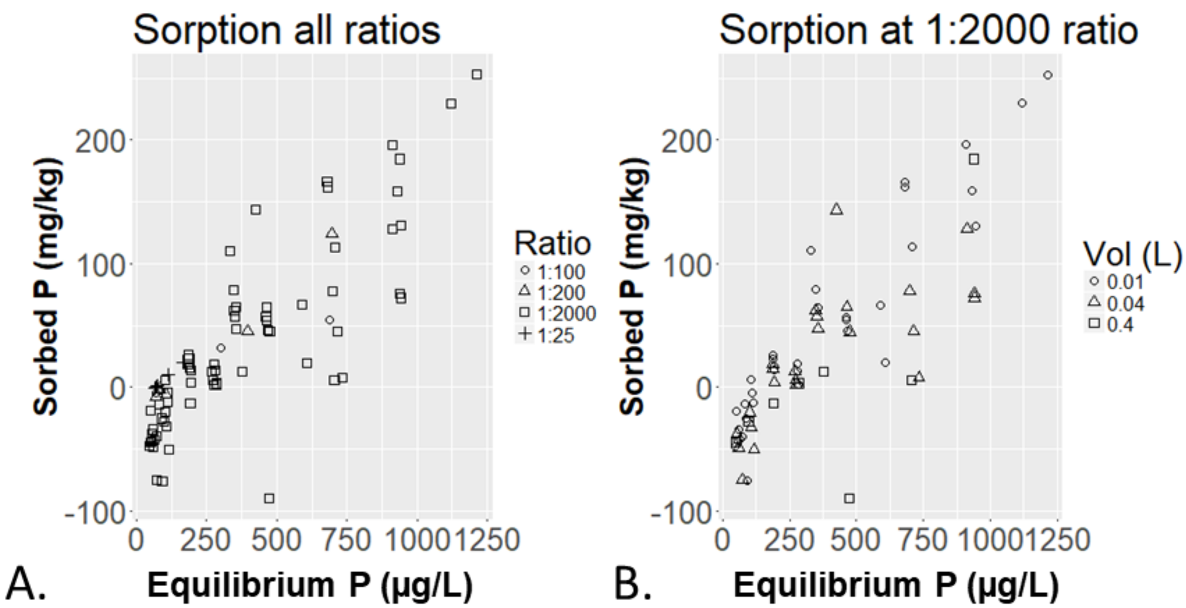
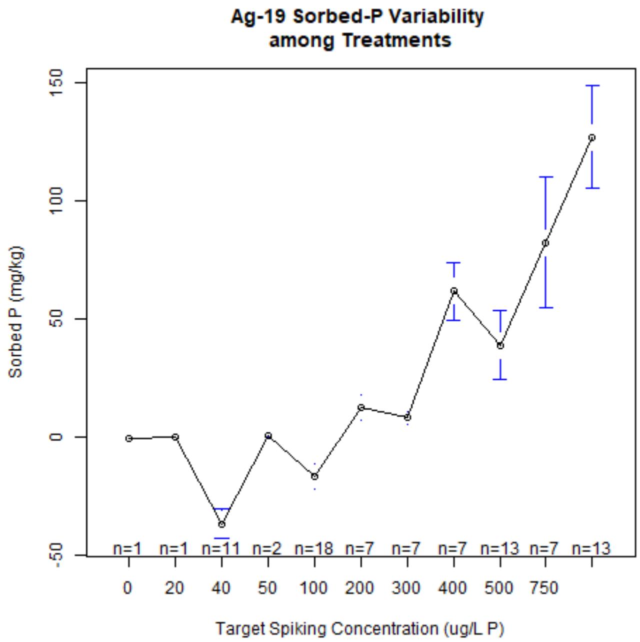
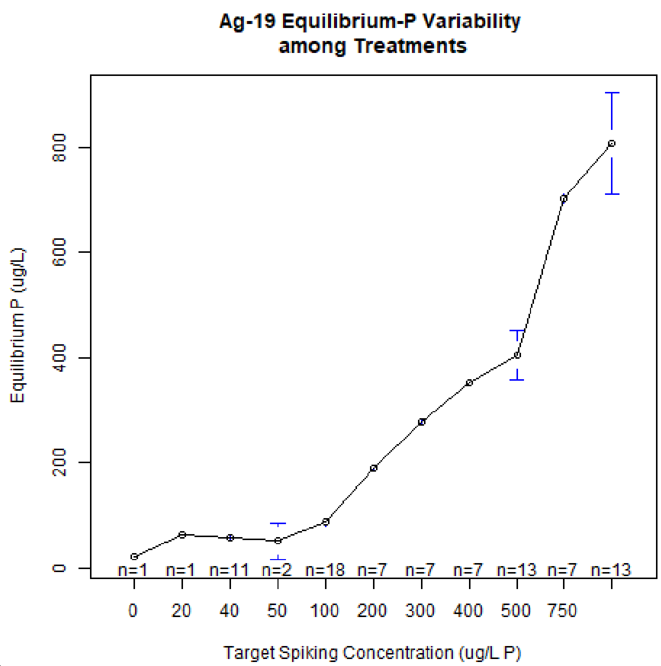


Figure B2. Sample Ag-19 sorption results at A) a range of ratios of sediment to solution and B) a range of spiking volumes for samples run at the environmentally relevant 1:2000 ratio.

The potential for inhomogeneity in our sediment sub-samples causing the variability was tested by running sample Ag-19 at the 1:2000 ratio but several different spiking volumes and subsequently masses of sediment. Results of these tests showed that variability in this relationship occurred at ratios of sediment to solution ranging from very high (1:25, equivalent to 40,000 mg/L, which is more than two orders of magnitude larger than the highest concentration observed in the Le Sueur river) to moderate (500 mg/L, a concentration which is in the 97th percentile of concentrations observed in the Le Sueur), and that even with an order of magnitude larger spiking volume and sediment mass (200 mg sediment to 400 mL of solution, 1:2000 ratio), the relationship between sorbed-P and equilibrium-P still exhibits variability (Figure B2-B). Examination of the standard deviation of replicate tests of sorptive capacity carried out on the same sediment sample at a given spiking concentration reveals that variability increases slightly with increasing spiking concentration (Figure B3-A and B).



A



B

Figure B3. Standard deviation about the means of A) sorbed phosphate concentrations B) Equilibrium Phosphorus concentrations for agricultural top soil sample Ag-19 plotted by target spiking concentration

Second, stock solutions of river water mixed with chloroform and spiked with orthophosphate showed declining phosphorus concentrations over the course of several days since creation (Figure B4). To address this, fresh solutions were made immediately preceding the spiking of each batch, and a series of blank samples of each stock solution was run with each batch to account for background changes that may be taking place in the solutions over the 24-hour equilibration. Solution concentrations were found to be unstable over the course of 24-hour equilibration, most commonly showing a decrease in concentration from initial creation of the stock solution to final equilibrated stock solution concentration (Figure B4), though some increased. To determine if precipitation was driving these changes, we measured total DOP on filtered and unfiltered stock solutions following 24-hour equilibration. These tests demonstrate that precipitation was occurring in our stock solutions at high phosphate concentrations (Figure B5), suggesting that the complex matrix ionic chemistry may play a role in generating variability in our sorption test results. In order to correct for these transformations occurring in the stock solution over the course of the tests, the final, equilibrated stock solution P concentration was used as “initial” concentration in finding sorbed P concentration.

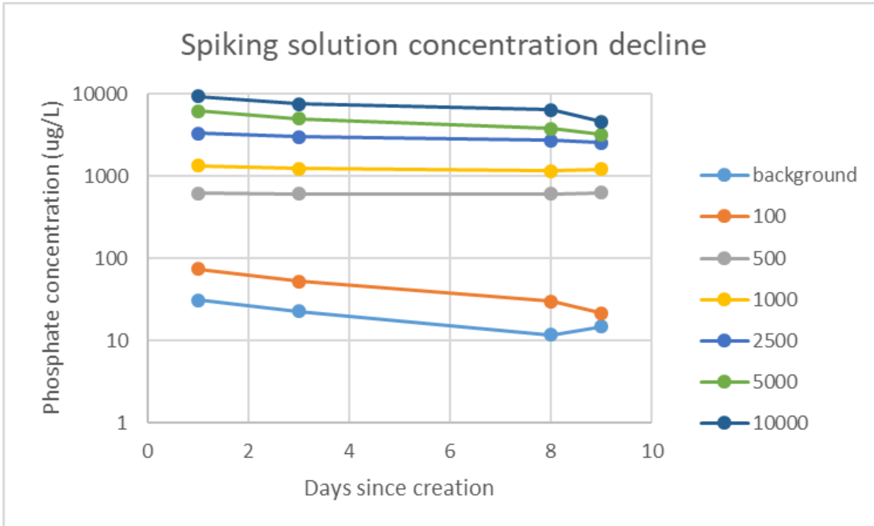
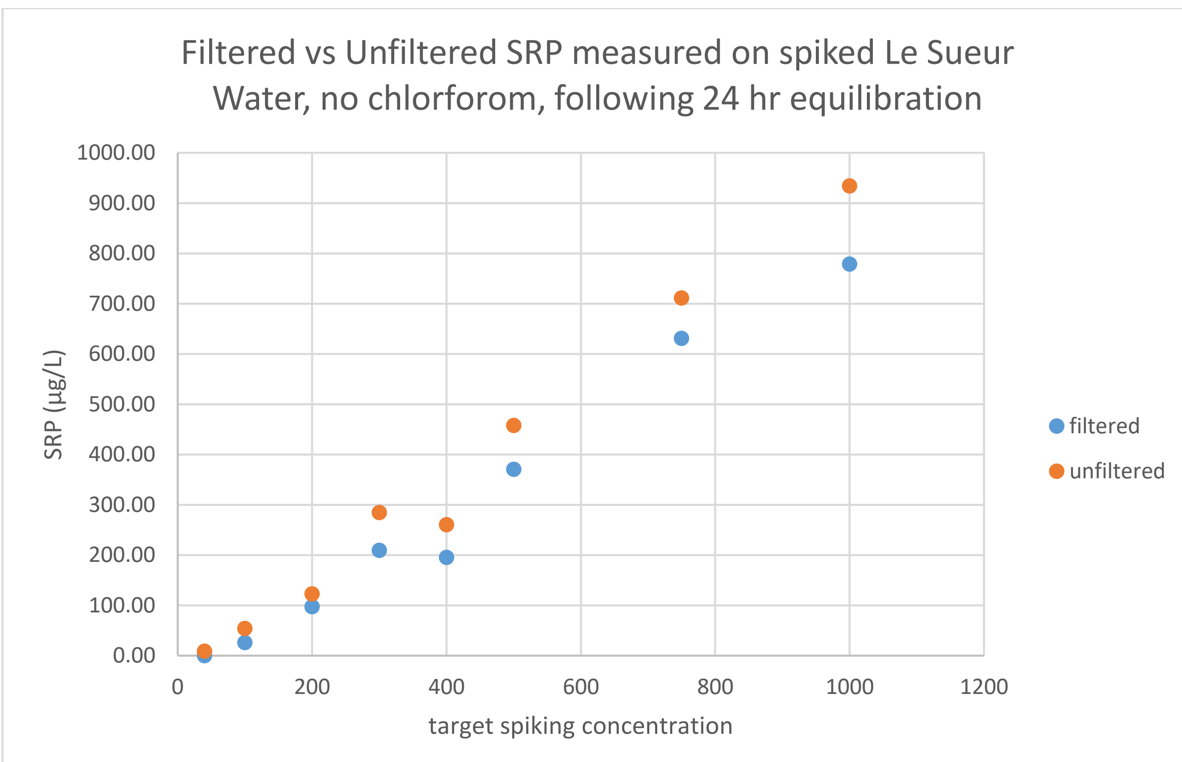


Figure B4. Spiking solution phosphate concentration decline over 9 days since creation.



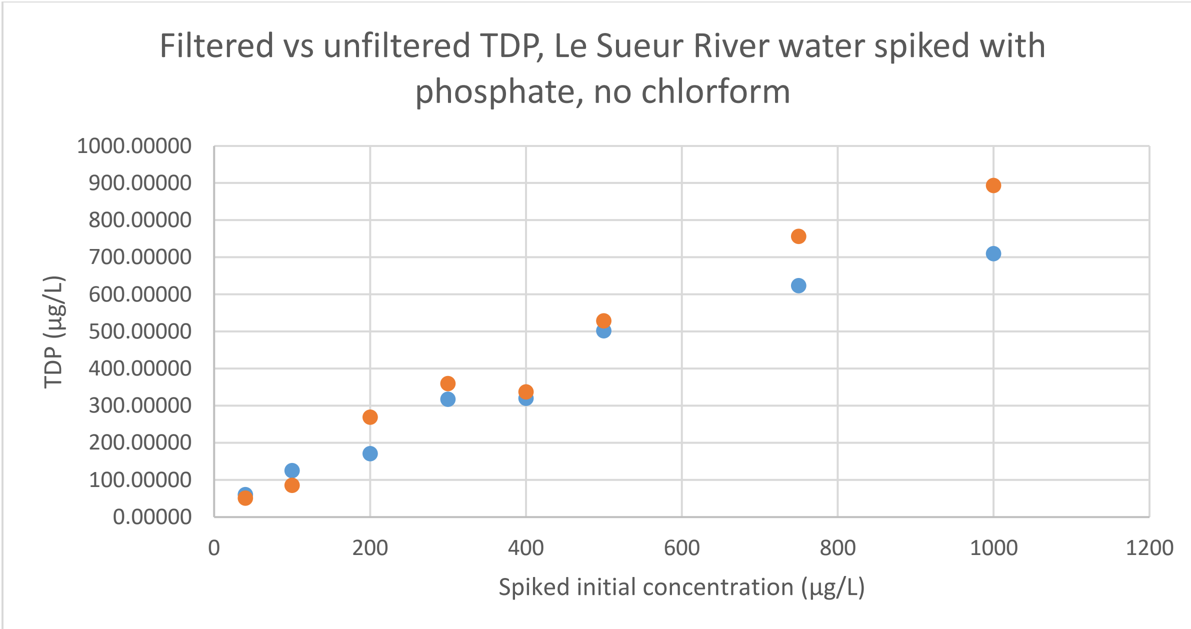


Figure B5. Filtered versus unfiltered SRP and TDP following 24-hour equilibration. Test was used to quantify precipitation of phosphates from solution.

Lastly, the samples were run in two different solutions to determine if matrix effects were playing a role in generating variability in this relationship. These tests were also run up to very high concentrations to see if sorptive capacity could be reached beyond the environmentally relevant range of phosphorus concentrations. Results of these tests suggest that spiking to a higher phosphate concentration and using a larger ratio of sediment to solution (1:100, equivalent to 10,000 mg/L sediment, an order of magnitude larger than the Le Sueur's highest concentration) produces a less noisy relationship than is observed within the environmentally relevant range (Figure 1 chapter two). However, these tests did not include the same amount of replication and had lower resolution (less spiked concentrations) in the environmentally relevant (0-1000 µg/L) phosphate range than the tests run at 1:2000 in Le Sueur River water, and thus may be missing some of the variability within the environmentally relevant range.

Though further investigation would help to further elucidate the ultimate source of the observed variability, results of our investigation suggest that the combination of complex ionic chemistry of natural waters and the low sediment to solution ratio generate high variability in sorption test results. These results suggest that isolating equilibrium exchange between phosphorus and sediment may overlook some of the drivers of stream DOP concentrations, such as precipitation and other effects. The complexity of these waters and difficulty of isolating equilibrium in natural systems calls into question the applicability of traditional controlled sorption test data to questions of phosphorus dynamics in stream environments. In this thesis we therefore have presented results of the application of controlled experiments by Grundtner (2013) as a maximum (Table B1), and of our experiments as a lower bound on the potential contribution of equilibrium processes to development of particulate phosphorus in this watersheds TP budget (Table 9).

Table B1. Sorbed phosphorus budget using sorptive capacity (Smax) from Grundtner, 2013.

Sorbed P using Smax from Grundtner, 2013

	Le Sueur River Annual Sorbed-P load (g/yr)		
	Uplands	**Incised Zone**	**Watershed Outlet**
Upland	8,015,630	10,109,282	16,582,679
Ravine	0	2,096,099	10,889,938
Bluff	1,082,455	10,670,610	36,818,214
Streambank	2,800,250	7,929,083	26,359,727
Lake	1,590,642	3,233,402	6,243,605
Flood plain	1,638,990	1,638,990	13,950,193
Predicted	**8,668,703**	**25,932,683**	**70,456,760**
Observed	56,842,980	82,350,750	290,719,250
Pred/Obs	**15.3%**	**31.5%**	**24.2%**

Appendix C: Data Tables

This appendix consists of data tables containing chemical and physical properties of sediments collected from the Le Sueur River Basin between August 2014 and July 2017.

Sediment Chemistry Data

The Sediment Chemistry Data table presents the results of analyses of sediment total phosphorus and extractable dissolved phosphorus (soluble reactive phosphorus, SRP, or dissolved orthophosphate, DOP) and other parameters with potential influence over the phosphorus content of these sediments. This data set consists of 91 samples collected from both erosional source areas and from target sinks such as channel beds and fluvial suspended sediment. See the definitions tab of the spreadsheet for a description of the sediment sample types. Methods of analysis for total phosphorus and elemental concentration, water extractable soluble reactive phosphorus (SRP, also referred to as dissolved orthophosphate, DOP), grain size, organic matter percent via loss on ignition (LOI), and pH are described in the methods section of Chapter 1 of this thesis. Total dissolved phosphorus was obtained via water extraction of sediments described in chapter one. Analysis of the extracts was performed via the ascorbic acid method previously referenced, but the filtered samples were digested prior to analysis (SRP/DOP analysis). Samples were digested by adding equal parts sample to 0.2M potassium persulfate and autoclaving for 30 minutes. Bray and Olsen phosphorus and buffer index were analyzed by the University of Minnesota's Research Analytical Lab. Bray and Olsen phosphorus are found first by extracting the phosphorus from 1 g of sediment and then analyzing the extractant using the molybdate blue ascorbic acid method. Bray phosphorus extraction is performed by shaking 1 g of sediment in a mixture of 10 mL of 0.025 M HCl and 0.03 M NH4F for 5 minutes (Research Analytical Lab, 2018c). Olsen phosphorus is extracted from 1 g of sediment by shaking in a mixture of 20 ml of 0.5 M NaHCO3 for 30 minutes (Research Analytical Lab, 2018d). Olsen phosphorus analysis is intended for calcareous soils. Buffer index was assessed only for samples with pH less than 6. This analysis involved adding 5 mL of Sikora buffer solution to the soil slurry upon which pH was measured, and subsequently measuring pH at 5-minute intervals for 15 minutes (Research Analytical Lab, 2018e). Total carbon and total nitrogen were analyzed via high combustion on an elemental analyzer.

Sorption Experimental Data

This data table presents all experimental data collected as a part of our examination of the sorptive properties of sediments including those collected from erosional features and suspended sediments from the Le Sueur River Basin. These features included bluffs (largely comprised of glacial till with smaller amounts of alluvium), streambanks (alluvial features approximately 2-4 meters in height, underlain by glacial till), agricultural fields, and suspended sediments from a pair of gages - one above the incised zone of the Le Sueur River at St. Clair, capturing sediment and phosphorus exported from uplands, and at the outlet of the Le Sueur River at Minnesota Highway 66.

Over the course of our experiments we observed that our stock solutions were changing concentration after creation (largely losing P over time), so we started running stock solution blanks with every batch of sorption test samples and using the equilibrated concentration after 24 hours of shaking as the “initial” concentration in our calculations. This served to correct our estimates of sorbed concentration by removing the effect of these changes in the matrix of the stock solutions from the equilibrium.

Sorption table column descriptions

- **Sample_type:** type of sediment collected, where Ag = agricultural topsoil; Bluff = bluffs sampled greater than 10 m above the wetted channel; SB = streambanks 2-4 m tall, sampled within this distance from above the wetted channel; SS = suspended sediment
- **Sample_subtype**: categories within each broad sample_type category. Categories include Ag (indicating that there was not a subtype for agricultural topsoil), till (corresponding to bluff samples), alluvium (corresponding to streambanks), upland (corresponding to streambanks, these are banks of upland agricultural ditches), upper (indicating suspended sediment from the upper gage on the Le Sueur River at St. Clair), and lower (indicating suspended sediment from the lower gage on the Le Sueur River at Minnesota Highway 66).
- **Sample:** the sample name, indicating type and the sequence in which the sample was collected
- **Ratio:** the ratio of sediment to solution
- **Matrix:** the solution used, where LS = Le Sueur River water collected from the gage at St. Clair on January 9^{th}, 2016, background soluble reactive phosphorus concentration of approximately 40 µg/L, with 20 g/L chloroform added to inhibit

biological uptake of phosphorus; and CaCl2= 0.005 M calcium chloride solution with 20 g/L chloroform.

- **Sieve_size_um:** the size of the sieve mesh used in preparation of the samples, corresponding to the maximum grain size in the sample analyzed.
- **target_P_conc_ugL**: target phosphorus spiking concentration for stock solution
- **target_sed_mass_kg**: target sediment mass
- **actual_sed_mass_kg**: actual sediment mass
- **target_solution_vol_L**: target spiking solution volume
- **solution_vol_L**: actual spiking solution volume
- **initial_stock_batch_creation_ugL**: stock solution soluble reactive phosphorus concentration, measured upon creation of the stock solution
- **Initial_conc_ugL**: initial soluble reactive phosphorus concentration of spiking solution used to dose sediments in the sorption tests. Our method for obtaining initial was adjusted following the discovery that stock solution SRP concentrations were not stable over time, so the method used is indicated in the column "initial_desc". This field is used in find the amount sorbed by subtracting equilibrium concentration from initial concentration.
- **inital_descr:** description of the method used to obtain initial SRP concentration at the beginning of the tests where "24hr shake initial" indicates that initial concentration was measured on spiking solution blanks that were run alongside the sorption test samples and allowed to equilibrate for during 24 hours of shaking, while "fridge initial" refers to measurements made on the stock solutions freshly removed from the refrigerator at the initiation of the test. The use of "24hr

shake initial" removes the effect of background changes occurring in the stock solution from the calculation of change due to sorption.

- **equilibriumP_ugL:** soluble reactive phosphorus concentration in solution after 24 hour equilibration with sediment.
- **pH_sample:** pH measured on equilibrated samples following removal of a subsample for measurement of soluble reactive phosphorus.
- **pH_stocksltn_start:** pH of the spiking solution measured at the beginning of the tests.
- **pH_stocksltn_end:** pH of spiking solution measured at the end of the tests.
- **Notes:** comments about the experiment