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High flow events as hot moments of reactive Fe and P export: impacts of land cover and seasonality

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HIGH FLOW EVENTS AS HOT MOMENTS OF REACTIVE Fe and P
EXPORT: IMPACTS OF LAND COVER AND SEASONALITY

A Thesis Presented

by

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Abstract

High flow events often comprise the majority of annual discharge and riverine geochemical flux of phosphorus (P) and metals such as iron (Fe) and manganese (Mn) due to glacial melt, snowmelt, and storm-driven sustained high flow. Aquatic ecosystem productivity in receiving water bodies such as Lake Champlain and the Gulf of Alaska (GoA) are impacted by the riverine import of nutrients. The magnitude of these high flow events can be a strong predictor of receiving water body conditions, and in some cases can contribute to eutrophication. We explore the intersection of high flow events and land cover in contrasting catchments in Vermont and Alaska, covering a range of land covers including glacial, boreal-forested, mixed hardwood-conifer forested, and agricultural.

In Vermont, we explore the hypothesis that riverine dissolved and suspended sediment P loads during spring runoff have a particularly high proportion of reactive species due to unique hydrologic pathways and the association of P with Fe. We compared spring runoff and summer storm concentrations and distribution of dissolved P (DP), dissolved and colloidal metals, and redox sensitive suspended sediment P (RSP). Agricultural catchments in Vermont were characterized by enrichment in RSP and DP during both spring runoff and summer storms, particularly at the onset of snowmelt. In 2014, 82% of the annual DP and 74% of annual RSP loads were delivered to Missisquoi Bay during spring runoff, with the majority of suspended sediment significantly more redox sensitive, and carrying potentially bioavailable P, than typical inputs to limnological models, suggesting that the reactivity of this load is systematically underestimated.

In Alaska, we investigate Fe size partitioning and flux throughout the hydrologic year, with additional high-resolution sampling during discrete storm events in adjacent forested and glacierized catchments typical of coastal Alaska. There are clear differences between these catchments during individual storm events, and across seasons, reflecting widely varying source environments for Fe. The geochemical character of river water exported from the forested catchment, dominated by dissolved Fe and DOC, reflects the influence of peatlands and organic-rich soil as the dominant source of Fe and P, while the glacial catchment exports significantly more material derived from glacial weathering of bedrock, reflected in higher sediment and colloidal concentrations. Phosphorus concentrations in both watersheds are very low throughout the year, but significantly higher in the forested catchment, driven by organic matter decomposition.

Both Vermont and Alaska are likely to be significantly impacted by climate change, with an increase in the frequency of heavy precipitation events, and continued glacial recession in Alaska driven by rising temperatures. Changes in the timing, provenance, and severity of high flow associated with climate and land cover change will have dramatic impacts on total riverine P and Fe loads, and their potential reactivity and bioavailability in receiving water bodies. Development of conceptual models that incorporate the intersection between high flow events (hot moments) and land cover source environments (hot spots) is critical to understanding how these systems are likely to change in the future.

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Chapter 1: Introduction and Project Context

Of critical importance to understanding aquatic ecosystem health is developing a better conceptual model of the interaction of hydrology and land cover on the flux of nutrients, pollutants, and other constituents from rivers to receiving water bodies.

Numerous studies over the past few decades have identified the impact of land cover on riverine geochemistry, and on nutrient, pollutant, and contaminant concentrations in lakes and coastal environments. It is also well known that high flow events deliver the majority of water and associated geochemical constituents to receiving water bodies, disproportionately affecting annual loads compared to baseflow conditions. The majority of climate models predict an increase in the frequency, severity, and duration of heavy precipitation events across much of the northern hemisphere, particularly in temperate forested systems. As such, it is expected that climate change will likely affect the timing and magnitude of riverine nutrient flux to receiving water bodies. An investigation of high flow event geochemistry across land covers and seasons would enhance our ability to project how phenology and event severity may affect water quality and ecosystem function in rivers and their receiving waters under climate change.

Riverine input of water and associated loads of soluble and suspended nutrients, metals, pollutants, and contaminants significantly affect the geochemistry of receiving water bodies. The geochemistry of river water is determined in part by the distribution of land covers within the watershed and by *in situ* processing of materials in the river.

Anthropogenic alterations to the land surface, primarily as a result of agricultural and urban development, significantly alter riverine geochemistry when compared to pristine natural environments [Ahearn *et al.*, 2005; Dillon and Molot, 1997; Owens and Walling,

2002]. In addition, the flux of geochemical constituents is controlled by hydrologic conditions, such as soil saturation, runoff intensity, and changing flowpaths, which are impacted by land surface development and alteration [*Grant et al.*, 1996; *Hansen et al.*, 2000; *Haygarth et al.*, 1998; *Monaghan et al.*, 2007]. The objective of this research is to characterize the influence of land cover and seasonality on the export of P, Fe, and Mn during high flow events, targeting both soluble and suspended phases.

High Flow Events

High flow events comprise a dominant component of the overall water flux coming from watersheds, particularly in temperate climates, and therefore drive annual geochemical loads. In temperate snow dominated catchments such as Vermont, the spring melt period, which is characterized by sustained high flow, usually delivers an amount of water disproportionate to the amount of time, accounting for up to 80% of the annual water in less than 25% of the year [*Shanley and Chalmers*, 1999; *Shanley et al.*, 2002]. Even in catchments with less snowpack, such as those in the Great Lakes region, recent research has shown that high flow events control annual nutrient loads [*Dalgolu*, 2012; *Richards et al.*, 2001; *Richards et al.*, 2008; *Yuan et al.*, 2013]. High flow events are common in many other temperate climates as well. In regions with glacial coverage, such as coastal Alaska, summer temperatures drive glacial melt, which results in steadily increasing discharge into the summer, decreasing into the fall. Individual storm events result in rapid increases in discharge on top of the glacial melt component of the hydrograph. Regardless of the cause of increased discharge, high flow events drive riverine export and therefore receiving water body geochemistry. In addition to high

discharge and associated high soluble and suspended loads, high flow events exert significant control on active hydrologic flowpaths, which can determine the source environment for material entering the river [e.g., *Sebestyen et al.*, 2009]. However, due to difficulties associated with sampling these events due to their episodic nature and potentially hazardous sampling conditions, there is still much to learn about their biogeochemical nature, and how this varies seasonally and based on watershed land cover.

The mobilization of material from the land surface during high flow events is hypothesized as an important control on downstream water quality through the delivery of organic matter and nutrients in both the dissolved and suspended forms [*Beaulieu et al.*, 2012; *Jamieson et al.*, 2003; *Langendoen et al.*, 2012; *Shanley et al.*, 2002; *Singh et al.*, 2009]. High flow conditions during snowmelt and spring and summer storms can encourage net erosion throughout a catchment both from the land surface and from river channel features such as streambanks and the channel bottom, especially when surface and shallow subsurface flow dominates over deep subsurface and groundwater flow (baseflow) [*Pellerin et al.*, 2012; *Sebestyen et al.*, 2009; *Shanley and Chalmers*, 1999]. In temperate climates, the transition from deep subsurface flow to runoff occurs as soil becomes progressively more saturated [*Campbell et al.*, 1995; *Pellerin et al.*, 2012; *Sebestyen et al.*, 2009], resulting in the intersection of active hydrologic flowpaths with nutrient “hot spots” [*Vidon et al.*, 2010]. The majority of suspended sediment in rivers is mobilized during these periods of overland and shallow subsurface flow, creating a tight relationship between total suspended solids and discharge in surface water. In addition, pools of soluble-phase elements, often present in organic-rich upper soil horizons, can be

mobilized as a result of changing flowpaths [Novak *et al.*, 2003; Sharpley *et al.*, 2003]. A conceptual model of riverine flux, and its impact on receiving water body geochemistry, must include these hydrologically critical high flow events, which may be important in the development of eutrophic conditions in lakes and coastal waters.

Land Cover

There is a fundamental link between terrestrial and aquatic environments. Land surface conditions influence riverine and receiving water body geochemistry by controlling the source environment, the routing of precipitation to rivers, and to some degree the partitioning and speciation of soluble and suspended geochemical constituents. In addition, terrestrial biota are responsible for consuming nutrients, decreasing the relative abundance of these nutrients in river water, and anchoring sediment on the land surface, thereby decreasing the amount of erosion that occurs, particularly during precipitation events [Lane, 1997; Wang *et al.*, 2008; Zheng, 2006]. The mobilization of sediment from the land surface and stream bed during high flow events is an important control on downstream water quality, as sediment from different source environments can vary dramatically in biogeochemical reactivity [Abdala *et al.*, 2015; Delgado and Scalenghe, 2008; Kaiser and Guggenberger, 2000]. However, this is rarely considered in watershed studies of suspended sediments, or when estimating loads. The characteristics of the land surface, and subsequent effects on riverine geochemistry, are predominately controlled by land use and land cover, and changes in land cover can have profound impacts on aquatic geochemistry.

A major portion of the Vermont economy involves agriculture, be it dairy or crop production. It is well known that the amendment of soils with manure and fertilizer increases the export of nutrients including P from agricultural fields [*Carpenter et al.*, 1998; *Dupas et al.*, 2015; *Haygarth and Jarvis*, 1999; *Monaghan et al.*, 2007; *Walter et al.*, 2001], and that some tilling practices, and the installation of tile drains, can significantly alter hydrologic pathways, resulting in increased erosion and increased export of farm runoff directly to rivers [*Edwards and Hooda*, 2008; *Haygarth et al.*, 1998; *Hively et al.*, 2005]. By contrast, pristine forested environments have significantly lower concentrations of P, both SRP and sediment-bound, and abundant understory vegetation anchors soil to the land surface, decreasing erosion relative to an exposed agricultural field. Runoff, shallow subsurface flow, and erosion during high flow events have the potential to mobilize large pools of dissolved and sediment-bound nutrients often present in upper soil horizons, particularly in agricultural fields. As such, it is necessary to conduct targeted research of these high flow events to determine how they differentially affect land covers common in temperate forested catchments.

In a region such as coastal Alaska, watershed land cover is impacted much less by human development and much more by climate change. This region has seen significant amounts of glacial recession in recent decades, driven by rising winter and summer temperatures [*Milly et al.*, 2005; *Neal et al.*, 2010]. High-latitude locations have seen a larger increase in average annual temperature than the rest of the planet, exacerbating glacial mass loss [*Chapin et al.*, 2014]. As the rapid retreat of glaciers is a relatively recent phenomenon, it is unclear how the landscape will respond, and more critically how riverine and coastal geochemistry may be affected by significant, rapid land cover

change. It is important to consider these rapidly changing landscapes, and specifically how they respond to high flow events, when trying to understand the flux of critical nutrients to receiving water bodies.

Seasonality

The geochemistry of riverine loads is clearly impacted by season [Adhikari *et al.*, 2010; Beaulieu *et al.*, 2012; Dupas *et al.*, 2015; Hood *et al.*, 2009; Malard *et al.*, 1999; Sebestyen *et al.*, 2008], particularly in systems where spring is characterized by a prolonged snowmelt period with high river discharge throughout. The same can be said for glacial systems, where river export is strongly coupled to glacial melt that occurs during the summer. In temperate environments with cold winters, annually frozen soils may also influence riverine geochemistry at the onset of snowmelt. Frozen/saturated soils are known to encourage surface and shallow subsurface flow as snow melts [Bayard *et al.*, 2005; Gburek and Sharpley, 1998; McGlynn *et al.*, 1999; Sebestyen *et al.*, 2009], so riverine geochemistry is disproportionately influenced by the land surface and upper soil horizons during this time period, where constituents have built up either in snow, or below the snowpack in near surface soil horizons. In addition, the springtime landscape in temperate climates is often occupied by senescent vegetation, particularly during snowmelt, and materials exported during this period may have a unique biogeochemistry as they are flushed out of the system prior to extensive uptake, transformation, and sequestration by vegetation. By contrast, the summer period in temperate climate, excluding glacial systems, is characterized by baseflow with intermittent storm events [Shanley *et al.*, 2002]. Only sustained storm events are able to saturate soils and connect

nutrient-rich upper soil horizons to rivers. As land surface conditions change with the seasons, so will riverine geochemistry, and the timing of this change has important ramifications for receiving water bodies.

Phosphorus and Metals Partitioning

Watershed loading of nutrients and contaminants is often partitioned into solute and sediment fluxes, which differ in terms of their fate and reactivity in the environment. Most load estimates for P in rivers are made using a total phosphorus (TP) concentration, which includes all species of phosphorus in both soluble and suspended phases. However, certain forms of phosphorus are much more bioavailable than others, making it useful to separate P loads based on reactivity and potential bioavailability. Orthophosphate, operationally defined as soluble reactive phosphorus (SRP), is generally tightly cycled in forested systems and will not be present in very high dissolved concentrations in oxic circumneutral waters [*Lijklema*, 1980; *Withers and Jarvie*, 2008]. However, studies have shown that certain metal oxides, particularly Fe and Mn (oxy)hydroxides can provide abundant sorption surfaces for oxyanions such as orthophosphate due to their high surface area and net positive surface charge [*Borggaard*, 1983; *Mayer*, 1995; *Sposito*, 1986]. As such, the riverine suspended sediment load may contain a large amount of P adsorbed to the surface of these metal (oxy)hydroxides, but this fraction is rarely quantified in suspended sediment samples. As discussed before, high flow events are known to mobilize significant amounts of sediment, and may therefore also carry significant loads of sediment-bound P in addition to SRP. Numerous studies have identified a relationship between P and certain metals, primarily Fe and Mn, in fluvial

systems [Borggaard, 1983; Lijklema, 1980; Sposito, 1986], making an understanding of the fundamental association of nutrients and metals, and the potential reactivity of P-metal complexes in receiving water bodies, critical to developing a conceptual model of riverine nutrient flux. Different species of Fe and Mn are present within river water, with the chemical form of these metals exerting a strong influence on their geochemical behavior and role in nutrient cycles [Meyer and Likens, 1979; Schroth *et al.*, 2011; Schwertmann and Taylor, 1989; Sposito, 1986].

The relationship between P and carrier phases such as metal (oxy)hydroxides, which are known to be an internal source of P in some lakes such as Lake Champlain in Vermont [Christophoridis and Fytianos, 2006; Schwertmann and Taylor, 1989; Smith *et al.*, 2011; Sondergaard *et al.*, 2003]. These oxidized metal precipitates also tend to be metastable and susceptible to dissolution due to changes in pH [Schwertmann and Taylor, 1989] and redox chemistry [Lijklema, 1980; Smith *et al.*, 2011], which can lead to the release of scavenged adsorbed nutrients, resulting in an increase in the concentration of bioavailable P [Smith *et al.*, 2011]. As such, estimating the redox sensitivity of suspended sediment Fe and Mn species may be critical to the transport and cycling of nutrients in rivers and in receiving water bodies, particularly during high flow events that export the overwhelming majority of suspended sediment to receiving waters. Anoxic to suboxic conditions, which are common at the sediment-water interface in stratified lakes, promote the reductive dissolution of Fe and Mn minerals, releasing both dissolved Fe and any sediment-bound P into the water column [Lovley *et al.*, 2004; Schwertmann and Taylor, 1989; Smith *et al.*, 2011]. The association of SRP with reactive metal (oxy)hydroxides has been hypothesized as a potential internal driver of eutrophication and associated algae

blooms [*Christophoridis and Fytianos, 2006; Smith et al., 2011; Sondergaard et al., 2003*].

Eutrophication and Micronutrient Delivery

Eutrophication is defined as excessive nutrient richness that causes an increase in primary productivity and a subsequent decrease in dissolved oxygen content, thereby reducing aquatic biodiversity [*Sharpley et al., 2003*]. It is thought to be the main cause of impaired surface water quality [*USEPA, 2006*], as it results in the proliferation of algae and aquatic weeds. Large algal blooms also pose a health hazard due to the presence of cyanobacteria, which can release harmful toxins that impact drinking water supplies. The development of eutrophic conditions is often attributed to excessive phosphorus (P) loading, as P is considered the limiting element for primary productivity in aquatic organisms due to tight cycling of P in soils and related low concentrations of bioavailable P in rivers and lakes [*Anderson et al., 2002; Schindler and Eby, 1997*].

There has been a significant amount of research on the causes of eutrophication in Lake Erie, which annually struggles with severely degraded water quality and large algal blooms [*Richards et al., 2001; Richards et al., 2008*]. High flow events related to large storms in the Cuyahoga River watershed in Ohio account for 20% of the annual water load, yet deliver 80% of the total phosphorus [*Yuan et al., 2013*]. Other studies in similar watersheds in the region have identified similar high flow-event derived loads of SRP and TP to Lake Erie, primarily driven by the spring storm period [*Richards et al., 2001; Richards et al., 2008*]. As such, the magnitude of spring runoff in watersheds draining into Lake Erie has recently been determined to be the most consistent predictor of the

severity of summer algal blooms [Michalak *et al.*, 2013]. Throughout the Lake Erie watershed, abundant agricultural activity, a major economic sector in the region, is the likely source for much of the SRP and TP delivered to the lake, as point source discharges from urban centers have decreased drastically since legislation mandated reductions in wastewater treatment plant releases and the use of phosphorus-based detergents. Lake Champlain in Vermont also struggles annually with algal blooms, which have increased in size and frequency throughout the century. Studies have suggested that agricultural fertilizer application is the primary source of excess P to receiving water bodies [Ghebremichael and Watzin, 2011; Jamieson *et al.*, 2003], and other studies have established a relationship between high flow events and sediment/nutrient/solute delivery [McGlynn *et al.*, 1999; Pellerin *et al.*, 2012; Sebestyen *et al.*, 2009]. However, few studies in Vermont have investigated the relationship between land cover and high flow events on the riverine flux of P, or on the possible link between metals and P in river water.

In addition to being an important transport vector for both pollutants and nutrients (e.g., P, As), iron itself is an essential micronutrient that can limit phytoplankton productivity in ~40% of the ocean due to its role in nitrogen assimilation during photosynthesis. In Gulf of Alaska (GoA), Fe has been identified as a limiting nutrient that can encourage primary productivity in coastal waters [Chase *et al.*, 2007; Hickey *et al.*, 2010]. The primary source of iron to GoA phytoplankton is glacial weathering-derived Fe [Lippiatt *et al.*, 2009; Schroth *et al.*, 2011; Wu *et al.*] The export of Fe from rivers draining into the GoA is important in maintaining a healthy ecosystem, and changes in the geochemical character and magnitude of Fe loads due to ice loss may affect aquatic

ecosystem health [Moore *et al.*, 2009; Raiswell *et al.*, 2008; Schroth *et al.*, 2014; Schroth *et al.*, 2011]. Very little is known about the impact of storms on the geochemical nature of macro and micronutrient loads in glacial rivers typical of the GoA, even though their impact on water flux from these systems is well-defined based on hydrologic monitoring. Insight into the impact of storms on glacial river Fe and P loads would improve our understanding of how these systems impact the base of the food chain in the productive marine waters that they feed.

Project Justification

The purpose of this study is to investigate the geochemical character of high flow events, specifically snowmelt and summer storms, to determine how the concentration and size distribution of critical micro and macro nutrient Fe and P vary over time and across a range of land covers. Few studies have focused on how critical hydrologic periods, specifically snowmelt and storm events, drive riverine geochemistry across a range of land covers. Furthermore, studies that quantify the potential reactivity of these storms over time and space are particularly sparse in the literature, but essential to understanding how their impact propagates through the receiving water lacustrine or marine ecosystem. Furthermore, climate change is likely to change the nature of these hydrologic events, with most projections indicating earlier onset of snowmelt and increased storm severity during the spring and summer. Understanding riverine geochemistry during high flow events is critical to developing a conceptual model of how changes in watershed processes may affect receiving water quality and aquatic ecosystems required in the ever changing Anthropocene.

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Chapter 2: Manuscript for *Biogeochemistry*

Coupling of reactive riverine phosphorus and iron during high flow events: impacts of land cover and seasonality

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ABSTRACT

Spring runoff often comprises the majority of annual discharge and riverine phosphorus (P) export due to storm and snowmelt driven sustained high flow. Furthermore, the magnitude of spring runoff can be a strong predictor of receiving water summer harmful algal bloom severity. Yet the loading of reactive forms of P during this time period remains poorly-characterized in time, space and geochemical partitioning. We explore the hypothesis that riverine dissolved and suspended sediment P loads during spring runoff have a particularly high proportion of potentially reactive species due to unique hydrologic pathways and P association with iron (Fe). We compared spring runoff and summer storm concentration and distribution of dissolved P (DP), dissolved and colloidal metals, and redox sensitive suspended sediment P (RSP), Mn and Fe during high flow events in forested and agricultural catchments. The dominant carrier of RSP was Fe (oxy)hydroxides across land cover and season, but Fe(oxy)hydroxide particles and colloids in agricultural catchments were strongly enriched in RSP and DP during spring runoff and summer storms, particularly at the onset of snowmelt. In 2014, 82% of DP and 74% of RSP were delivered to Missisquoi Bay during spring runoff, and most suspended sediment was significantly more redox sensitive than typically input to limnological models, suggesting that the reactivity of this load is systematically underestimated. Changes in the timing, provenance and severity of spring runoff associated with climate or land cover change will have dramatic impacts on total riverine P loads and their potential reactivity in receiving water ecosystems.

INTRODUCTION

High flow events are known to be important drivers of riverine loading of both dissolved and suspended sediment forms of nutrients and pollutants to receiving water bodies, as these events deliver much of the annual water budget in temperate climates [Barnett *et al.*, 2005; Easterling *et al.*, 2000; Shanley and Chalmers; Shanley *et al.*, 2002]. The increased erosion and river discharge associated with these events contribute a disproportionately large amount of sediment, nutrients, and when present, contaminants to annual riverine loads [Grant *et al.*, 1996; Jamieson *et al.*, 2003; Ontkean *et al.*, 2005; Richards *et al.*, 2008; Su *et al.*, 2011; Zhu *et al.*, 2012]. In addition, the activation of specific flowpaths during periods of increased flow may result in a biogeochemically distinct load compared to baseflow, in terms of the reactivity of suspended sediment as well as the concentration and size distribution of nutrients and metals [Bayard *et al.*, 2005; Gburek and Sharpley, 1998; McGlynn *et al.*, 1999; Sebastyen *et al.*, 2008]. However, it is notoriously difficult to sample rivers that are, in many cases, inaccessible at high discharge and/or predict the magnitude and duration of these events, especially when bulk grab samples are needed to characterize suspended sediment.

The geochemistry of riverine loads is clearly impacted by season [Adhikari *et al.*, 2010; Beaulieu *et al.*, 2012; Dupas *et al.*, 2015; Hood *et al.*, 2009; Malard *et al.*, 1999; Sebastyen *et al.*, 2008], particularly in systems where spring is characterized by high discharge and prolonged snowmelt. The spring runoff period, comprised of both snowmelt and frequent rain events, in catchments in northern forests delivers of up to 75% of the annual water in less than 25% of the year [Gburek and Sharpley, 1998; McGlynn *et al.*, 1999; Sebastyen *et al.*, 2008; Shanley *et al.*, 2002]. The snowmelt period

may also have a unique biogeochemistry, as materials that accumulate in and below the snowpack are flushed out of the system prior to extensive uptake, transformation, or sequestration by senescent local vegetation. Frozen/saturated soils encourage surface and shallow subsurface flow during melting [Bayard *et al.*, 2005; Gburek and Sharpley, 1998; McGlynn *et al.*, 1999; Sebestyen *et al.*, 2009], so riverine geochemistry is disproportionately influenced by the land surface and upper soil horizons. Numerous studies have linked snowmelt to unique riverine geochemistry in terms of DOC [Dawson *et al.*, 2008; Sebestyen *et al.*, 2008], nitrogen [Pellerin *et al.*, 2012; Sebestyen *et al.*, 2009], phosphorus [Jamieson *et al.*, 2003; Royer *et al.*, 2006 2011], and trace metals [Dahlqvist *et al.*, 2007; Rember and Trefry, 2004]. While the spring runoff period is characterized by sustained high discharge and associated runoff/shallow subsurface flow, summer in temperate climates such as Vermont is characterized by baseflow conditions with intermittent storm events [Shanley *et al.*, 2002]. During this time, the activation of runoff/shallow subsurface flowpaths is dependent on the duration and magnitude of specific storms and antecedent conditions (e.g., soil moisture); unsaturated soils may not encourage abundant runoff and associated mobilization of surface materials [Kollet and Maxwell, 2006]. As such, summer riverine geochemistry may be influenced more by deeper flow paths, riparian zones, and baseflow geochemical processes than pooling of material and processes within the upper soil profiles [Fisher *et al.*, 2004; Lapworth *et al.*, 2009].

Watershed loading of nutrients and contaminants is often partitioned into solute and sediment fluxes that differ in their fate and reactivity in the environment. As a nutrient, phosphorus (P) is considered readily bioavailable as dissolved orthophosphate

(PO_4^{3-}). Excessive loading of dissolved P has been linked to eutrophication in rivers and receiving water bodies [Anderson *et al.*, 2002; Michalak *et al.*, 2013; Yuan *et al.*, 2013], and is derived from both point-sources (wastewater treatment, sewage and industrial effluent) and diffuse sources (e.g., agricultural runoff) [USEPA, 2006; Van Drecht *et al.*, 2009]. Non-point sources and runoff are of particular interest to this study, as the export of DP is known to differ across land covers, particularly that of agricultural [Hansen *et al.*, 2004; Jamieson *et al.*, 2003; Walter *et al.*, 2001; Yuan *et al.*, 2013] and forested [Edwards and Withers, 2007; Meyer and Likens, 1979] catchments. In addition, the tight cycling of metal species, particularly Fe and Mn, has been shown to be important in the cycling, transport, and fate of P [Baken *et al.*, 2015a; Baken *et al.*, 2015b; Borggaard, 1983; Lijklema, 1980] in some systems. As Fe and Mn are ubiquitous components of natural soils, the export of metals from river systems is well studied [Dahlqvist *et al.*, 2007; Pokrovsky and Schott, 2002; Pokrovsky *et al.*, 2006; Pokrovsky *et al.*, 2010; Rember and Trefry, 2004; Schroth *et al.*, 2011; Stolpe *et al.*, 2013], but the interaction of different Fe and Mn size fractions with P during high flow events and across land covers has not been explored. This is critical, as recent studies found that redox cycling of Fe has a strong control on P mobility at the surface- groundwater interface in some environments [Baken *et al.*, 2015a; Baken *et al.*, 2015b; van der Grift *et al.*, 2014], suggesting the transport and fate of P may be closely related to the size distribution and speciation of Fe.

Given extensive erosion during high flow events, a relatively high fraction of many constituents are associated with suspended sediment [Richards *et al.*, 2008; Walling *et al.*, 2008; Dhillon, S. and Inamdar, S., 2013]. Sediment mobilized from the

land surface and stream bed during high flow events is an important control on downstream water quality through the delivery of nutrients and contaminants associated with suspended sediment [Pacini and Gachter, 1999; Walling *et al.*, 2008; Walter *et al.*, 2001; Withers and Jarvie, 2008]. The dramatic differences in biogeochemical reactivity of sediment from different source environments is well documented in soils and sediment literature [Abdala *et al.*, 2015; Delgado and Scalenghe, 2008; Hansen *et al.*, 2004; Kaiser and Guggenberger, 2000; 2003; Lovley *et al.*, 2004], but is rarely considered in watershed studies of suspended sediment, nor when estimating loads. Of particular interest are Fe/Mn (oxy)hydroxides, which are very effective scavengers of oxyanions such as phosphate as a result of surface charge and surface area [Borggaard, 1983; Delgado and Scalenghe, 2008; Lijklema, 1980; van der Grift *et al.*, 2014 2014]. These metal (oxy)hydroxides develop within the soil and river system depending on redox conditions and pH [Baken *et al.*, 2015a; Baken *et al.*, 2015b; Perret *et al.*, 2000; van der Grift *et al.*, 2014] and are highly susceptible to reductive dissolution in suboxic to anoxic environments [Baken *et al.*, 2015a; Baken *et al.*, 2015b; Lovley *et al.*, 2004; van der Grift *et al.*, 2014; Zinder *et al.*, 1986]. Dissolution results in the release of adsorbed P, making Fe/Mn (oxy)hydroxides a dominant internal P source to receiving waters that reach an/hypoxic sediment water interface conditions [Smith *et al.*, 2011; Schroth *et al.* 2015; Giles *et al.* in press]. More recalcitrant forms of sediment also exist, but are less likely a dominant source of nutrients, as dissolution occurs much more slowly in most natural systems and stability may not be impacted by redox dynamics (e.g., apatite-derived P). While high flows increase sediment loads, the biogeochemical nature and ramifications of that sediment for receiving waters may differ across land covers, particularly between

agricultural and forested environments [*Owens and Walling, 2002; Walling et al., 2008; Withers and Jarvie, 2008*].

In this study, our objective is to examine the geochemical nature of Fe, Mn, and P in high flow events associated with spring runoff in comparison to high flow events during the summer after vegetation across the landscape becomes active. Specifically, our sampling strategy and analyses allow us to assess the hypotheses that: 1) land cover has a significant impact on snowmelt suspended sediment and solute concentrations during spring runoff compared to summer high flow events; 2) soluble and potentially reactive P in suspended sediment are associated with reactive Fe and Mn carrier phases, which differ between snowmelt and summer high flow events and across land covers; 3) the concentrations and loads of soluble and suspended sediment P, Fe, and Mn systematically evolve during spring runoff and during the summer across landscapes; and 4) seasonal high flow events disproportionately impact the delivery of reactive forms of P to Lake Champlain. The conceptual model of high flow event Fe and P geochemistry herein developed has important ramifications for understanding loading of reactive Fe and P species during these high flow events, as well as their potential impact on receiving water quality and ecosystems threatened or impacted by cultural eutrophication.

METHODS

Field sites and sampling design

Sampling locations, located in northern Vermont within the Missisquoi River watershed, drain into Lake Champlain at Missisquoi Bay (Figure 1). The Missisquoi River watershed can be partitioned into regions of low and high elevation. The lowlands contain the majority of the Champlain Valley agricultural land, and higher elevations are primarily montane-forested catchments of the northern Green Mountains (Figure 1). Throughout the lower elevations, much of the agriculture is concentrated near the river within floodplains. Individual monitoring locations were chosen to utilize pre-existing USGS and EPSCoR infrastructure including gages and ISCO auto-samplers. Two sampling locations are located on the Missisquoi River: the outlet at Swanton (OUT) and the uplands at North Troy (FOR); and two sites, located on tributaries in the sub-watersheds of Hungerford Brook (AGR) and Wade Brook (FOR), were selected to cover the two dominant watershed land covers, forested (FOR) and agricultural (AGR) (Figure 1). The sample location OUT provides an integrated biogeochemical and hydrologic signal of the entire watershed export. Samples from Missisquoi River in North Troy and Wade Brook are grouped as FOR for discussion purposes to increase data available for that forested land cover, as both catchments have very similar land covers.

A sampling design targeted high-flow events with additional baseflow sampling from the onset of snowmelt, during both temperature-driven melt and rain-on-snow events, to the end of the summer in 2014. Meteorological data and resulting forecasts of rising hydrographs at multiple sites helped design sampling strategies for days following above-freezing nights, and during or immediately after precipitation events (Figure 2).

Sampling in mid to late afternoon helped capture peak discharge typical of a snowmelt-driven hydrograph. The spring runoff period was defined as the onset of melt (3/28/2014) to the end of sustained high discharge and the growth of vegetation (5/2/2014). Following spring runoff, weekly to bi-weekly baseflow samples were collected, with targeted storm event sampling from May to September. Metals samples were collected in 250mL acid-washed bottles from stream channel center using an acid-washed bucket sampling rig. Suspended sediment and SRP samples were collected in a 20L acid-washed carboy using the same sampling rig, with care taken not to disturb channel bottom sediment.

Sample preparation and analysis

Sample splits for metals analysis were filtered in a laminar flow hood with 0.45 μ m PES disposable filters and 0.02 μ m Anotop[®] Plus nonsterile PES filters within 24 hours of sampling and stored in 15mL bottles soaked in trace metal grade HCl and rinsed with dDI water following the method in Shiller [2003]. After filtration, sample for trace metal (TM) analysis was acidified to 0.1% HNO₃ using Optima[®] ultra-pure concentrated nitric acid [Shiller, 2003]. Remaining unfiltered sample was also acidified to 0.1%. The acidified and filtered samples were analyzed by ICP-MS at Woods Hole Oceanographic Institution's plasma facility. A spike of Sc and In was used to calculate Fe and Mn concentrations for the <0.45 μ m and <0.02 μ m fractions (truly dissolved = <0.02 μ m; colloidal = 0.02-0.45 μ m) [Shiller, 2003]. Because 0.02 μ m filters leach P, only the <0.45 μ m fraction for P was used, consistent with Shiller 2003's observation. Filter contamination was checked using full process filtered blanks and was always less than 10% of the lowest concentration counts for each analyte measured. We used the

international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) to validate daily ICP-MS runs, with material measured once for every 10 uncharacterized samples. Standard concentrations were used to calculate ICP-MS error for each analysis day, with triplicate SLRS-4 measurements all within 10%. Thus, any colloidal value <10% of the measured total <0.45 μ m fraction was considered insignificant, and removed from analysis.

River samples were analyzed for SRP following filtration through a 0.45 μ m PES filter within 24 hours. Concentrations were measured using the spectrophotometric molybdenum blue method [*Murphy & Riley, 1962*] following EPA Method 365.1. In addition, the <0.45 μ m fraction was analyzed on the ICP-MS as explained above. Concentrations determined by SRP and ICP-MS were combined to increase sample count.

To extract suspended sediment, known sample volumes were poured into Nalgene[®] vacuum filtration rigs containing pre-weighted 0.45 μ m PES filters and connected to a fume hood vacuum system. Additional sample was added in 250mL aliquots until the filtration rate dropped drastically, indicating the filter was clogged. Following filtration, the filtrate was discarded and the filters were air-dried in the fume hood for a minimum of 48 hours. Dry weight was then measured to determine the sediment mass and suspended sediment concentration (in mg/L). When possible sediment extractions were optimized for a target mass of 0.1-0.2g dry sediment for each analysis; it was not possible to extract this amount of sediment during some sampling events, particularly during the summer.

Following collection of suspended sediment, two preparations targeted different geochemical pools of particulate P, Fe, and Mn: 1) ascorbic acid extraction following Anschutz et al. (2000) (referred to subsequently as the 'redox sensitive' pool); and 2) Aqua Regia digestion following EPA Method 3050B, which targets all non-silicate bound P, providing a measure of total P. Both methods were modified for use on sediment-laden filters rather than loose material to ensure full contact of extraction/digestion solution with the filters. For the extraction, multiple filters with sediment totaling 0.1-0.2g were placed in 15mL acid-washed tubes with 10mL of extracted solution and placed in a shaker for 24 hours. The ascorbic acid extraction targets easily reduced metal (oxy)hydroxides within sediment by simulating anoxic conditions that may occur at the lake bottom or within a saturated soil. The forced reductive dissolution of metal (oxy)hydroxides also releases adsorbed P. No volume modifications were made to the Aqua Regia acid digestion method, although whole filters with sediment were folded and placed within digestion tubes, along with filter blanks to ensure no leaching of TM or P. NIST standards for phosphorus were used as positive control to develop a method error for each run. Solutions from both the extraction and digestion procedures were analyzed with an ICP-OES.

Calculation of spring runoff and annual loads

Annual and seasonal loads of geochemical constituents were estimated using the USGS EGRET package. This recently developed R-script employs a weighted regression on time, discharge, and season using approved daily USGS discharge measurements and user-provided sample concentrations. We used our data and the EGRET script to model

daily TSS and SRP loads. Using these daily TSS estimates and the suspended sediment time series data, we determined the daily reducible and digestible P loads by assigning the suspended sediment P concentrations for individual days to that day's TSS load. To assign values of suspended sediment P concentration to days that were not sampled, we averaged adjacent sampling days.

RESULTS

Spring Runoff Period

The 2014 Vermont spring runoff period was characterized by sustained high discharge supplied by a near-average (65-year record) high-elevation snowpack that melted rapidly [*UVM-EcoInfo, 2015*]. A large percentage of the total study (March – September) water budget was exported from the system during this spring runoff period, accounting for 59% at OUT, 71% at AGR, and 60% at FOR (Figure 3). In 2014, snowmelt in northern Vermont began around 3/28/14 at low elevations, identified by flowing rivers and active USGS gages. This was also a time when temperatures remained above freezing for extended periods (Figure 2) and a thick snowpack remained throughout the watershed. Snowmelt at higher elevations did not begin until 4/7-4/10 [*UVM-EcoInfo, 2015*], although safety concerns prevented sampling until 4/11 (Figure 3c). Samples were collected at periods of temperature-driven melt when river levels were high compared to baseflow (Figure 3). In addition, a number of large rain-on-snow events were captured at all sites, including a 10-year flood on 4/15 (Figure 3).

Suspended Sediment

During the 2014 spring runoff, total suspended sediment (TSS) concentrations were generally high with peak values associated with rain-on-snow events (Figure 3). At all sites, the TSS loads were high throughout snowmelt, driven by consistently high (and positively correlated with) discharge ($p < 0.05$); TSS dropped rapidly as conditions trended toward baseflow (Figure 3). Redox sensitive P concentrations varied across sites with a mean concentration of 0.11, 0.03, and 0.05 mg/L for AGR, FOR, and OUT respectively. Digestible P was also variable with mean values of 0.27, 0.12, and 0.15 mg/L for AGR, FOR, and OUT, respectively. Redox sensitive and digestible Fe concentrations were much higher than P at all sites with mean reducible Fe values of 0.90, 0.63, and 0.58 mg/L for AGR, FOR, and OUT, respectively. The concentrations of both redox sensitive and digestible Mn were low and very similar across streams draining different land covers.

Dissolved and Colloidal Constituents

Mean DP concentrations during the spring runoff period were 102.8, 5.6, and 20.8 ppb for AGR, FOR, and OUT, respectively. At all sites, DP concentrations were highest within 1-2 days of the onset of snowmelt and decreased over time, with minimum values occurring near the end of the defined spring runoff period (Figures 4a-c). Maximum DP concentrations at AGR were nearly two orders of magnitude greater than at FOR. Mean truly dissolved and colloidal Fe concentrations were similar across land covers (10-20 and 55-60ppb respectively) and did not display the same degree of variability as DP values. The same was true for truly dissolved Mn, which had mean values of 37.3, 10.1,

and 19.9 ppb for AGR, FOR, and OUT respectively. Colloidal Mn values were generally low with the exception of two very high concentrations occurring during a large rain-on-snow event at OUT (Figure 4c). Peak truly dissolved Fe and Mn concentrations occurred at all sites approximately one week into snowmelt and decreased rapidly over time (Figure 4). Colloidal Fe concentrations varied with discharge at OUT and AGR, but decreased over time at FOR (Figure 4). The same trends exist in colloidal Mn with the exception of AGR, where colloidal Mn values are generally insignificant. Across all sites, the majority of Fe is colloidal and the majority of Mn is truly dissolved.

Post-Snowmelt Period

The end of the spring runoff period marks the hydrological transition from sustained high discharge and associated runoff/shallow subsurface flow to groundwater-fed baseflow conditions with intermittent storms. From May to September, samples were collected weekly to bi-weekly during baseflow conditions with targeted sampling during storm events. Characterization of suspended sediment was only possible during storm events, as baseflow did not result in sufficiently high TSS concentrations.

Suspended Sediment

From May to September, TSS concentrations were generally low, peaking only during intermittent storm events (Figure 3). (Low summer sediment loads were especially noticeable at the FOR forested site, where water ran clear even during larger storm events.) Therefore, characterization of suspended sediment in the forested catchments during the summer was conducted only on samples from FOR. Summer storm RSP

concentrations were high at AGR relative to the other sites, with mean concentrations of 0.06, 0.01, and 0.01 mg/L for AGR, FOR, and OUT respectively; digestible P was also high at AGR and relatively low at the other sites with mean values of 0.14, 0.04, and 0.03 mg/L for AGR, FOR, and OUT respectively. The concentrations of redox sensitive and digestible Fe were much higher than P at all sites and similar across sites with mean reducible Fe concentrations of 0.47, 0.26, and 0.24 mg/L and mean digestible Fe values of 1.7, 1.1, and 1.0 mg/L for AGR, FOR, and OUT respectively. The concentrations of both redox sensitive and digestible Mn were low across all land covers. Since suspended sediment could not be extracted during periods with very low TSS concentrations, the biogeochemical nature of suspended sediment during baseflow conditions is unknown; however, this also makes baseflow essentially irrelevant to sediment-bound nutrient budgets.

Dissolved and Colloidal Species

Mean DP concentrations during the late spring and summer period were 86.1, 4.8, and 13.6 ppb for AGR, FOR, and OUT, respectively (Figure 4). At all sites, DP concentrations were highest during storm events and at least one order of magnitude lower at baseflow (Figure 4). At AGR, the concentration of DP increased rapidly during storm events, with peak concentrations preceding the peak discharge during some storm events (Figure 4a). Maximum DP concentrations at AGR were nearly two orders of magnitude greater than at FOR. The mean truly dissolved Fe concentrations were 24.0, 12.0, and 4.93 mg/L and mean colloidal Fe concentrations were 82.0, 122.0, and 64.1 mg/L for AGR, FOR, and OUT, respectively (Figure 4). Across all sites, truly dissolved

Mn had a mean concentration of 74.1, 14.4, and 35.7 for AGR, FOR, and OUT, with very low or insignificant colloidal Mn concentrations. Truly dissolved Fe concentrations increased over time, while truly dissolved Mn concentrations were more variable (Figure 4). Colloidal Fe and Mn concentrations varied with discharge at all sites with the exception of AGR, where colloidal Mn values were generally insignificant (Figures 4a-c). Across all sites, the majority of Fe was colloidal and the majority of Mn was truly dissolved during spring runoff, summer storms, and baseflow conditions. No discernable pattern appears between concentrations of soluble-phase Fe and Mn at baseflow and discharge (Figure 4).

DISCUSSION

Our targeted sampling across seasons and comprehensive geochemical analyses of solutes and sediment P, Fe and Mn concentration during different hydrologic conditions allow us to: 1) compare the impact of land cover on suspended sediment and solute concentration during spring runoff and summer high flow events, 2) characterize and compare the coupling or decoupling of solute and suspended sediment P to reactive Fe and Mn phases exported in snowmelt to summer high flow events across land covers, 3) describe the temporal evolution of these constituents during the poorly-described spring runoff period and compare to summer temporal dynamics across land covers, and 4) model P species loading to Lake Champlain and assess the relative importance of seasonal high-flow events on delivery of reactive dissolved and redox sensitive forms of P to the lake ecosystem. We integrate these analyses to establish a broadly applicable conceptual model of riverine P and Fe loading across seasons, with focus on reactive

forms in both suspended and dissolved/colloidal loads. Our data suggest that season, flow regime and land cover are strong drivers of the proportion of reactive P in soluble and suspended sediment loads and its association with Fe, and that the Missisquoi River delivers the majority of labile P to Lake Champlain during the spring runoff period, derived in large part from lowland agricultural sub-catchments in the Champlain Valley.

Land Cover and Seasonal Impacts on P, Fe, and Mn Concentrations

Suspended Sediment

Spring runoff

During spring 2014, the suspended sediment concentrations at all sites are characteristic of this hydrological runoff period (Figure 3) when extensive erosion and elevated flows produce relatively high sustained suspended sediment loads [Gao *et al.*, 2004; Lane, 1997]. In addition, variably frozen and saturated soils were common throughout the lowland portion of the watershed. These soil conditions are known to isolate water at and within the soil surface and upper horizons that are actively melting [Bayard *et al.*, 2005; Groffman *et al.*, 2001; Hardy *et al.*, 2001]. Total suspended sediment was highest at AGR, likely a result of easily eroded and abundant bare agricultural soils from 4/11 through the remainder of spring (Figure 3a), and due to a combination of streambank and riverbed erosion that likely contributes to TSS loads [Langendoen, 2012]. As a result of erosion from the land surface, streambanks, and riverbeds, the spring runoff TSS loads are likely characteristic of the land surface and upper soil horizons. Conversely, TSS concentrations were lowest in the forested system

due to root network and soil O-horizon anchoring of mineral soil and stream banks (Figure 3c). Since thaw and snowmelt occur at different times across the range of elevations studied (30-1140m), the temporal evolution of suspended sediment composition measured at the Missisquoi River outlet is likely representative of the dynamic biogeochemical nature of basin loads from the highlands of the northern Green Mountains to valley lowlands. The difference in TSS concentrations across land covers suggests that the Champlain Valley lowland agricultural systems contribute disproportionately to the sediment-derived P, Fe, and Mn loading to Lake Champlain during spring runoff.

Summer storm TSS

During summer baseflow, it is not unusual that the average TSS concentrations at all sampling sites were much lower than the spring runoff period (Figure 3), given the increased anchoring of vegetation and decreased flows. Unlike the spring runoff period, summer riverine geochemistry has been shown to be characteristic of deeper flowpaths except under conditions when groundwater tables become high and surface soils become saturated; the latter promotes an increase in the relative proportion of surface runoff to stream discharge [Gburek *et al.*, 1999]. Throughout the Lake Champlain Basin, leaf out in 2014 was coincident with the change in dominant flow regime from spring to summer, enhancing the role of terrestrial biota on biogeochemical dynamics relative to the snowmelt period. Therefore the increased TSS concentrations observed during summer storm events were likely due to some component of increased in-stream, land surface, and streambank erosion (Figure 3) [Langendoen *et al.*, 2012]. Consistent with conditions

during the spring runoff period, average TSS concentrations during storms were highest in AGR (Figure 3a), presumably as a result of cut and till schedules known to increase soil susceptibility to erosion during storm events [Hansen *et al.*, 2000; Panuska *et al.*, 2008; Su *et al.*, 2011] combined perhaps with the relatively high erodibility of the Champlain Valley glacio-lacustrine surficial geology. Summer average TSS concentrations were again lowest in the forested system (Figure 3b), likely due to abundant root networks and understory anchoring. Summer TSS concentrations at OUT lie between the forested and agricultural systems (Figure 3c), but are closer to AGR. Higher TSS concentrations in the lowland agricultural systems, across all seasonal high flows, suggest that these regions are disproportionately important in the loading of suspended sediment (and associated sediment bound nutrients or pollutants) to Lake Champlain, irrespective of season.

Spring runoff P, Fe, and Mn

Since it has been suggested that the magnitude of P loading during spring runoff drives the severity of algal blooms in many lakes [Michalak *et al.*, 2013; Stumpf *et al.*, 2012] and that sediment redox chemistry drives the onset and propagation of summer algal blooms in Lake Champlain [Pearce *et al.*, 2013; Smith *et al.*, 2011, Giles *et al.*, 2016], characterization of metal and P redox sensitivity in riverine suspended sediment loads is critical to describe the potential mobilization of these constituents in receiving waters. Previous research identified an extractable P fraction of ~30% in agricultural runoff that can be considered potentially bioavailable [Dupas *et al.*, 2015; Poirier *et al.*, 2012; Sharpley *et al.*, 1992]. The relatively high concentration of redox sensitive and

digestible P at AGR during the 2014 spring runoff is consistent with other studies showing higher P concentrations in soils from manure-amended fields [Abdala *et al.*, 2015; Hansen *et al.*, 2004; Walter *et al.*, 2001], and agricultural surface soils enriched in labile P [Huang *et al.*, 2011; Jamieson *et al.*, 2003; Pacini and Gachter, 1999]. The low RSP concentrations in the forested system (FOR) suggest that not only is less total P exported from these catchments, but the suspended sediment load is inherently less reactive, presumably due to the lack of P amendment in these forested soils. . While the RSP concentrations at OUT reflect the variable land cover of the Missisquoi watershed, the RSP concentrations are much closer in magnitude to AGR, reflecting the disproportionate influence of lowland agricultural fields on the suspended sediment P geochemistry and loading in the Missisquoi River during spring runoff . Since the Hungerford Brook sub-catchment (AGR) is characteristic of the Lake Champlain lowland region (Figure 1), it follows that reducible sediment-bound P exported from agricultural land during spring runoff will disproportionately influence and elevate the potential redox sensitivity of spring sediment loads and contribute to internal P loading once deposited to the lake bed. Unlike sediment-bound P, the average concentration of either redox sensitive or digestible Fe or Mn in suspended sediment during spring runoff does not appear to differ statistically ($p \gg 0.05$) across our sampled land covers. Importantly, our selective extractions demonstrate an enrichment of reducible Fe relative to Mn in spring runoff suspended sediment, irrespective of catchment land cover, suggesting these relatively abundant Fe (oxy)hydroxides have the potential to be the dominant carrier of RSP in spring suspended sediment loads.

Summer storm P, Fe, and Mn

Across all sites, summer storm RSP concentrations were much lower than spring runoff as a result of lower TSS concentrations, confirming the disproportionate importance of the spring loading. However, RSP concentrations were highest at AGR for all summer storms (Wilcoxon test: $p=0.047$, $\chi^2=6.111$, $DF=2$), confirming a similar land cover-driven impact on phosphorus partitioning in summer when manure was applied intermittently on these fields, sustaining high P concentrations in the suspended sediment and stream water. In addition, streambank erosion has been identified as a major source of labile P in the Champlain Valley, especially in regions with long-term P amendment, resulting in pools of legacy soil P in easily erodible soils [Langendoen *et al.*, 2012]. The decrease in reducible and digestible P, Fe, and Mn concentrations at all sites during summer storms relative to spring runoff was primarily the result of decreased erosion and TSS concentrations. Enrichment in reducible Fe relative to Mn in the summer storm suspended sediment load at all land covers also further suggests that Fe(oxy)hydroxides are the dominant redox sensitive phase in high flow event suspended sediment loads in this catchment across both time and space.

Dissolved and Colloidal P, Fe, and Mn Concentrations

As with suspended sediment forms of P, the AGR spring runoff waters were typical of heavily fertilized agricultural environments in that SRP concentrations were 10-20 times those at other sites (Figure 4a) [Abdala *et al.*, 2015; Hansen *et al.*, 2004]. Unlike the agricultural catchment, spring runoff waters exported from the forested catchments were characterized by very low mean and maximum DP concentrations

(Figure 4b), even during snowmelt; but this is expected because: 1) forested soils are not amended with labile P; 2) primary mineral weathering only produces low background concentrations of DP [House, 2003; Owens and Walling, 2002]; and 3) available P is relatively tightly cycled by northern forest biota [Meyer and Likens, 1979; Stelzer et al., 2003]. Similar to suspended sediment RSP dynamics, SRP concentrations in spring runoff waters at OUT range between the AGR and FOR site concentrations, but with a mean closer to AGR despite 74% of the upstream land cover being forested (Figure 4c). The relatively high mean DP concentration at OUT during spring runoff further demonstrates that the P loading is relatively enriched in labile P (in both dissolved and particulate fractions) derived from the agricultural lowland of its catchment. The ranges in dissolved and colloidal Fe and Mn concentration across land covers during spring runoff are consistent with the suspended sediment Fe and Mn data, in that these metal species concentrations were not statistically different by catchment land cover (agricultural vs. forest). While the amendment of soils with labile P appears to be the main driver of elevated riverine P (both suspended sediment and soluble reactive forms), it does not affect the concentration and distribution of colloidal and ‘truly’ dissolved Fe and Mn. The elevated concentrations of colloidal Fe compared to Mn suggest that ample reactive colloidal Fe(oxy)hydroxides in river loads that have the potential to carry sorbed P species, irrespective of land cover, further implicating the critical role that reactive iron species play in P transport during spring runoff.

The lower summer DP concentrations across all sites (compared to spring runoff), suggests less dissolved P is exported from the entire landscape as biological uptake increases in the warmer months. However, similar to the snowmelt period, DP

concentrations at AGR were high relative to other land covers, which is expected in manure-amended systems, particularly during storms, when pathways enriched in labile amended P are activated [Dupas *et al.*, 2015; Royer *et al.*, 2006; Walter *et al.*, 2001]. Given continued manure application during the summer, the maximum concentration of DP in river water derived from agricultural runoff during summer storms appears similar in magnitude to early spring storm runoff concentrations. Consistent with trends during spring runoff, water exported from forested catchments during summer storms had very low DP concentrations, in terms of both mean and maximum values, characteristic of these relatively pristine environments [Meyer and Likens, 1979; Owens and Walling, 2002; Stelzer *et al.*, 2003]. Additionally, concentrations measured at OUT during summer storms were also characterized by intermediate DP values similar to spring runoff, reflecting the integrated watershed geochemical signal evident at the Missisquoi River outlet. This differs from RSP concentrations at OUT during summer, which, as a result of generally low TSS concentrations, were more similar to FOR. This indicates an important seasonal impact on high flow event P loads because summer storms still export large amounts of amendment-derived SRP in runoff and shallow subsurface flow from agricultural fields. However, anchoring of sediment by crops and understory vegetation reduces the export of labile particulate RSP during the summer in comparison to spring runoff. Additionally, monitoring confirmed no statistical difference in Fe and Mn concentration and partitioning across overall catchment land covers during high summer flow events.

P Association with Fe

Suspended sediment

Indeed, the strong positive and statistically significant correlations between the concentrations of RSP and Fe in suspended sediment (AGR: $R^2=0.802$; FOR: $R^2=0.989$; OUT: $R^2=0.875$; $p<0.001$ for spring samples only) at all sites suggests that Fe (oxy)hydroxides serve as a critical sorption surface and transport vector for RSP in spring runoff suspended sediment (Figure 5). This is not surprising, as Fe (oxy)hydroxides are known to be highly effective scavengers of oxyanions such as P in typical oxic mildly acidic-neutral freshwater systems [*Baken et al.*, 2015a; *Baken et al.*, 2015b; *Borggaard*, 1983; *Lijklema*, 1980; *Mayer*, 1995; *van der Grift et al.*, 2014]. Yet analysis of the correlation shows the slope of association between RSP and Fe differs dramatically by land cover, due to a wide range in RSP concentrations across landscapes and a relatively similar range in redox sensitive Fe concentrations (Figure 5). We interpret this to reflect the varying amounts of RSP associated with Fe (oxy)hydroxides in each system's spring runoff suspended sediment load, which is driven by land cover effects on Fe(oxy)hydroxide enrichment in sorbed P (Figure 5). In AGR there are high but variable RSP concentrations with less variable reducible Fe concentrations, producing a relatively high slope (slope=0.262) compared to the forested catchment (slope=0.059) (Figure 5). During this spring runoff period, the relationship between RSP and Fe at OUT appears similar to AGR, again reflecting a disproportionate influence of lowland agricultural regions on the redox sensitivity of P in suspended sediment loads (slope=0.195) (Figure 5). These trends suggest that a similar fraction of reducible Fe exists in the suspended sediment from both forested and agricultural sub-catchments, but the dramatic difference

in P concentrations associated with reducible Fe phases reflects the abundance of P in suspended sediment sources in agricultural soils and stream bank sediments having a history of P amendment. These trends confirm that during spring runoff: 1) Fe (oxy)hydroxides are the dominant carrier of RSP across forested and agricultural catchments; and 2) reducible Fe mineral phases in sediments from agricultural fields are relatively rich in RSP, which ultimately elevates the RSP loading from the entire Missisquoi River Basin. The lack of a statistically significant correlation between RSP and Mn (oxy)hydroxides ($p >> 0.05$) at any site is interesting in the context of internal P loading studies on Missisquoi Bay lake sediments, where Mn (oxy)hydroxide reduction near the sediment water interface has been demonstrated to be the best indicator of P release from sediment and initiation of harmful algal blooms [*Pearce et al.*, 2013; *Smith et al.*, 2011; *Giles et al. in press*].

Similar to suspended sediment loads during spring runoff, the RSP and reducible Fe concentrations during summer storms show strong positive correlation ($p < 0.001$) at each site, suggesting these iron phases remain the dominant carrier of RSP across seasons (Figure 5). Also consistent with spring runoff suspended sediment, there is no statistical relationship between Mn (oxy)hydroxides and RSP during summer storms. The small sample size for summer storm suspended sediment prevents statistically sound regression analysis for these samples; however, the addition of summer samples does not change the previously discussed relationship (i.e., slope) between RSP and Fe at AGR or FOR. Interestingly, the addition of summer storm suspended sediment samples resulted in a significant change to the relationship between RSP and Fe at OUT when comparing the high spring runoff samples (slope=0.195) to the relatively low slope (0.062) for all

samples over the entire year. The annual slope at OUT is comparable to the FOR suspended sediment (Figure 5). These data may suggest that the proportional provenance of suspended sediment in the Missisquoi Basin during high flow events changes during the seasons, with less disproportional impact of the agricultural lowlands during the summer relative to the spring. Alternatively, in the larger Missisquoi River system represented at OUT, it is possible that some internal process depletes the amount of RSP in storm event suspended sediments (e.g., biological cycling, desorption, or redox dynamics) as water temperatures warm and the riverine/riparian ecosystem becomes more active. We cannot conclusively identify a mechanism through analysis of our dataset; and this warrants further research. Yet these watershed data demonstrate that Fe (oxy)hydroxides are the dominant carrier of particulate RSP during all seasons, and a systematic variation across season and land cover exists in the concentration of RSP associated with Fe(oxy)hydroxides in suspended sediment loads, with the more RSP concentrated on Fe phases in the spring runoff load from the agricultural Champlain Valley lowlands. As such, we can conclude that spring sediment P loads may exert disproportionate impact on receiving water quality, not only due to higher sediment concentrations, but because the suspended sediment loads bear particularly P-rich redox sensitive mineral phases sourced in the agricultural regions of the watershed.

Colloidal and dissolved phases

Previous studies have identified colloidal Fe(oxy)hydroxides as transport vectors for an array of nutrients and pollutants as a result of high surface area and charge at typical freshwater pH ranges [Dahlqvist *et al.*, 2007; Stolpe *et al.*, 2013], and as highly effective scavengers of dissolved inorganic P similar to particle-sized metal (oxy)hydroxides. In the Missisquoi River basin in 2014, the majority of soluble-phase Fe was colloidal, although there were intermittent events with relatively high concentrations of ‘truly dissolved’ Fe, and the overwhelming majority of Mn was always in the ‘truly dissolved’ form. This size distribution and inferred Fe and Mn speciation is consistent with that observed in relatively pristine and well-studied boreal-forested catchments [Dahlqvist *et al.*, 2007; Pokrovsky *et al.*, 2006; Pokrovsky *et al.*, 2010; Rember and Trefry, 2004; Stolpe *et al.*, 2013], and suggests that operational partitioning by size does not vary systematically among our sites.

Since trace metal size partitioning data suggest that abundant, Fe-rich organic and inorganic colloidal phases were present during spring runoff, we explored the relationship with these various fractions and SRP to better understand when and where these constituents may be following similar pathways and when soluble P transport may be driven by the flushing of metal colloids formed in soil, riparian or hypohreic environments. When separated by site, interesting trends appear in the relationship between DP and various soluble Fe size fractions. There were no statistically significant relationships (at $p=0.05$) between DP and colloidal or truly dissolved Fe in the agricultural system, but a strong positive correlation between DP and colloidal Fe at the forested sites ($n=5$, $R^2=0.904$, $p=0.013$) (Table 1). The latter suggests that these colloids

may be important carriers of soluble P in non-P amended systems, or to a 'natural' soil P saturation level, but it is unclear to what degree these highly reactive metal colloids transport amended P in agricultural systems during spring runoff. The lack of relationship between DP and colloidal Fe in AGR waters is inconsistent with the association of these elements in suspended sediment of spring runoff, which showed a strong relationship between RSP and reducible Fe at all sites. Our data may indicate that P from manure amendment is flushed from the agricultural system as dissolved orthophosphate not associated with metal carriers when there is excess DP relative to available colloidal Fe (oxy)hydroxides. As Fe colloids are known to be strong sorbents of dissolved organic matter at circumneutral pH [Pokrovsky *et al.*, 2006; Stolpe *et al.*, 2013], it is possible that colloid-sized Fe (oxy)hydroxides are coated with manure-derived OM, decreasing available binding sites for DP, although our data cannot determine this conclusively. Our data clearly suggest that in some systems, Fe(oxy)hydroxide colloidal phases are likely important for transport of P, but more detailed study of riverine Fe and P colloidal speciation in forested and manure-amended catchments is clearly warranted.

The general size partitioning of Fe and Mn during summer storms and baseflow remains consistent with spring runoff, and with previously discussed studies, supporting the interpretation that Fe and Mn size distributions are controlled by watershed conditions that are not altered by the agricultural practices in these catchments. The strong correlation between DP and colloidal Fe in forested summer samples confirms that, across the seasons, much of the DP exported from forested systems is likely associated with colloidal Fe (Table 1). Furthermore, the strong correlation between dissolved P and dissolved Fe suggests these constituents are following similar pathways during high flow

summer events. Surprisingly, the strong relationship ($R^2=0.795$, $p=0.007$) between DP and truly dissolved Fe in summer samples collected from the agricultural system (Table 1) suggests these constituents share similar source environments and geochemical pathways during the summer; a relationship not evident during spring runoff (Table 1). Additionally, while high concentrations of truly dissolved Mn and DP in Lake Champlain are often coupled, reflecting the reductive dissolution of Fe/Mn minerals at the sediment water interface [Schroth *et al.* 2015; Giles *et al.* *in press*], this relationship is not evident in our riverine data as a whole or partitioned by land use. This suggests that P fluctuations during high flow events across the region are not likely driven by reductive dissolution of secondary Fe/Mn minerals.

Inter and Intra-Seasonal variability

Suspended sediment geochemistry

We interpret the temporal changes in Asc:AR P, Fe, and Mn ratios as representing the changing redox sensitivity of the constituents in suspended sediment loads throughout the spring runoff period, and then later in the summer. As previously discussed, the limitations of collecting suspended sediment at FOR during spring runoff prevents our detecting any trends in sediment reactivity within each season, so this discussion will be focused on the more robust time series collected at AGR and OUT. Suspended sediment at the onset of snowmelt was particularly enriched in RSP (high Asc:AR ratio) with a systematic decrease in redox sensitivity over time (Figure 6), independent of discharge ($p \gg 0.5$), suggesting an initial flush of particularly redox sensitive suspended sediment

from these AGR and OUT catchments that had accumulated in frozen soils and streambanks. Yet the entire time series of spring runoff suspended sediment at these sites indicates more than 30% of the particulate P is present in the redox sensitive form (Figure 6). Similar to trends in particulate P, the decrease in the Asc:AR Fe ratio over time at AGR and OUT during spring runoff occurs independent of discharge. This reflects the large scale depletion of a pool of particularly reactive sediment enriched in Fe (oxy)hydroxides bearing high concentrations of adsorbed P (Figure 6) over time. The similarity in these within season trends of AGR and OUT suspended sediment composition further highlights the temporal geochemical similarities between stream water draining the agricultural catchment and that of the entire Missisquoi Basin outlet early in snowmelt. We suggest this reactive pool is likely sourced from surface flow paths of the agricultural landscape that are most active during the initial onset of snowmelt and lowland thaw. At all sites, the ratio of Asc:AR P and Fe is lowest at the end of the spring runoff period, indicative of a ubiquitous depletion of reducible phases in suspended sediment throughout this spring time period (Figure 6). However, the proportion of reducible phases (relative to total digestible) in summer storm event suspended sediment increases dramatically after basin-wide green up and prolonged baseflow conditions (Figure 6). We believe that this pool of particularly redox sensitive sediment developed basin-wide during baseflow conditions when anoxic Fe(II) rich groundwater likely interacted with oxic surface water in riparian interfaces [Baken *et al.*, 2015a], causing the precipitation of relatively P-rich Fe (oxy)hydroxides to be subsequently flushed during periods of high-flow events (Figure 6). Indeed, the development of such Fe deposits often manifests as discontinuous orange flocs along

riverbeds and banks where strong redox gradients are common under baseflow conditions [Lapworth *et al.*, 2009; van der Grift *et al.*, 2014; Vidon *et al.*, 2010]. These abundant redox sensitive suspended sediment phases likely scavenged available soil/hyporheic water P [Baken *et al.*, 2015a; Baken *et al.*, 2015b; van der Grift *et al.*, 2014], as reflected by the increase in the proportion of RSP and Fe in suspended sediment at all sites during the summer. Furthermore, the progressive increase in the redox sensitivity following prolonged periods of baseflow suggests that antecedent conditions (time since the last high flow event), which promote riparian redox gradients and facilitate Fe(oxy)hydroxide generation, may have a dramatic effect on high flow event suspended sediment redox sensitivity during summer storms.

Colloidal and dissolved phase geochemistry

Previous studies have identified a large spring flush of various soluble-phase geochemical constituents including metals [Dahlqvist *et al.*, 2007; Rember and Trefry, 2004], DOC [Dawson *et al.*, 2008], and nitrate/phosphorus [Jamieson *et al.*, 2003; Michalak *et al.*, 2013; Royer *et al.*, 2006; Sebestyen *et al.*, 2009; Yuan *et al.*, 2013], highlighting the importance of this time of year on annual loads. Very similar temporal changes in dissolved P concentrations occurred across all our study sites, where DP decreases over time independent of discharge ($p \gg 0.05$) following an initial flushing event early in snowmelt (Figure 4). This is consistent with the decrease in the flux of RSP identified at AGR and OUT independent of discharge (Figure 6), and suggests that both DP and RSP are flushed from upper soil horizons and the land surface during the onset of the spring runoff period. This same flushing, albeit at different concentration scales,

occurs across the montane forests and the agricultural lowlands of the Missisquoi Basin during spring runoff. Similar to DP, truly dissolved Fe and Mn concentrations at all sites are highest early in snowmelt and decrease as a function of time (Figure 4). There is a slight lag (~1 week) between peak SRP and peak dissolved Fe/Mn concentrations at AGR and OUT, with DP concentrations rising earlier, suggesting that the flush of highest dissolved metal concentrations does not necessarily come from the same source as the highest P concentrations. Unlike DP and truly dissolved Fe/Mn, colloidal metals exported from the lowland agricultural systems are coupled to discharge and do not change as a function of time during the spring runoff. This may indicate the rapid *in situ* development of colloids in soils, streams or wetlands, which are more abundant in the lowland Hungerford Brook sub-catchment relative to forested catchments [Kerr *et al.*, 2008; Lapworth *et al.*, 2009; Soto-Varela *et al.*, 2015; Young *et al.*, 2012]. Interestingly, there was a systematic decrease in colloidal Fe concentration in forested catchments over time and independent of discharge (Figure 4b), which is consistent with other studies [*e.g.*, Dahlgvist *et al.*, 2007]. It is likely that different processes control the development and flushing of colloidal material in the watershed lowland regions relative to the mountains during spring runoff.

In stark contrast to spring runoff DP dynamics, characterized by concentrations that decreased over time independent of discharge (Figure 4), summer DP is strongly coupled to discharge ($p < 0.05$), suggesting flow-derived mobilization and export of DP during summer storms (Figure 4). The high-frequency ISCO-derived DP dataset captures rapidly increasing concentrations during increased discharge associated with substantial rain events, confirming the relationship between flow and DP export. Indeed, flow

induced flushing of DP is typical of agricultural runoff during intermittent storm events in P amended catchments, and highly dependent on flow and fertilizer application timing [Hively *et al.*, 2005; Panuska *et al.*, 2008; Zhu *et al.*, 2012]. Peak DP concentrations during the summer at AGR correspond to manure application that occurred just prior to rain events on July 28th and August 12th (Figure 4a). The increase in DP during storm events is evidence of the flushing of surface and shallow subsurface flowpaths during these high-flow events, with ample DP replenished in these pathways by manure application between storms. The truly dissolved Fe concentrations across all sites were generally lower than the spring, with the exception of two isolated high flow events at AGR (Figure 4a). This flushing is presumably associated with enhanced connectivity to source environments enriched in Fe-OM complexed dissolved species like wetlands or riparian organic rich soil solutions. Unlike changes in truly dissolved Fe throughout the summer, colloidal Fe concentrations increase following the end of the spring runoff period (Figure 4). This is consistent with previous studies in pristine boreal forests that identified the development of colloidal material at the hyporheic or riparian interface and wetlands where anoxic groundwater rich in Fe(II) and oxic surface water mix [Pokrovsky and Schott, 2002; Pokrovsky *et al.*, 2006; Stolpe *et al.*, 2013] which is then flushed from these Fe (oxy)hydroxide floc-rich interfaces during storm events [Kerr *et al.*, 2008; Lapworth *et al.*, 2009; Soto-Varela *et al.*, 2015]. Our data suggest that the processes controlling the development and flushing of colloidal Fe(oxy)hydroxides during summer are similar between pristine forested environments and the more developed lowlands of the Missisquoi Basin, but may be fundamentally different from those occurring during spring runoff. Data also suggest that summer storm loads are more concentrated in

Fe(oxy)hydroxide colloids relative to high spring flows, presumably due to different provenance and antecedent conditions that promote relative enrichment of summer storms in iron (oxy)hydroxide colloids relative to spring runoff and truly dissolved iron fractions.

Seasonal Loading Estimates

While our targeted high flow data illustrate a fundamental difference in the biogeochemical nature, magnitude, and temporal evolution of riverine sediment and soluble phase P exported during spring runoff and summer storm events, it is useful to quantitatively model the loading of reactive P species delivered to Lake Champlain from the Missisquoi River over the course of the 2014 hydrologic year to estimate the fractions of P that are delivered to the lake across the seasons. Annual nutrient loads are traditionally generated for TP and DP, which fail to account for the variable reactivity and bioavailability of P within suspended sediment. Our study employed the recently developed USGS R-Script EGRET package to model daily loads of TSS, TP, DP, and RSP [Hirsch *et al.*, 2010]. To our knowledge, we are the first study to incorporate the redox sensitivity of solid phase P (TP) to load estimates. Results from the EGRET modeling showed a very large difference between seasons in the DP, TSS, RSP loadings, and total digestible P, with spring runoff defined in the modeling as 3/28 to 5/2. During spring runoff, an estimated 83.3% of the total TSS loading was exported at OUT, with estimates of 73.89% and 77.01% of the annual RSP and total digestible P, respectively. Spring runoff in 2014 was also responsible for 81.65% of the annual SRP load. Overall, this highlights how critical the spring runoff period is when estimating annual loads of

immediately and potentially bioavailable P to Lake Champlain, reflecting the unique biogeochemical and hydrologic nature of this time period. It is clear that the spring runoff period was the main driver of the annual export of both dissolved and RSP in 2014, and is likely responsible for the majority of the annual reactive P load to some varying degree during typical hydrologic years in this and other similar systems, although there is certain to be large inter-annual variability in the relative contribution of individual seasons based on inter-annual variability in weather. These model results highlight the importance of this time period in understanding and managing eutrophication.

Conceptual Model

Our unique dataset and subsequent modeling effort demonstrate that the reactivity of high flow event P loads varies significantly in time and space and that significant seasonal changes in high flow event load geochemistry are driven in part by antecedent conditions and land cover. Periods of prolonged baseflow conditions (cold frozen soils or dry summertime baseflow conditions) appear to promote the development of abundant redox sensitive iron and sorbed P that can be ‘flushed’ during a storm event or the onset of snowmelt. Whereas prolonged or closely successive high flow events appear to deplete the pool of labile redox sensitive sediment, making Fe and P suspended sediment loads progressively less redox sensitive, with similar behavior of SRP and colloidal Fe. Iron (oxy)hydroxides present in both the suspended sediment and colloidal loads of high flow events appear to be dominant carriers of reactive P across the landscape, illustrating the strong coupling of Fe-P behavior during events that dominate the annual load of both constituents across seasons and land covers. In general, the remarkably high P

concentrations associated with redox sensitive Fe phases, particularly during the onset of spring when discharge when TSS concentrations are particularly high, suggests that there may be systematic underestimation of the redox sensitivity of spring runoff and summer storm event-derived suspended sediment, particularly from P amended catchments. The high RSP concentrations in suspended sediment early in snowmelt relative to the summer reflect the increased influence of lowland agricultural sub-catchments during spring, when the more inert elevated forested catchments are disconnected from the rest of the watershed due to snow and ice. This lowland suspended sediment appears more conducive to the reductive release of P from lake sediment that promotes algal blooms and degrades water quality when compared to the significantly less redox sensitive sediment exported from the relatively pristine forested catchments that cover 71.6% of Vermont. A similar dynamic impacts DP loads during spring runoff as DP pools in agricultural soils are depleted and water derived from forested catchments increases as the snowmelt progresses to higher elevations. DP pools are then intermittently replenished due to manure application, and flushed during subsequent storm events. In general, sustained high flow and erosion, low ecosystem productivity, large pools of available labile P, and particularly reactive suspended sediment make the spring runoff period disproportionately important to the annual load of these constituents to Lake Champlain, and likely other systems with similar catchment configurations. Changes in the severity, timing and provenance of spring runoff, as well as summer storms, will likely have dramatic impact on not only the flux and temporal distribution of P loading, but also the timing and magnitude of the delivery of riverine particles and colloids with the most potential to impact summertime harmful algal bloom development.

This should be taken into account when developing future P targets and best management practices for impaired or potentially impaired systems. If possible, sampling schemes similar to ours that target high flow periods and characterize redox sensitivity should be employed to develop useful and realistic management objectives for systems of concern.

ACKNOWLEDGEMENTS

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FIGURES AND TABLES

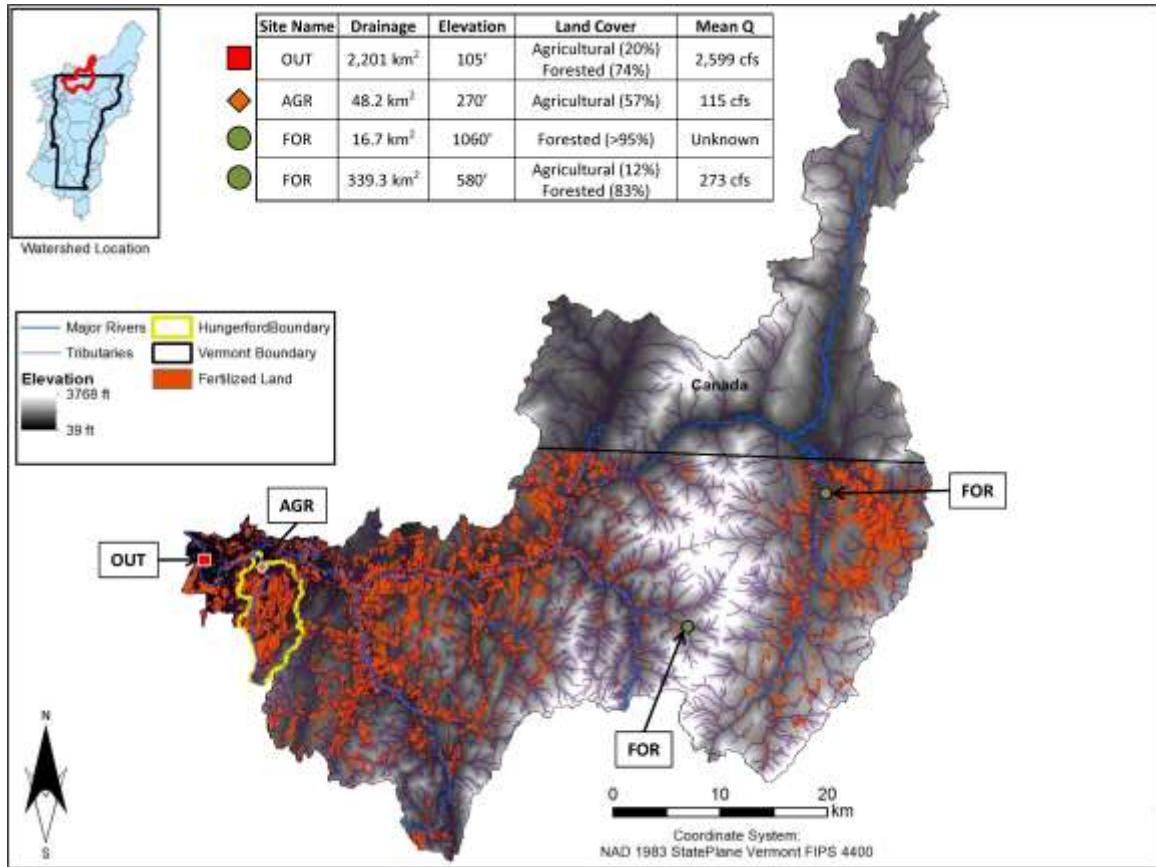


Figure 1. Site locations and agricultural land within the Missisquoi Basin in Vermont. Major rivers and tributaries are shown for reference. Agricultural land was defined as either cultivated crops or pasture/hay. The Hungerford Brook sub-catchment is highlighted for reference.

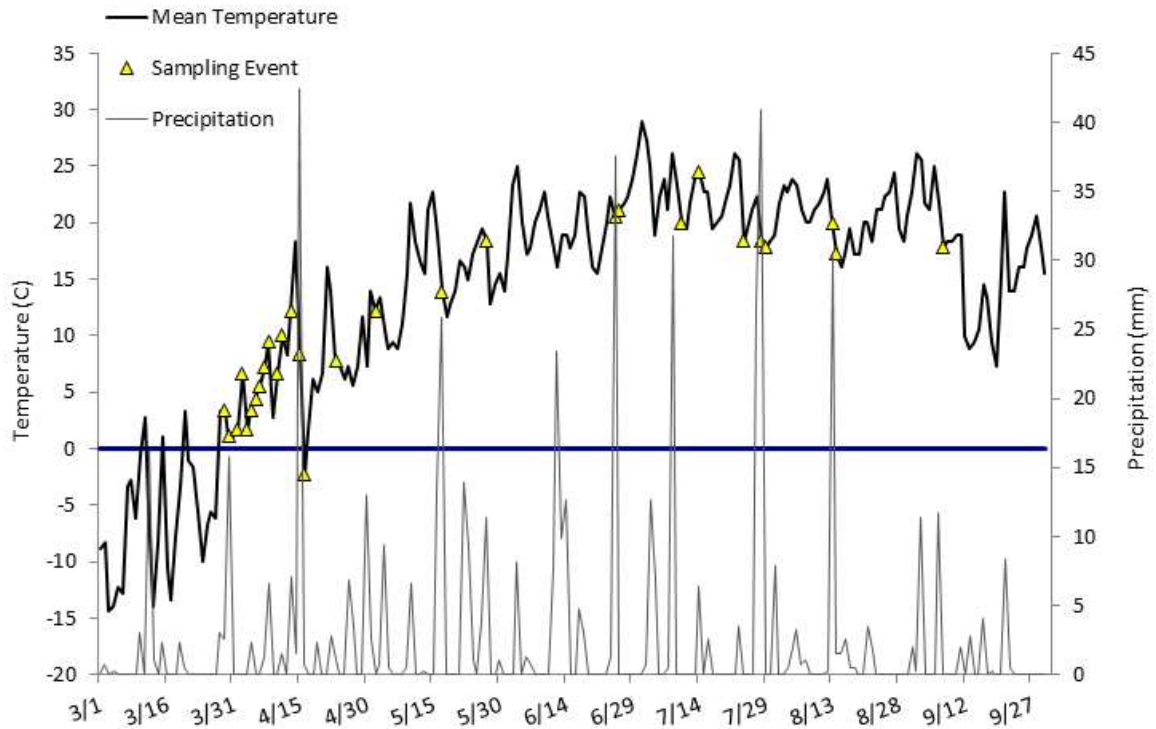
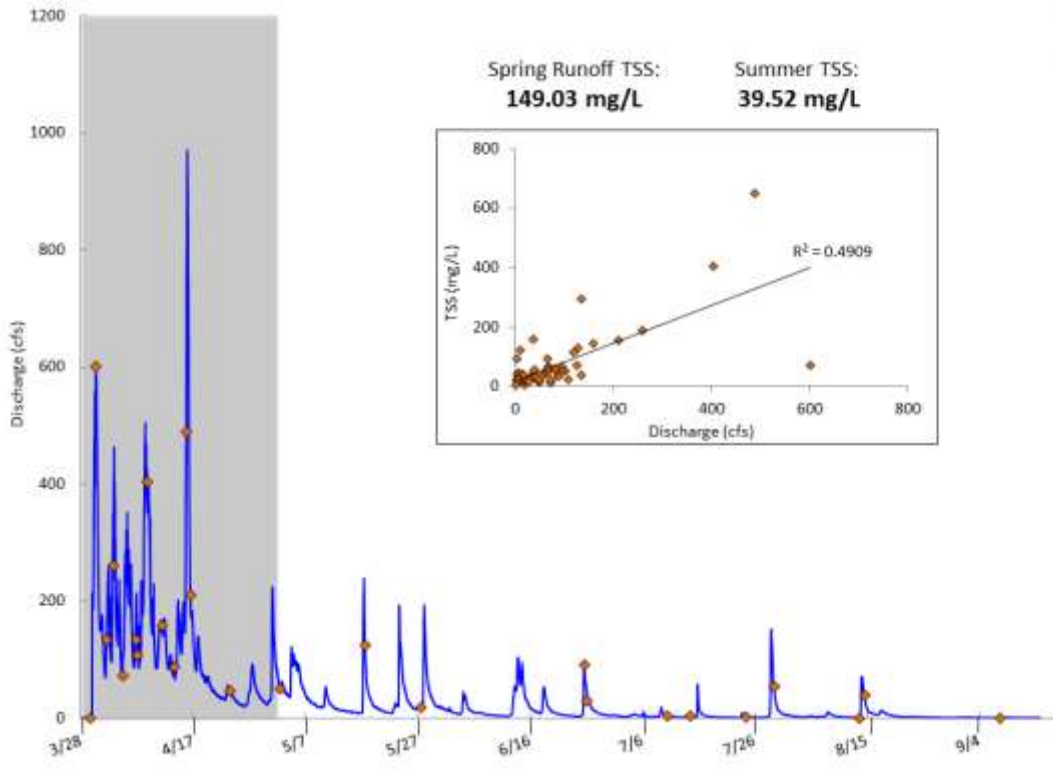


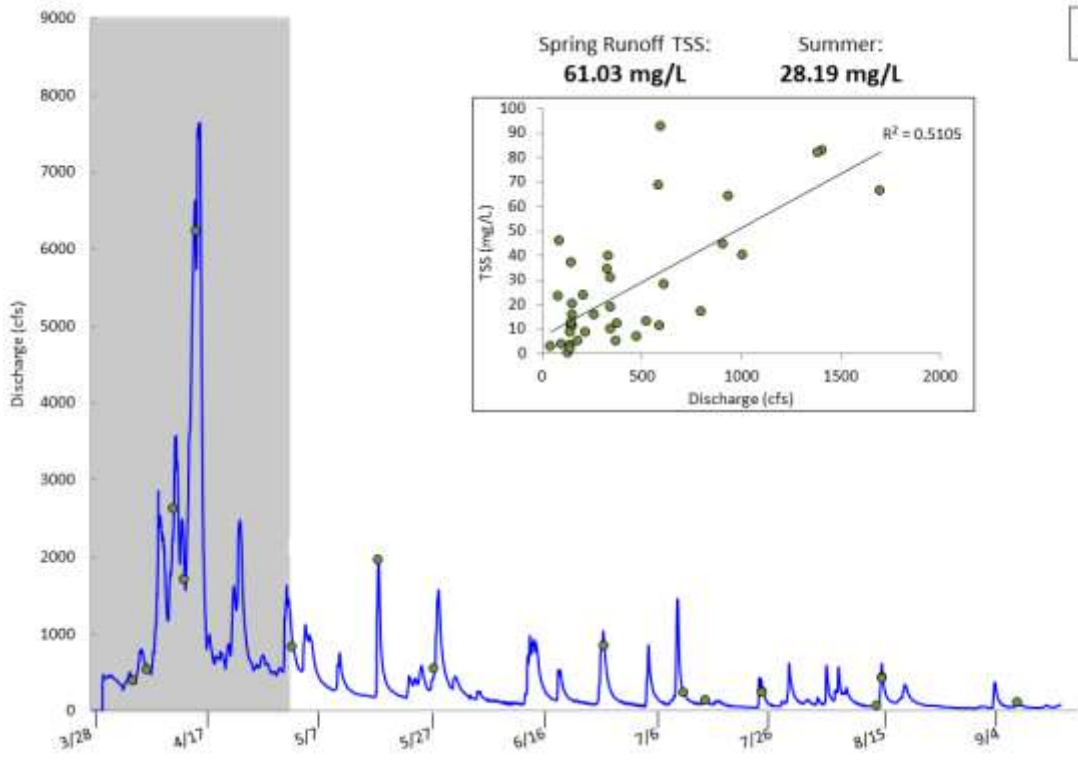
Figure 2. Weather history from Burlington, VT within the Champlain Valley. Daily temperatures and precipitation are shown with sampling events. No similar weather history was available near our sampling locations, but the Burlington Airport weather is a good approximation for the Champlain Valley.

AGR



A

FOR



B

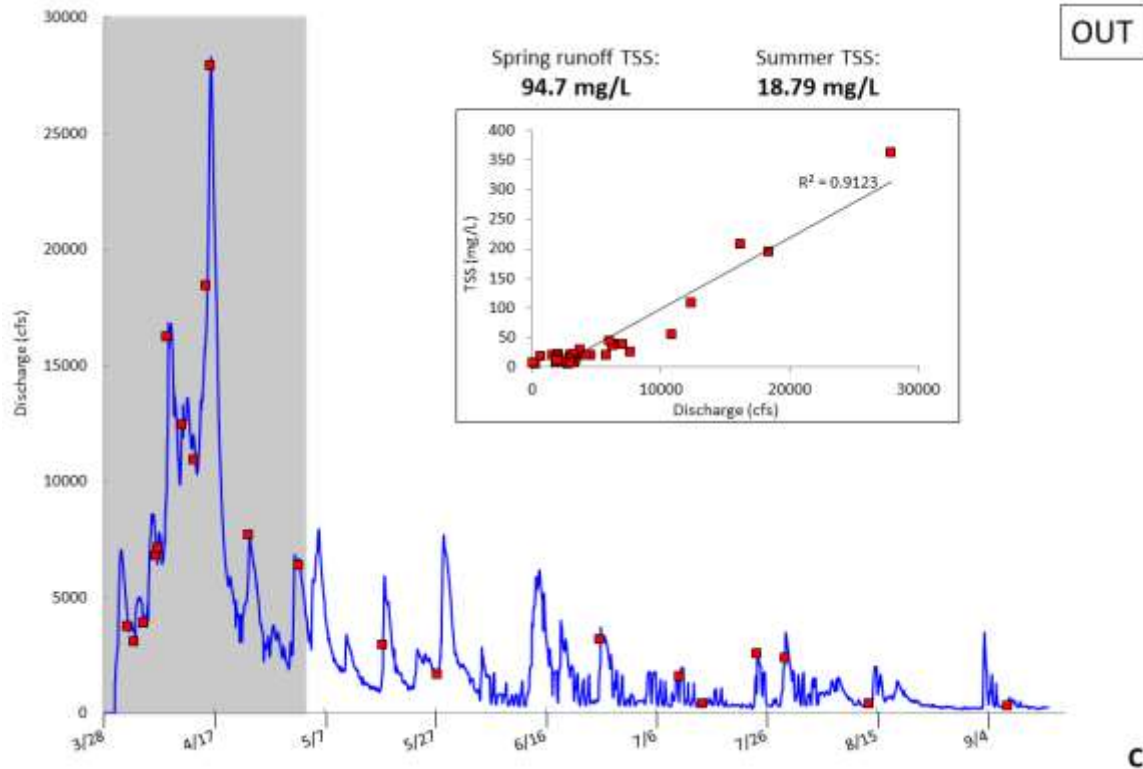
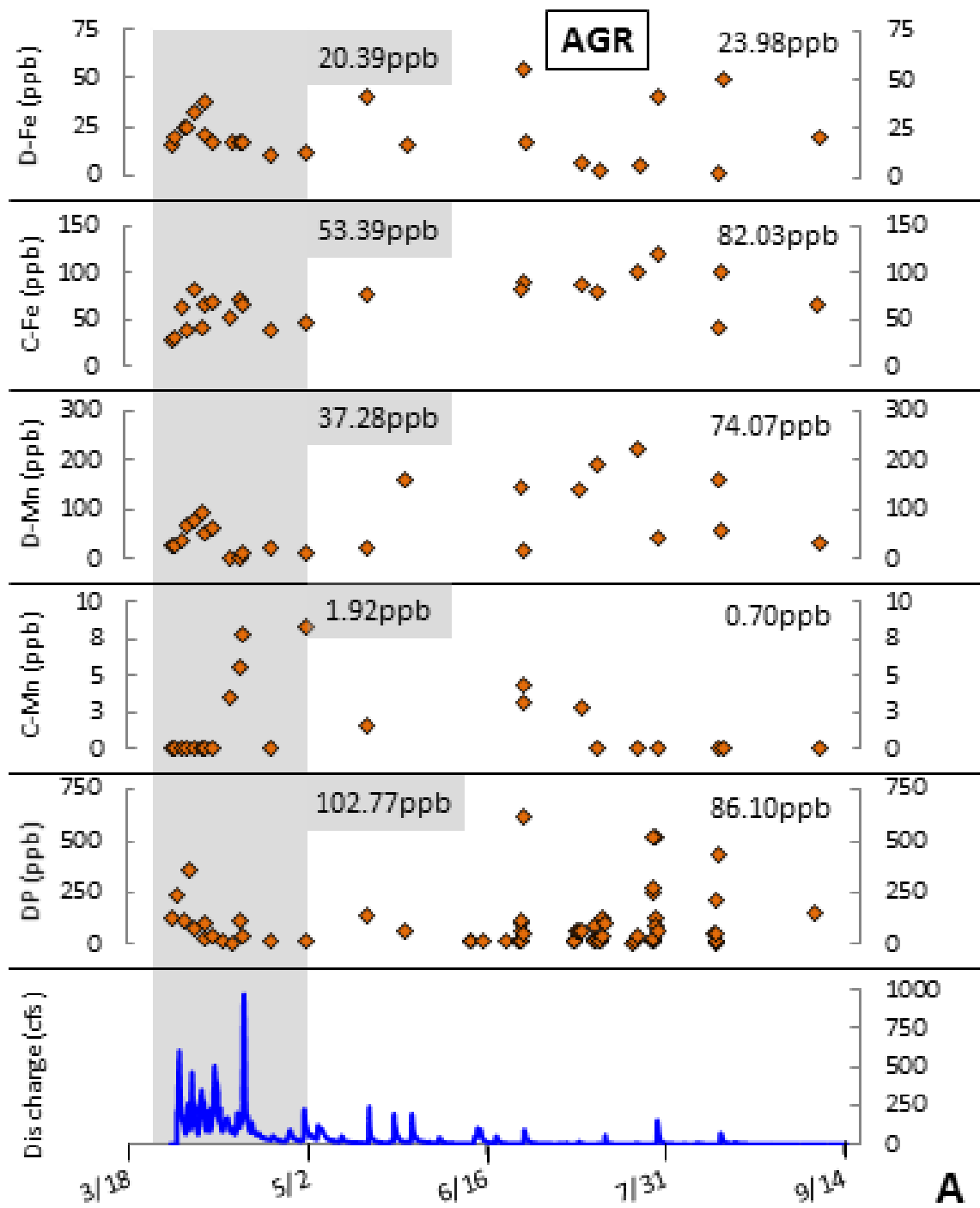
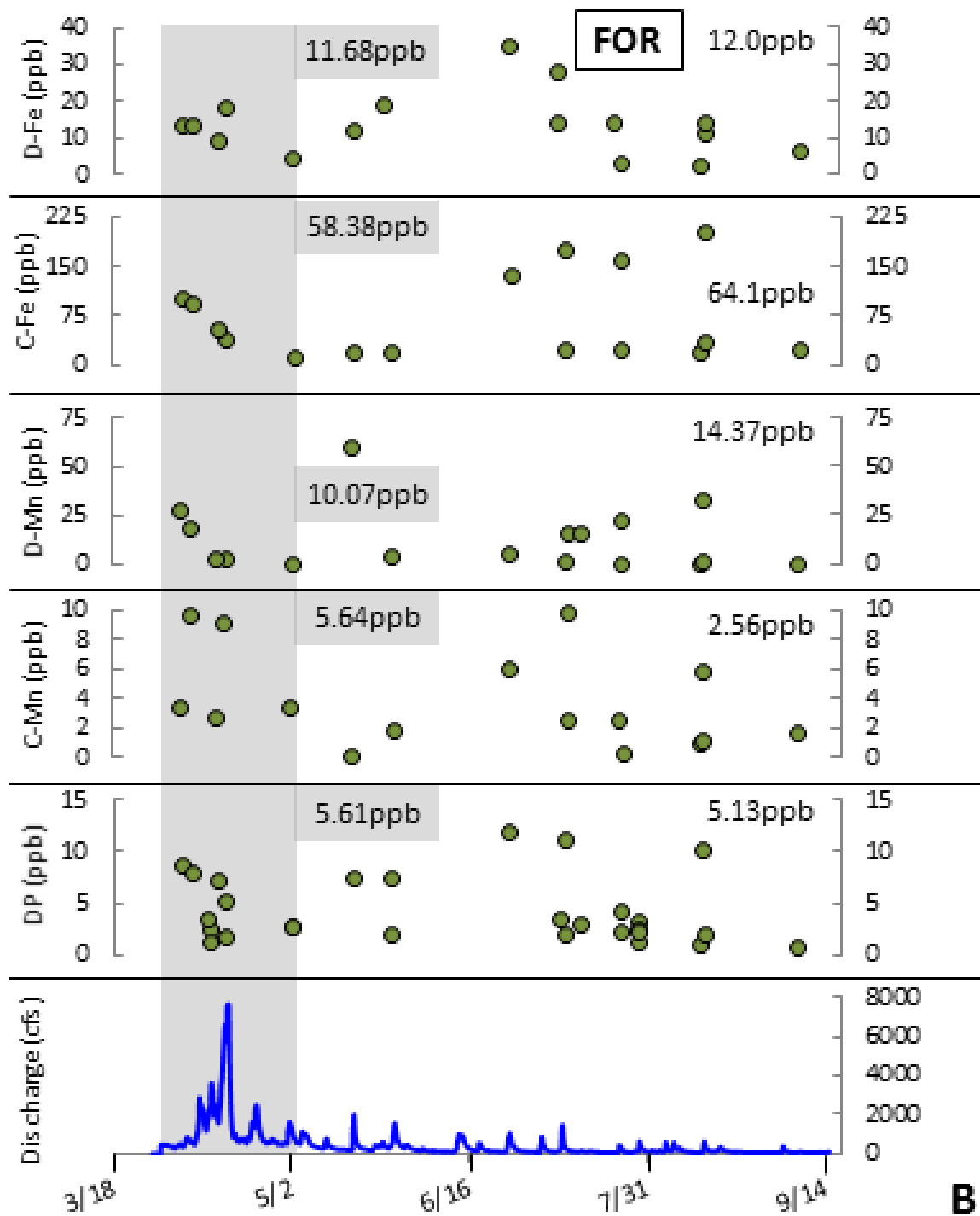


Figure 3. Discharge for each of the gaged sites during the 2014 sampling period. Sampling events are marked along the discharge plot. The inset shows the TSS to discharge relationship at each site. The spring runoff period is shown in grey. Average TSS values for spring runoff and summer are shown above the inset plot.





B

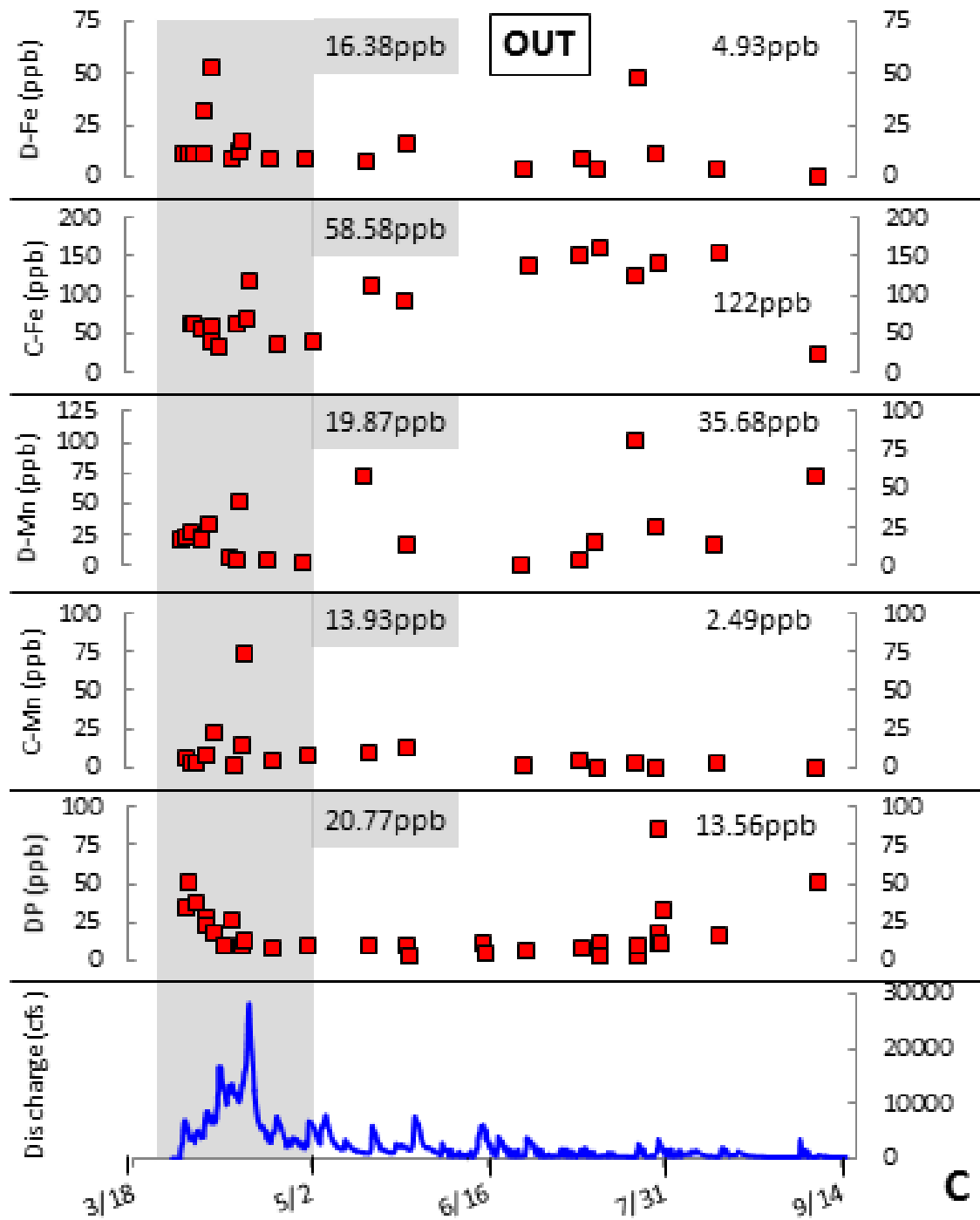


Figure 4. Soluble P and TM concentrations over time at each site. Dissolved P values in the summer include both ICP-MS P and SRP. Mean concentrations for each constituent during spring runoff are shown in grey boxes, and summer concentrations are presented on the right side of each figure.

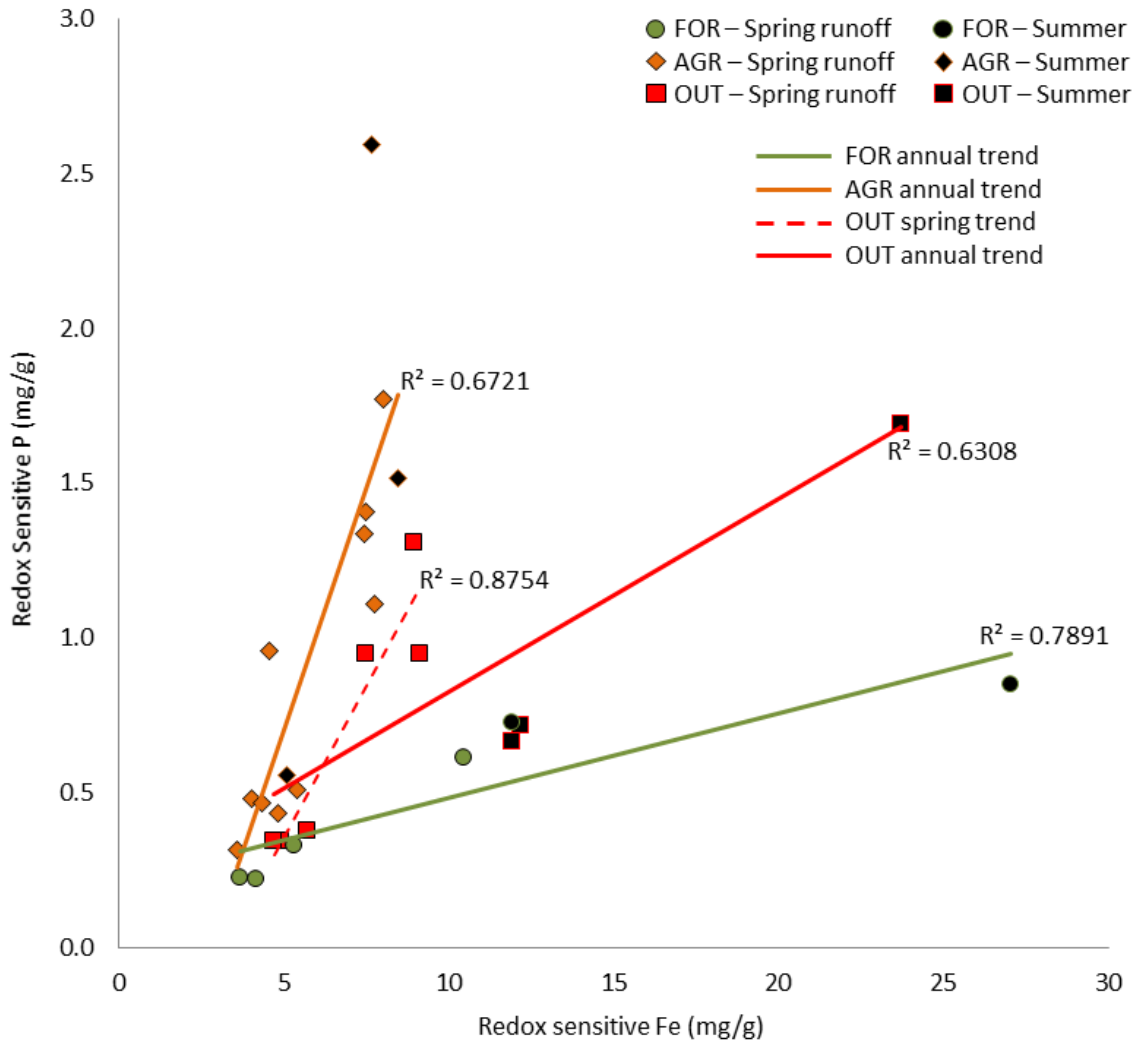
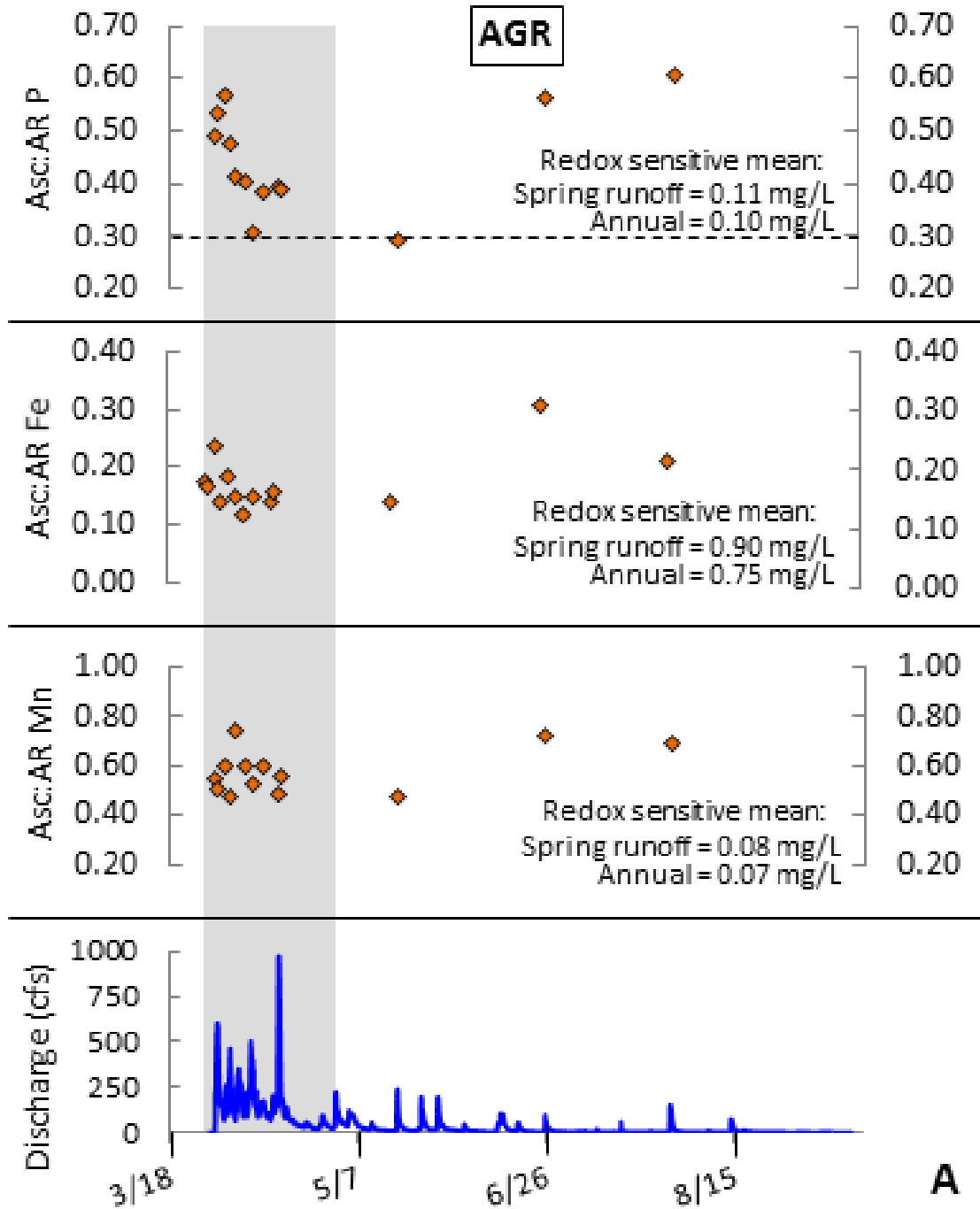
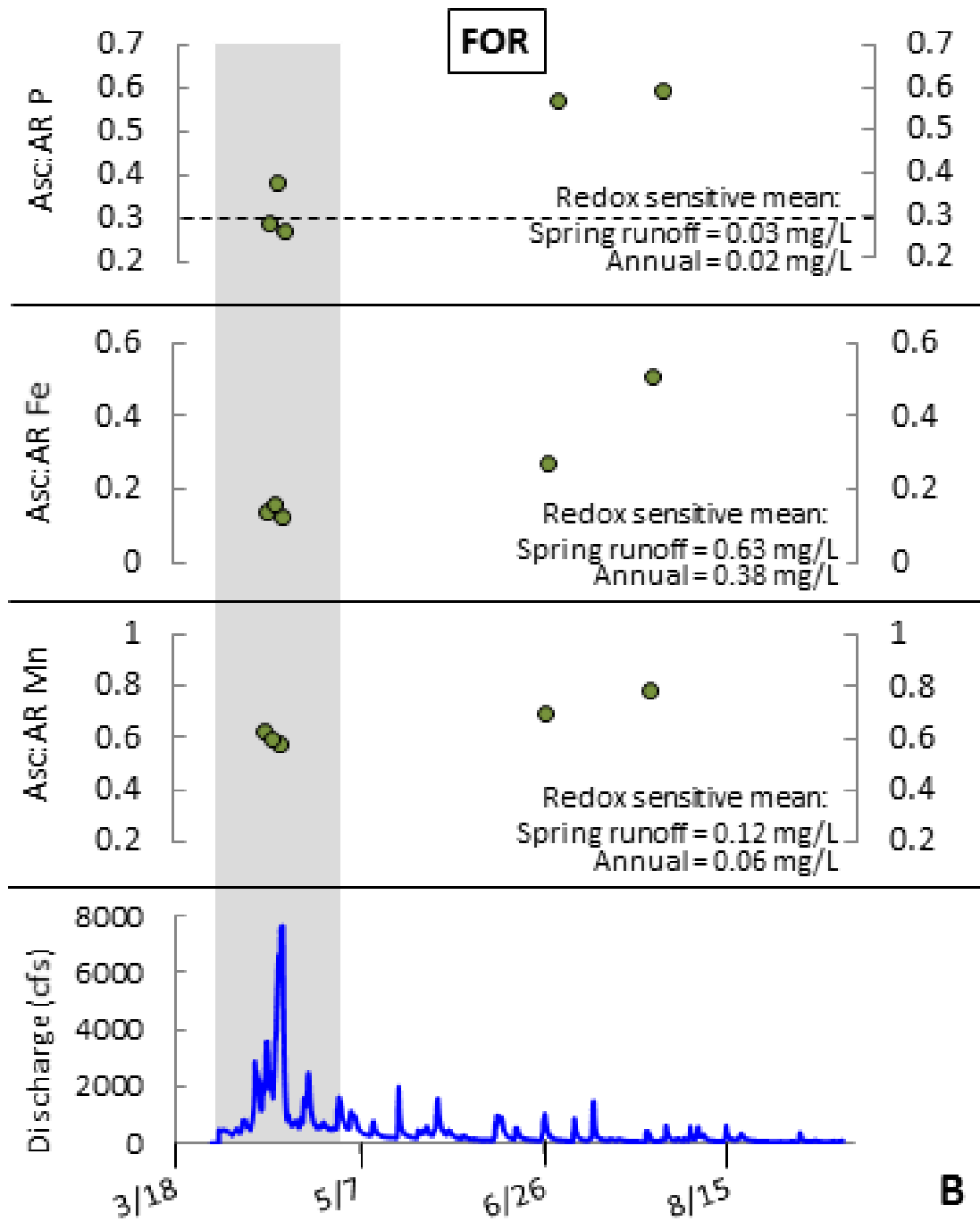


Figure 5. Redox sensitive P vs. redox sensitive Fe at all sites. Colored samples were collected during spring runoff. Samples in black were collected during summer storms. Annual trends are presented with solid lines. The trend for spring runoff at OUT is shown in a hashed line. There was no statistically significant difference between spring runoff and annual trends for AGR or FOR. Slopes for the various trend lines are presented in the discussion. All relationships are statistically significant (p-test; $p < 0.05$).





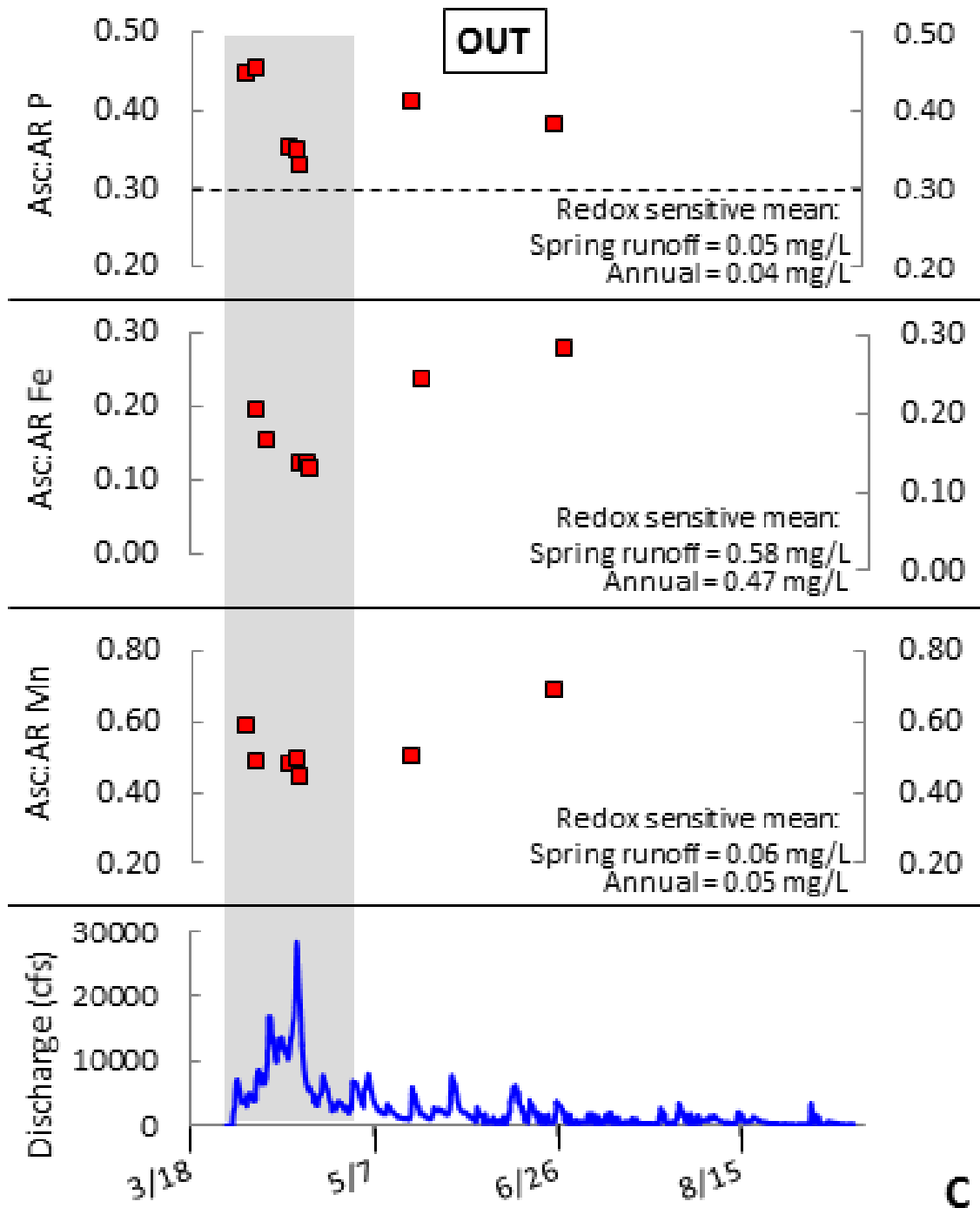


Figure 6. Asc:AR ratio for P, Fe, and Mn over time at each gaged site. Hashed line represents a literature-supported 30% particulate P bioavailability (Sharpley et al., 1992; Poirier et al., 2012). Mean concentrations for the redox sensitive fraction are shown in each plot for comparison.

Table 1. R² values for statistically significant correlations (p-test; p<0.05) between DP and soluble metals. These relationships correspond to those shown graphically in Figures 10 and 11.

		Spring Runoff (2014)			
		Truly Dissolved Fe	Colloidal Fe	Truly Dissolved Mn	Colloidal Mn
Dissolved P	AGR	-	-	-	-
	OUT	-	-	-	-
	FOR	0.2195	0.9041	-	-
	All Sites	0.2014	-	-	-
		Summer (2013 and 2014)			
		Truly Dissolved Fe	Colloidal Fe	Truly Dissolved Mn	Colloidal Mn
Dissolved P	AGR	0.7211	-	-	-
	OUT	0.4145	-	-	-
	FOR	0.705	0.5929	-	-
	All Sites	0.6228	-	-	-

Chapter 3: Preliminary Manuscript for TBD

Iron and phosphorus partitioning during high flow events in adjacent glacerized and forested catchments: impacts of land cover and seasonality.

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ABSTRACT

Aquatic ecosystem productivity in the Gulf of Alaska (GoA) is impacted by riverine input of nutrients, particularly during periods of high flow such as glacial melt, snowmelt, and storm events. We demonstrate that catchments in different stages of landscape progression, glacial and forested, respond differently to high flow events, with implications for the chemical nature and magnitude of Fe and P input to the GoA. We investigate Fe size partitioning and flux throughout the hydrologic year, with additional high-resolution sampling during discrete storm events in adjacent forested and glacierized catchments typical of coastal Alaska. Iron exported from the glacial catchment is predominantly colloidal, with very low dissolved Fe concentrations, indicating glacial weathering is the primary source of Fe in this catchment. Conversely, there is a much larger amount of dissolved Fe exported from the forested catchment, reflecting the influence of peatlands and organic-rich soil as the dominant source of this fraction of Fe during high flow conditions. There are clear differences between these catchments during individual storm events, and across seasons, reflecting widely varying source environments for Fe. Phosphorus concentrations in both watersheds are very low throughout the year, but significantly higher in the forested watershed, driven by organic matter decomposition. As climate change drives continued glacial recession in Alaska and similar environments, we predict continued change in the Fe and P source environments, with impacts on the timing, magnitude and speciation of their riverine flux to the GoA.

INTRODUCTION

The transition of subarctic environments, particularly along the glaciated coasts, from primarily glaciated to forested land cover has implications on the delivery of soluble and suspended constituents such as nutrients and trace elements. Glacial melt and weathering influences the flux of nutrients, sediment, and water, affecting coastal ecology [Fellman *et al.*, 2014; Hood and Scott, 2008; Hood and Berner, 2009; Hood *et al.*, 2009; Moore *et al.*, 2009; Schroth *et al.*, 2014; Schroth *et al.*, 2011]. Deglaciation and subsequent changes in riverine discharge and geochemistry have the potential to affect coastal productivity due to the importance of glacially-derived nutrient fluxes, particularly those of the micronutrient iron (Fe) [Hickey *et al.*, 2010; Ware and Thomson, 2005]. Studies in proglacial streams have shown that primary productivity and biodiversity are lower compared to non-glacial streams [Friberg *et al.*, 2001; Milner *et al.*, 2000; Robinson *et al.*, 2001]. However, it is unclear how riverine biogeochemistry changes as catchments transition from glaciated to forested landscapes. Understanding the impact of large-scale glacial retreat on landscape conditions and riverine biogeochemistry is integral to developing models of riverine export from arctic and alpine environments under a changing climate.

Glacial retreat has occurred rapidly over the past century, with retreat rates particularly high in low-elevation temperate environments like coastal Alaska [Barry, 2006; Dyurgerov and Meier, 2000]. Significant amounts of water ($410\text{km}^3 \text{ yr}^{-1}$) are delivered to the Gulf of Alaska from regional ice sheets and alpine glaciers [Neal, 2010]. The Juneau ice sheet in particular has melted significantly in the past 50 years. Thinning rates of glaciers fed by the ice sheet can be as high as 6-8 m/year [Larsen *et al.*, 2007],

and nearly all of the glaciers fed by the ice sheet have decreased in mass over the past few decades. There is tremendous uncertainty in the response of coastal aquatic ecosystems to changes in sediment, nutrient, and trace element flux from glacial watersheds, which deliver the majority of water annual to the Gulf of Alaska. However, changes in watershed land cover, and associated changes in the timing, form and magnitude of riverine nutrient loads, are very likely to significantly affect downstream aquatic ecosystems.

Previous studies have shown that Fe is an important limiting nutrient for phytoplankton [*Chase et al.*, 2007; *Hickey et al.*, 2010] in the GoA. Glacial weathering has been identified as the primary source of Fe to the Gulf of Alaska, and may also drive the flux of P and OM [*Hood and Scott*, 2008; *Wu et al.*, 2009; *Lippiatt et al.*, 2009]. As such, changes in the relative contribution of glacial meltwater to discharge are likely to alter the flux of these constituents to coastal environments. Despite this, relatively few studies have investigated the effects of changing land cover, driven by changes in glacial coverage, on the biogeochemical nature of Fe.

Some recent studies have investigated the influence of glacial coverage on riverine on organic matter biogeochemistry [*Fellman et al.*, 2014; *Hood and Berner*, 2009]. Studies on riverine Fe geochemistry have traditionally focused on very large ice sheets [*Raiswell et al.*, 2008; *Raiswell et al.*, 2008; *Raiswell et al.*, 2006], finding that meltwater runoff and iceberg calving deliver nearly 2900 Tg of sediment annually, with a major portion of that sediment in the form of Fe (oxy)hydroxide nanoparticles and aggregates. As these Fe species are susceptible to dissolution in some environments, this fraction is considered bioavailable [*Raiswell et al.*, 2006]. Recently, there has been

increasing interest on coastal alpine glacial retreat and riverine geochemistry, with a focus on understanding the impact of changing glacial coverage on riverine biogeochemistry, utilizing co-located watersheds in varying stages of glacial retreat as proxies for long-term temporal changes likely to occur as glacial retreat continues (a space-for-time substitution) [Fellman *et al.*, 2014; Hood and Berner, 2009; Lafreniere and Sharp, 2005; Milner *et al.*, 2000; Schroth *et al.*, 2011]. Significant differences in the partitioning and size fractionation of Fe across landscapes transitioning from glacial to boreal forested have been identified. In the glacial system, the majority of Fe flux is present in the colloidal form, with minimal dissolved Fe, while the boreal forested catchments export significantly more dissolved Fe, presumably derived from organic-rich soils and peatlands common in these temperate rainforests [Schroth *et al.*, 2011]. These same boreal forested catchments also export large quantities of DOC and organic matter [Fellman *et al.*, 2014; Hood *et al.*, 2009], often complexed with Fe and other metals [Schroth *et al.*, 2011], and in some cases, with P [Hood and Scott, 2008]. Suspended sediment export from glaciated catchments is known to be very high, potentially providing another source of micronutrients to the GoA [Crusius *et al.*, 2011; Hood and Berner, 2009; Schroth *et al.*, 2014]. Additional research is needed to understand the impact of glacial retreat on riverine geochemistry, specifically during high flow events, which are the main driver of annual loads of sediment, nutrients, and trace elements.

In this study, we use a space-for-time substitution approach to compare nutrient and iron dynamics in two adjacent catchments during high flow events to project how the chemical nature, timing and magnitude of iron and phosphorus riverine loads may evolve as ice loss continues throughout the GoA catchment. Specifically, we analyze Fe and P

time series geochemical data to understand how their concentration and size distribution vary in different environments during high flow periods; and how this may be related to changing watershed processes and related solute provenance. High-frequency, targeted sampling during sustained storm events gives us the opportunity to develop a conceptual model of how riverine geochemistry and the flux of Fe may change over time during discrete storm events or across seasons. Our findings have significant ramifications for understanding how micro and macronutrient dynamics may change as subarctic land cover and precipitation patterns evolve under a warming climate.

METHODS

The sampling locations for this study were located in southeastern Alaska and consist of the Herbert River (HR) and Peterson Creek (PC), both of which drain into fjords connected to the Gulf of Alaska (Figure 1). Both sites are relatively well-characterized by previous studies, which found major differences in riverine geochemistry between the glacial Herbert River and forested Peterson Creek [*Fellman et al.*, 2014; *Hood and Berner*, 2009] The Herbert River watershed is a 158km² mixed glacial/forested basin with approximately 49% glacial coverage with the majority of the forest in the lower-elevation portions of the watershed. High elevation portions of the watershed are characterized by recently exposed bedrock, alpine tundra, and glacial moraines. At lower elevations the watershed is primarily old-growth coniferous forest. The Peterson Creek watershed (24km²) drains a pristine forested catchment with abundant wetlands. The landscape contains mixed coniferous forest and very large peatlands. Both watersheds are within the temperate climate of coastal southeast Alaska,

and are underlain by similar bedrock. All samples in both watersheds were collected near the outlet, although parent material samples were collected throughout the basins. These sites were selected to represent different states of landscape evolution and to leverage previous and ongoing studies in the region.

A sampling strategy was developed to target high flow events in both watersheds with occasional intermittent low-flow sampling. Initial samples were collected at the onset of snowmelt in both watersheds and continued until snowfall in the fall. Samples were collected in both watersheds for every event. During the sampling season, temperature and weather were tracked to target sampling during peak discharge. In addition, for a number of storm events, numerous samples were collected during certain events to characterize the evolution of Fe and P concentration over different stages of the high flow event.

Metals samples were filtered in a clean space through 0.45 μm PES disposable filters and 0.02 μm Anotop® Plus nonsterile PES filters within 24 hours following the size partitioning scheme developed by Shiller, 2003. The acidified and filtered samples were analyzed at Woods Hole Oceanographic Institute on an ICP-MS. Internal spikes of Sc, Y, and In were used to calculate Fe and P concentrations for the <0.45 μm and <0.02 μm fractions. Samples with greater than 5% internal replicate error were re-analyzed or removed. The international geostandard SLRS-4 (Riverine Water Reference Material for Trace Metals) was used to validate daily ICP-MS runs and calculate error.

In addition to metals analysis, the concentration of dissolved phosphorus in <0.45 μm filtered samples was determined by ICP-MS. This particular measurement captures both organic and inorganic P. Samples were also analyzed for dissolved organic

carbon (DOC) on a filtered <0.45 μ m aliquot. For this analysis, samples were collected in combusted amber glass bottles and analyzed within 24 hours.

RESULTS

Hydrology

As expected, the hydrologic regimes in Herbert River and Peterson Creek were markedly different despite being influenced by the same storm events, reflecting the contribution of glacial meltwater in HR during the summer (Figure 2). HR was characterized by progressively increasing discharge as glacial melt began and increased into the summer (Figure 2a). Large storm events were superimposed on the glacial melt, resulting in short-lived spikes in discharge (Figure 2a). Glacial melt decreased in mid to late August as nighttime temperatures dropped. By contrast, discharge in Peterson Creek was characterized by a brief increase during snowmelt followed by baseflow conditions with frequent summer storms and corresponding spikes in discharge (Figure 2b).

Soluble-phase geochemistry

Mean truly dissolved Fe concentrations were 17.61 and 125.54ppb for HR and PC respectively. The first two samples collected from HR were enriched in truly dissolved Fe (150.1 and 110.6ppb) relative to the rest of the sampling period. Colloidal Fe concentrations were similar at both sites with a mean of 104.65 and 128.41ppb for HR and PC respectively. DP concentrations were generally low throughout the sampling period at both sites, with mean concentrations of 4.06 and 9.54 ppb, and ranges of 1.57 – 7.16 and 2.67 – 48.64 ppb at HR and PC respectively.

Parent material geochemistry

Parent material samples collected in the Herbert River watershed were characterized by statistically negligible redox sensitive P concentrations and low redox sensitive Fe concentrations. By contrast, parent material in the Peterson Creek watershed had higher redox sensitive P and Fe concentrations relative to Herbert River, particularly in the fine fraction (<63 μ m). In the digestible fraction, a measure of total non-silicate-bound sediment, the concentration of digestible P in HR parent material was much higher than in PC parent material. However, reducible Fe concentrations were below the detection limit in HR.

DISCUSSION

Streamflow and hydrologic regime

Discharge within the two rivers sampled for this study was consistent with previous studies in the region and showed a systematic difference between a glacial-melt dominated hydrologic regime controlled by temperature, and a precipitation-dominated regime driven by storm events and subsequent runoff [Collins, 2006; Hood and Berner, 2009; Kyle, 2001; Neal *et al.*, 2002]. In both watersheds, storm events resulted in a rapid increase in discharge in response to precipitation (Figure 2). At HR, these spikes in discharge were superimposed on top of glacial melt, and discharge remained relatively high after precipitation and storm discharge subsided (Figure 2a). In the boreal-forested PC watershed, precipitation resulted in a large transition from baseflow to stormflow and back, likely resulting in major changes in the source environment for water and geochemical constituents (Figure 2b). The contrasting storm response between these two

adjacent watersheds likely impacts the provenance of solutes and sediment, and suggests that the majority of the water exported during these events is derived from different flow paths based on land cover. Furthermore, both watersheds are impacted by a high flow event during snowmelt in May (Figure 2). However, the snowmelt input is more significant in PC relative to HR, where the onset of glacial melt quickly diminishes the relative contribution of snowmelt compared to glacial melt (Figure 2). As with storm events, the different seasonal hydrologic evolution of these two adjacent watersheds likely impacts the flux and speciation of Fe and P in both soluble and suspended phases.

Effect of land cover on riverine geochemistry

Our sampling strategy was designed to address our hypothesis that differences in solute provenance between glacierized and boreal forested catchments during high flow events cause differences in the concentration and partitioning of Fe and P in these systems, which could impact GoA nutrient dynamics. Indeed, there were very large differences in the concentration of truly dissolved Fe ($<0.02\mu\text{m}$) between the two watersheds (Wilcoxon test: $p < 0.0001$; $\chi^2 = 30.20$; $DF = 1$) presumably due to the different sources of this component of the iron load (Figure 3). It is important to note that the truly dissolved Fe fraction in these well oxygenated and circumneutral pH systems has been shown to consist primarily of complexes nano-organic colloids rather than dissolved Fe ions [Pokrovsky *et al.*, 2006; Stolpe *et al.*, 2013]. In HR, truly dissolved iron and dissolved organic carbon concentrations are extremely low, which is characteristic of glacial systems under peak discharge (Figure 3) [Hood *et al.*, 2009; Schroth *et al.*, 2011]. This indicates that limited available DOC likely limits the concentration of truly

dissolved Fe in the Herbert River watershed. Furthermore, the source of the dissolved organic carbon (ice) in glacial systems is decoupled from the source of dissolved iron (mineral dissolution), suggesting that flowpaths activated during high flow events may not concurrently mobilize each constituent. This is in stark contrast to PC, where the abundance of forests and wetlands provides a source for nanocolloidal Fe/OM complexes, which have been identified in similar pristine boreal forested systems in Siberia, where peatland provenance of enriched nanocolloidal and dissolved Fe river loads has been proposed [Dahlqvist *et al.*, 2007; Pokrovsky *et al.*, 2006; Rember and Trefry, 2004; Stolpe *et al.*, 2013]. In fact, there was a very strong correlation between DOC and truly dissolved Fe in PC, supporting the interpretation that Fe may be present complexed with organic matter and shares a similar source environment in the forested catchment, while there was no relationship between DOC and Fe in HR (Figure 4). The relatively small amount of forest and lack of organic-rich upper soil horizons within the Herbert River watershed are reflected in the much lower truly dissolved Fe concentrations.

As expected, concentrations of DP were low in both rivers, with concentrations significantly higher in PC compared to HR (Wilcoxon test: $p=0.0002$; $\chi^2=14.05$; $DF=1$). Low concentrations of DP (mean of 4.06 and 9.54ppb for HR and PC respectively) are expected in montane forested catchments because: 1) these are pristine watersheds with no agricultural or other anthropogenic activity; 2) primary mineral weathering only produces low background concentrations of P; and 3) P is tightly cycled by biota of the northern forest [Hood and Scott, 2008]. The DP concentrations in PC are higher than in HR due to increased levels of decomposition and soil processing. Two samples collected

in PC had spikes in DP concentration (Figure 9) that occurred during salmon runs, providing a highly temporary source for DP. Previous studies have identified a large flux of TP exported from glacial catchments, presumably driven by large amounts of glacial weathering liberating phosphorus from bedrock coupled with sustained high discharge [Hood and Scott, 2008]. The low DP concentrations measured in our study are reflective of the geochemical nature of the phosphorus load, and not the flux of TP. Although they were not analyzed in this study, it is expected that TP concentrations would be higher than DP concentrations in HR, as much of the P liberated from bedrock is likely to be present in sizes $>0.45\mu\text{m}$, and high TSS concentrations are known to be correlated with high TP concentrations in many catchments.

Suspended sediment concentrations in HR were orders of magnitude higher than in PC (Figure 5). This is expected as glacial activity produces very large amounts of sediment. There was a strong correlation between TSS and discharge in HR, indicating that increases in glacial melt and precipitation events mobilize large amounts of sediment throughout the hydrologic year (Figure 5). In the forested PC catchment, there are fewer sources of suspended sediment, in part due to the abundance of wetlands that act as traps for any mobilized sediment. In addition, export of sediment-sized material from PC is likely to be dominated by organic matter complexes, while in HR, the majority of suspended sediment is likely derived from bedrock weathering. As a result, TSS and discharge in PC do not appear to be significantly correlated. During individual high flow events, driven by storm events that affected both HR and PC, TSS concentrations did not rise significantly in PC, likely due to sediment trapping throughout the watershed. These same events in the HR catchment resulted in very large increases in TSS loads, likely

indicating that precipitation events encourage mobilization of glacially-derived sediment throughout the catchment. Although this study focused on soluble-phase geochemistry, it is clear that the suspended sediment phase is a major component in HR, delivering large amounts of suspended material to the Gulf of Alaska.

Parent material samples collected in multiple locations throughout both HR and PC catchments provide evidence of the composition likely source environments for suspended sediment. Assuming these samples are representative of suspended sediment composition, the nature of suspended sediment loads in HR and PC are very different (Figure 6). In PC, a large proportion, greater than 30% in the fine fraction (<63 μ m) and in peatland soil samples is redox sensitive P, defined as the reducible fraction. Previous studies investigating the bioavailability of sediment-bound P exported from agricultural fields have suggested that approximately 30% of the total sediment-bound P can be considered bioavailable [Poirier *et al.*, 2012; Sharpley *et al.*, 1992]. Interestingly, parent material in PC has a proportion of redox sensitive P greater than 30% (Figure 6). By contrast, the parent material collected from the HR catchment is almost exclusively digestible P, defined as a total sediment phosphorus measure. As such, the sediment exported to the GoA from HR is primarily in the non-redox sensitive phase that is characteristic of glacial flour (Figure 6). These data support previous Fe speciation studies that used synchrotron measurements to determine the geochemical nature of Fe loads in the GoA, and identified that glacial flour contains more recalcitrant forms of suspended Fe, compared to the more redox sensitive species exported from forested catchments [Schroth *et al.*, 2011]. A more comprehensive investigation of the

geochemical character of suspended sediment, particularly in terms of potential reactivity, is clearly warranted.

Temporal changes in riverine geochemistry during high flow events

The presence of adjacent catchments in different stages of landscape evolution gives us the opportunity to study how these contrasting landscapes respond to discrete storm events, with a specific focus on the size fractionation and flux of Fe during critical hydrologic events. The flux of Fe and P to the Gulf of Alaska has important ecosystem implications due to their role as micro and macronutrients critical to regional phytoplankton populations. Previous studies have identified large flushes of geochemical constituents during periods of high flow including DOC [*Campbell et al.*, 1995; *Hood et al.*, 2009; *Hornberger et al.*, 1994] and metals [*Dahlqvist et al.*, 2007; *Stolpe et al.*, 2013] in Alaska and similar environments, highlighting the importance of these hydrologic events on annual loads. For our study, two large storms were targeted for high-resolution sampling, presenting the opportunity to investigate the rising and falling limbs in terms of Fe partitioning and concentration. There are stark differences between HR and PC during each storm in both the dissolved and colloidal Fe fractions, suggesting that these catchments do not respond to precipitation events in the same way. During both storm events, dissolved Fe at PC is tightly coupled to discharge, with no evidence of a dilution effect or an initial flushing event (Figure 7). The concentration of dissolved Fe during these storms rises rapidly with discharge and tails off on the falling limb. The export of large amounts of dissolved Fe at peak discharge may indicate the connection of

peatlands, the likely source environment for this Fe fraction to the river when soil is saturated (Figure 7). Decreasing concentrations on the falling limb of the storm support this interpretation, as the river returns to baseflow conditions dominated by groundwater and deep subsurface flow. There is some continued flushing of dissolved Fe likely derived from these peatlands as discharge decreases, continuing until baseflow conditions dominate, and the system may be disconnected from this Fe hot spot. The high concentrations of dissolved Fe throughout the September storm event may indicate that soils in the PC catchment become sufficiently saturated during the year to directly connect upslope peatlands to the river, resulting in sustained export of dissolved Fe. The same trend exists in DOC flux, with high concentrations throughout the September storm, supporting the interpretation that the peatlands are connected to the river at this point in the year. In contrast to PC, the dissolved Fe concentration in HR during storm events was not coupled with discharge (Figure 7). Despite significant amounts of precipitation, there is no evidence of a systematic flushing or dilution effect in HR. This suggests that the primary source environment for Fe is glacial melt, and an increase in precipitation does not connect the river to a large pool of dissolved Fe.

Temporal trends in colloidal Fe during storm events are dissimilar from dissolved Fe trends in both HR and PC (Figure 8). In PC, particularly during the mid-July storm, there is clear evidence of dilution in colloidal Fe concentrations at peak discharge, followed by rising concentrations as discharge decreases (Figure 8). Peak colloidal Fe concentrations occur approximately 24 hours after peak discharge, although discharge at this time is still relatively high compared to baseflow (Figure 8). These data suggest that legacy water enriched in colloidal Fe, likely a combination of (oxy)hydroxides and

aggregates of Fe/OM complexes [Stolpe *et al.*, 2013], may be exported from peatlands that remain connected to the river as a result of soil saturation even after precipitation has subsided. The lag between peak dissolved Fe and peak colloidal Fe may reflect the more rapid mobilization of dissolved Fe during storm events, even if the fractions share a similar source environment. It is likely that the concentration of colloidal Fe would remain high until the river reaches baseflow conditions, when significant amounts of colloidal material are not expected. Interestingly, there is no evidence of colloidal Fe dilution during the early-September storm, however discharge during this event was approximately half of peak discharge during the mid-July storm (Figure 8). A threshold for dilution may exist that was not met during this late-season storm. Additionally, peak colloidal Fe concentrations during the September storm lag behind peak discharge by only 8 hours (Figure 8). The direct connection of peatlands to PC due to saturated soils is the likely cause for consistently high colloidal Fe throughout the September storm, reflecting the development of colloidal Fe/OM complexes and Fe(oxy)hydroxides throughout the summer that are easily flushed from the system during late-season storms, similar to the geochemical partitioning identified by studies in other boreal-forested systems [Dahlqvist *et al.*, 2007; Rember and Trefry, 2004; Stolpe *et al.*, 2013]. Similar to dissolved Fe, trends in colloidal Fe export from HR during both storm events are inconsistent, with no evidence of systematic dilution, as colloidal Fe is derived primarily from glacial melt (Figure 8). Our limited data from individual storms suggests that Fe fluxes from glacial systems during storm events do not exhibit a systematic response in concentration (dilution, enrichment, and hysteresis), presumably because the storm is having minimal effect on the source of these constituents, and their concentration is

overwhelmingly driven by glacial processes that are not necessarily varying in response to individual storms. High-resolution data collected at both watersheds during these storms make it clear that different landscape conditions between HR and PC are reflected in riverine geochemistry, indicating dissimilar responses to high flow events.

Seasonal trends in riverine geochemistry

The contrasting hydrologic regimes in HR and PC also provide the opportunity to compare the evolution of riverine geochemistry over time in catchments with different seasonal responses. Seasonal transitions have the potential to change both the source environment and magnitude of nutrient and sediment fluxes. This is particularly evident in HR, where discharge is derived primarily from glacial melt that increases in magnitude throughout the summer (Figure 2). Although the HR catchment contains a significant amount of glacial coverage (49%), there are still low elevation rain forests throughout. Interestingly, samples collected at the onset of snowmelt and prior to glacial melt in HR had truly dissolved Fe concentrations very similar to the samples collected from PC, suggesting a forested source of these outlier truly dissolved iron data from HR (Figure 9). The fact that these samples collected during snowmelt also have the highest DOC measurements collected from this system further suggests a forested component of the catchment as the Fe source. It appears that the soluble-phase Fe geochemistry in the Herbert River early in the hydrologic year is characteristic of the lowland forested portion of its watershed before glacial melt is active. At this time of the year, active flowpaths contributing water to the river are similar between the two watersheds, resulting in a similar Fe size distribution (Figure 3). Once significant glacial melt began and increased

during the summer, the relative proportion of water derived from the lowland forested regions of the watershed decreased, resulting in much lower stream water truly dissolved Fe concentrations that are characteristic of glacial meltwater (Figure 9) [Schroth *et al.* 2011, Schroth *et al.*, 2014]. In general, this suggests that, from an iron standpoint, the glacial system is behaving like a forested one immediately after ice break-up, but quickly transitions to one where glacial weathering-derived Fe dominates the load once the hydrology is driven by glacial melt.

Additional further seasonal evolution of riverine geochemistry throughout the hydrologic year is evident in both HR and PC. At both sites there was an increase in the concentration of colloidal Fe over time (Figure 9), consistent with previous studies [Dahlqvist *et al.*, 2007; Rember and Trefry, 2004; Stolpe *et al.*, 2013]. In PC, the increase in colloidal Fe is likely caused by a variety of factors including: 1) the development of Fe (oxy)hydroxides at redox interfaces and within wetlands; and 2) aggregation of smaller nanocolloidal Fe/OM complexes. In HR, the increase in colloidal Fe is consistent with glacial weathering that occurs throughout the summer, providing a source for colloidal Fe even as glacial melt subsides in the fall. Interestingly, truly dissolved Fe concentrations in PC increased significantly throughout the sampling period, but the same was not true in HR (Figure 9). The abundant wetlands and organic-rich soils throughout the Peterson Creek watershed are the dominant source for this truly dissolved Fe fraction, supported by the strong correlation between DOC and truly dissolved Fe in PC (Figure 8). The increases in dissolved Fe and DOC concentrations at PC throughout the hydrologic year indicate that soil saturation may progressively connect more peatlands directly to the

river throughout the year, resulting in sustained high concentrations by the end of the season.

CONCLUSIONS

Our findings suggest that landscape evolution during glacial retreat has pronounced impacts on stream water Fe, and to a lesser extent Mn and P, concentrations, and on the size distribution of Fe, which may affect the bioavailability of Fe in the Gulf of Alaska, where it is critical to the aquatic ecosystem. Glacial recession, which is occurring at very rapid rates currently, and is likely to increase as a result of climate change, fundamentally changes the source environments and catchment processes that determine riverine geochemistry and the flux of soluble-phase metals and P to the gulf of Alaska. A changing climate is likely to accelerate the transition of glacial watersheds to boreal forested watersheds, which will result in an increase in the relative loads of smaller-sized Fe fractions complexed with organic matter. In the short term, rapid glacial melt is likely to continue to deliver large amounts of colloidal and suspended material. However, over longer timescales, a large decrease in glacial coverage will result in fundamental changes to riverine biogeochemistry. An investigation of the bioavailability of different size fractions of Fe is critical to understanding the effect of landscape evolution of coastal aquatic ecosystems. Particulate Fe is known to be the primary source of bioavailable Fe to aquatic organisms, and is derived from a combination of re-suspended continental shelf sediments [*Lam and Bishop, 2008*], eddies [*Lippiatt et al., 2009*], and glacial flour dust storms [*Crusius et al., 2011*], with the riverine contribution also significant. A transition from glacial to boreal forested coastal watersheds will

significantly decrease the amount of particulate and colloidal Fe delivered to the Gulf of Alaska, with as yet unknown implications for coastal ecosystems.

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FIGURES AND TABLES

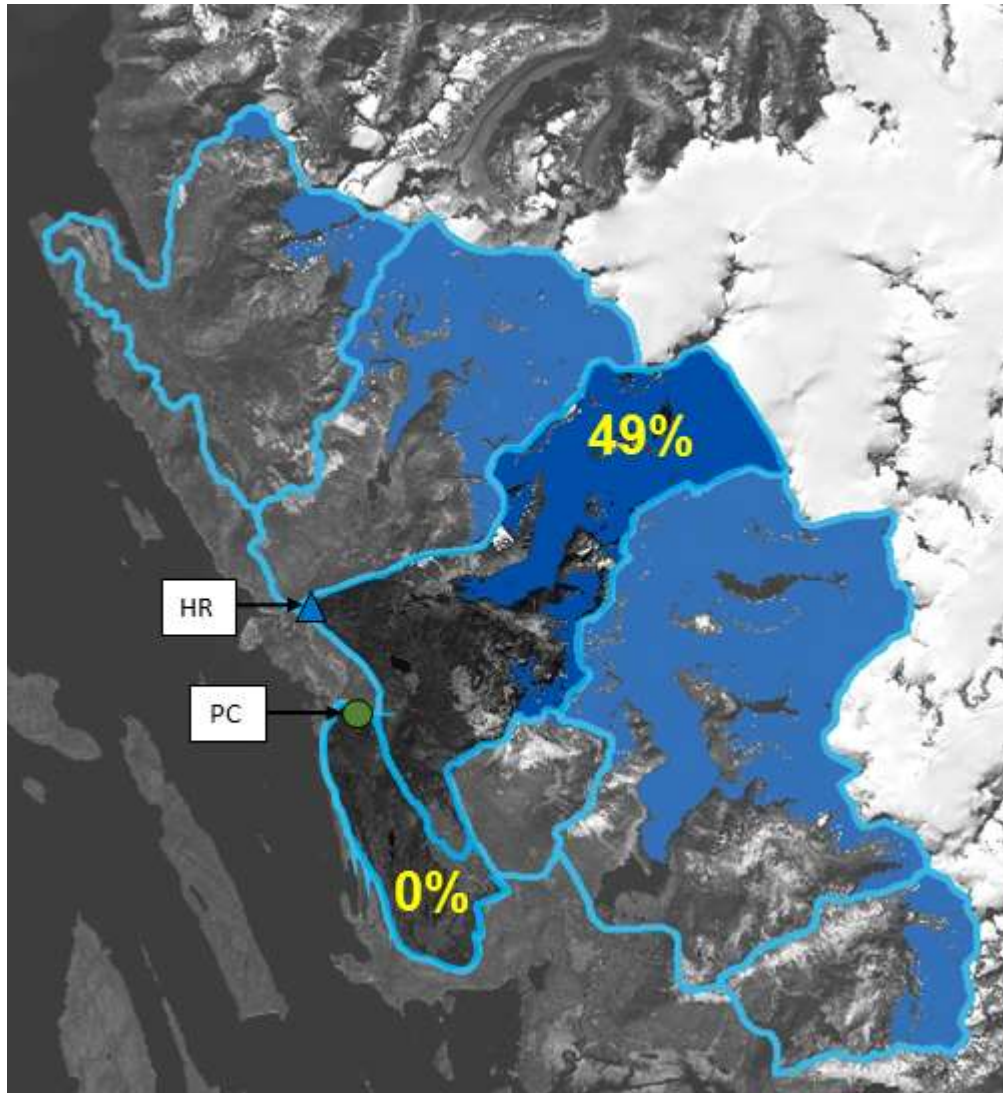


Figure 1. Sample locations and watershed glacial coverage. Thick lines denote the watershed boundaries, the dark blue identifies the extent of glacial cover, and the inset percentage is total glacial coverage within each watershed. Image courtesy of Andrew Schroth.

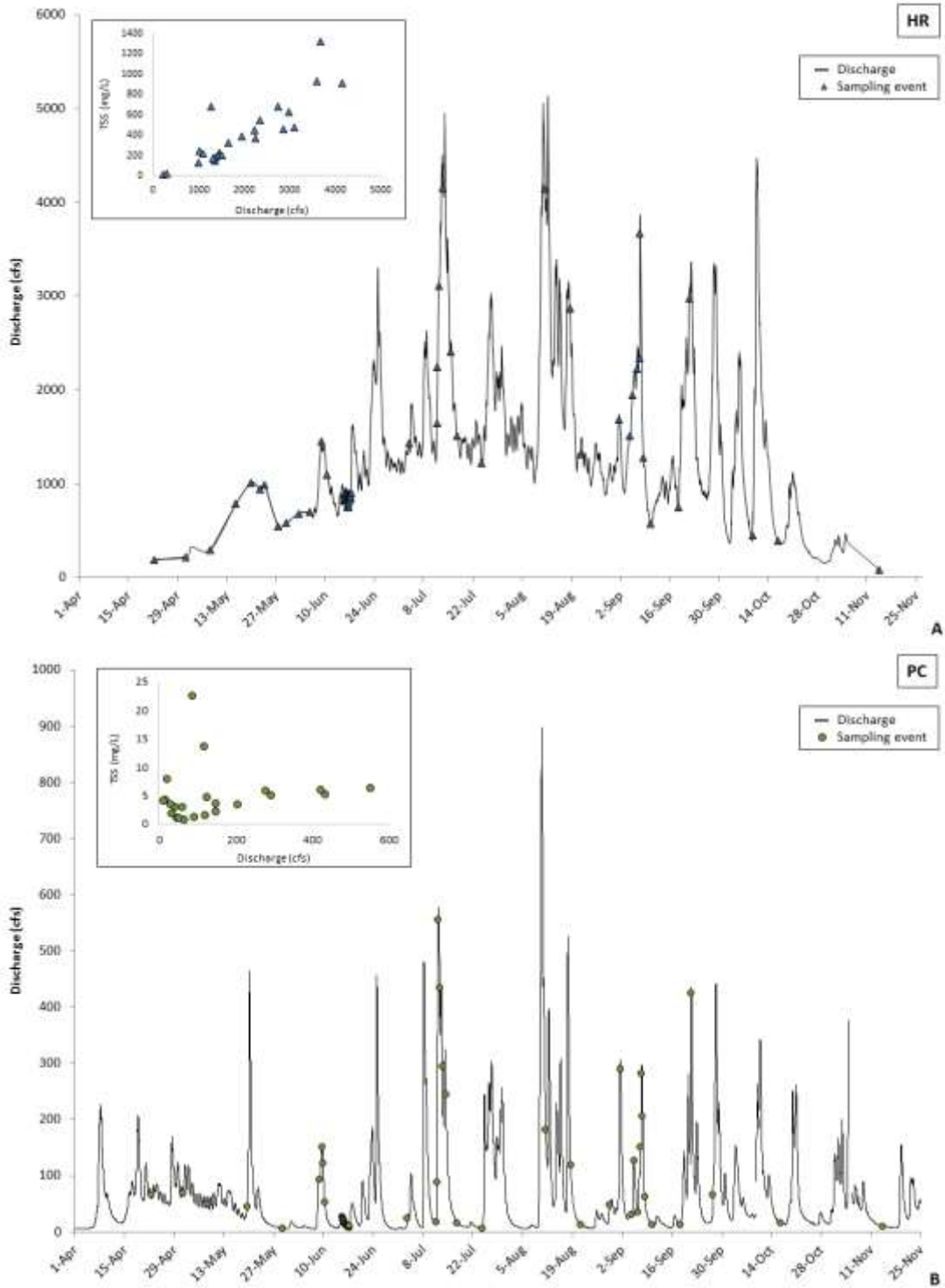


Figure 2. Discharge and sampling events for Herbert River (a) and Peterson Creek (b) during the 2014 sampling season. Samples were taken from both sites at each sampling event. The inset plot shows the relationship between discharge and total suspended solids (TSS) at each site.

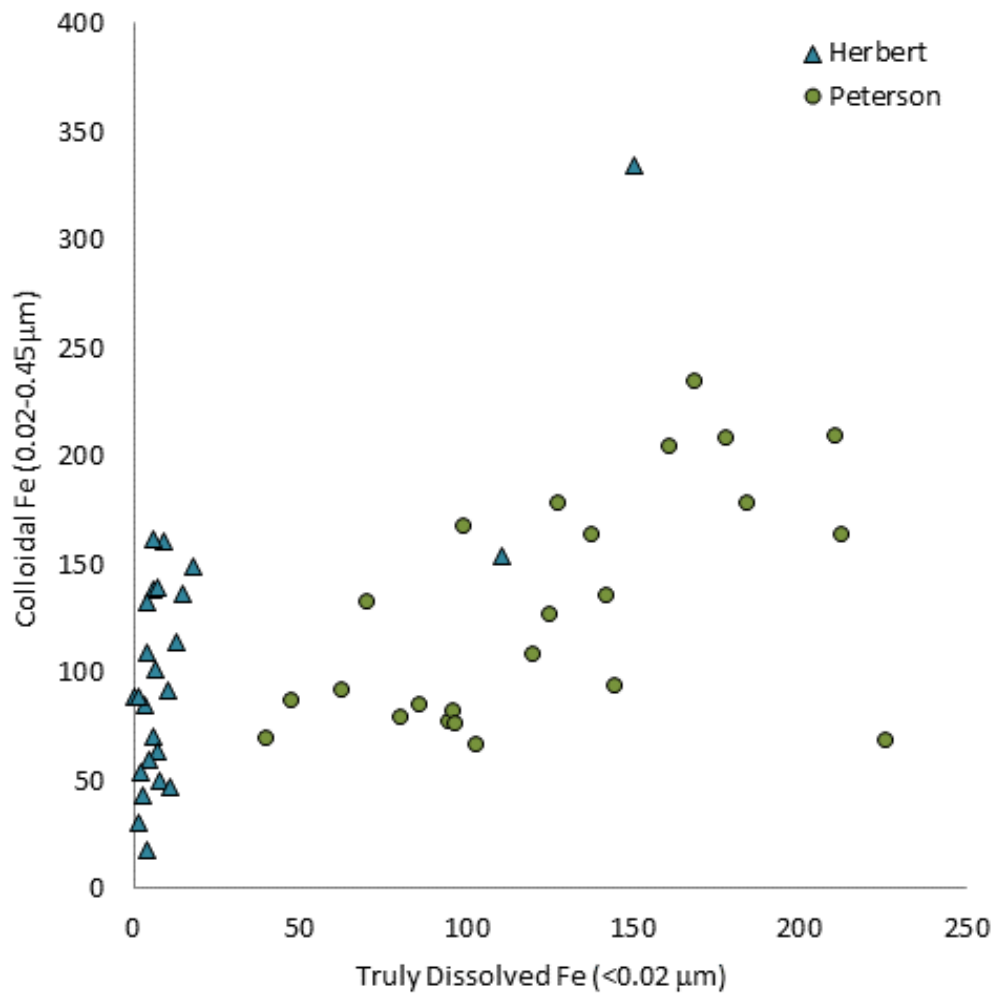


Figure 3. Size distribution of soluble-phase Fe in both sites. Two samples from Herbert River with high dissolved Fe concentration were the first 2 samples collected.

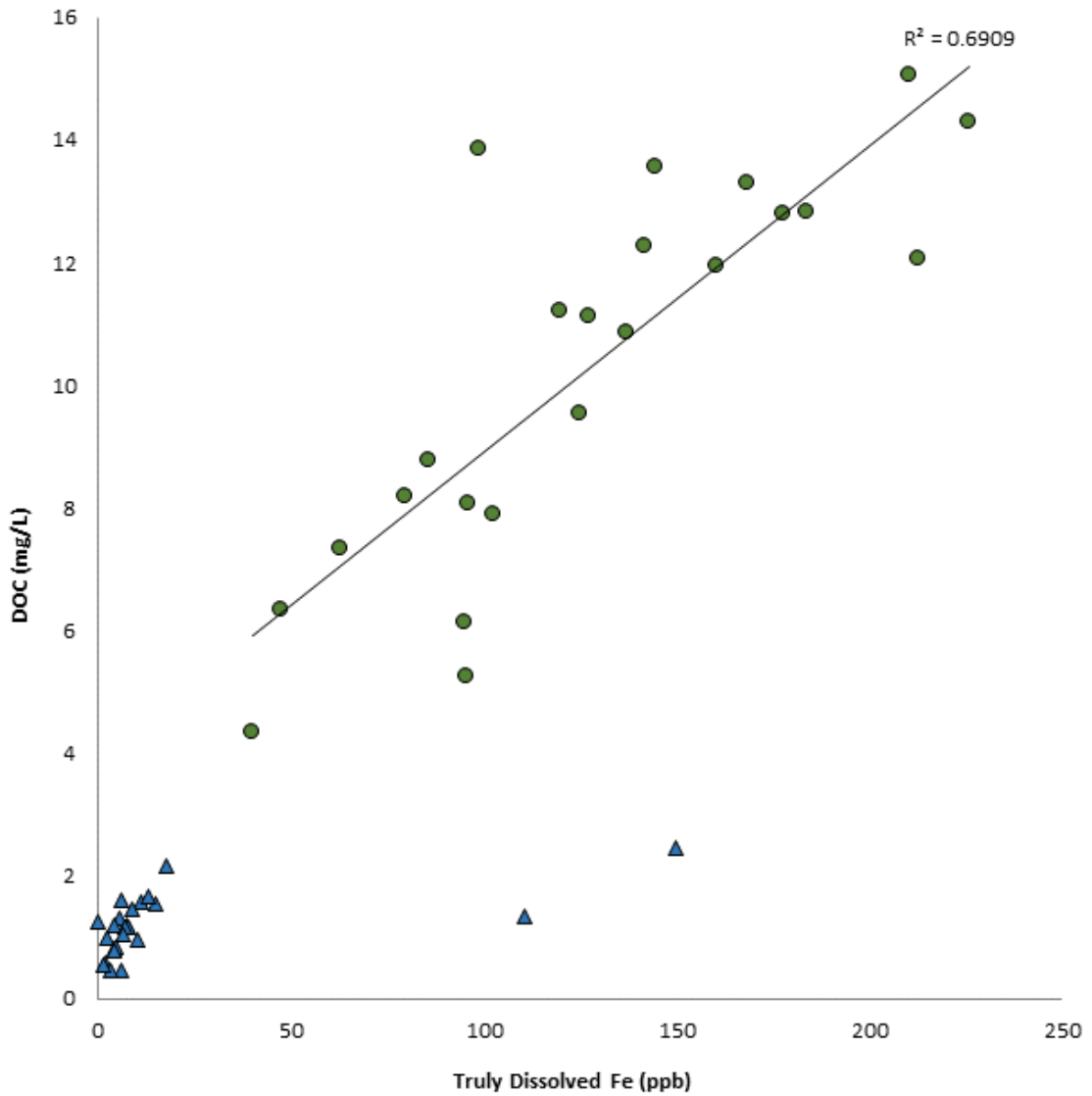


Figure 4. Relationship between truly dissolved Fe (<0.02 μ m) and DOC in Peterson Creek. The trend shown for Peterson Creek is significant at $p < 0.01$. There was no statistically significant relationship between DOC and Fe at the Herbert River site. Also note the significantly lower concentrations of DOC and truly dissolved iron in HR. Axes were not scaled to exaggerate the concentration difference.

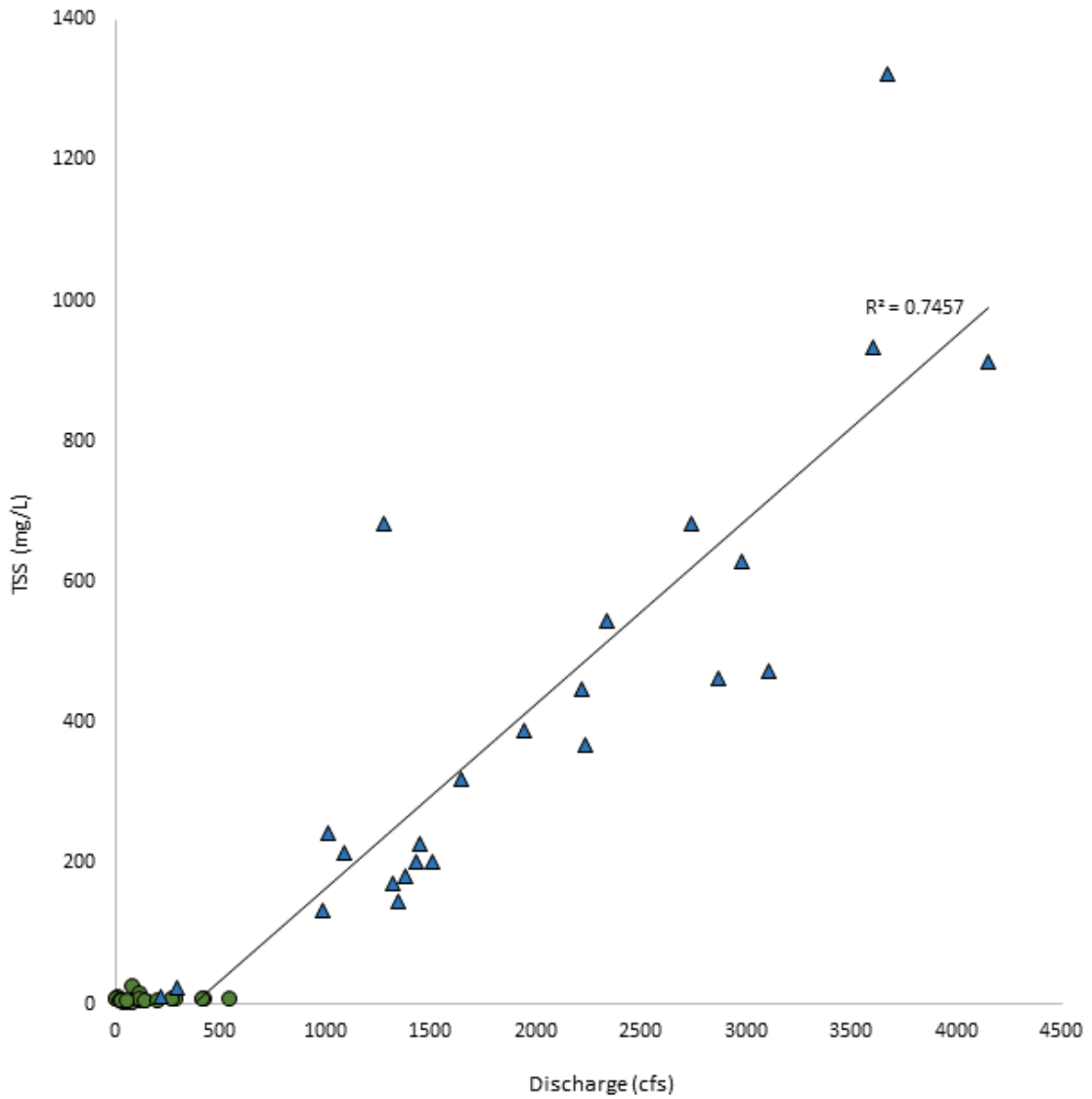


Figure 5. Total suspended sediment (TSS) concentrations for both HR and PC. The correlation displayed for HR is significant at $p < 0.01$, and there is no significant relationship between discharge and TSS at PC. For a closer view of the PC TSS and discharge data see Figure 1b.

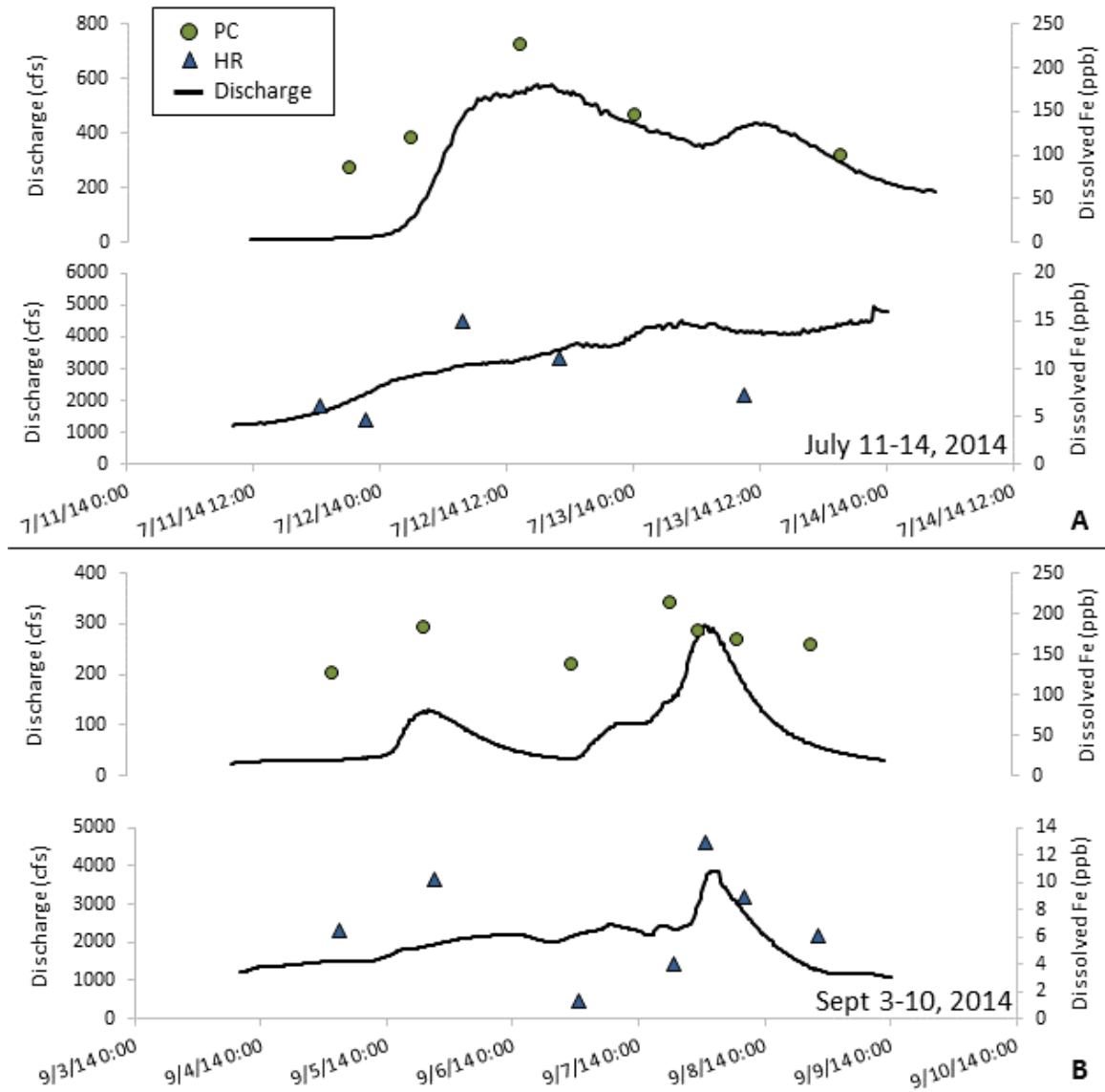


Figure 6. Trends in dissolved Fe during two storm events in 2014. In both (a) and (b) Peterson Creek is on top, and Herbert River is on the bottom. (a) Storm event from 7/11 to 7/14. (b) Storm event from 9/3 to 9/10.

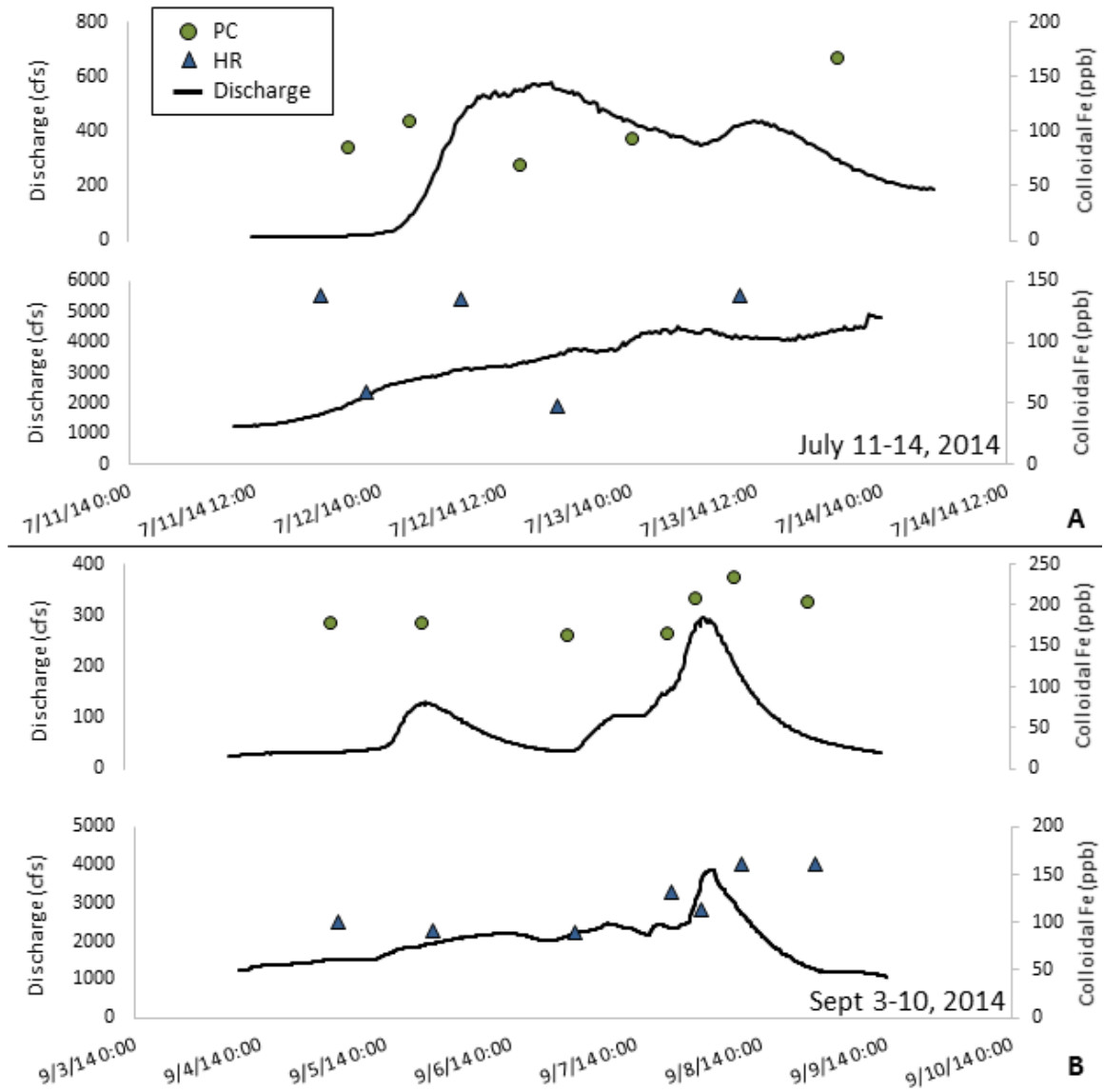


Figure 7. Trends in colloidal Fe during two storm events in 2014. In both (a) and (b) Peterson Creek is on top, and Herbert River is on the bottom. (a) Storm event from 7/11 to 7/14. (b) Storm event from 9/3 to 9/10.

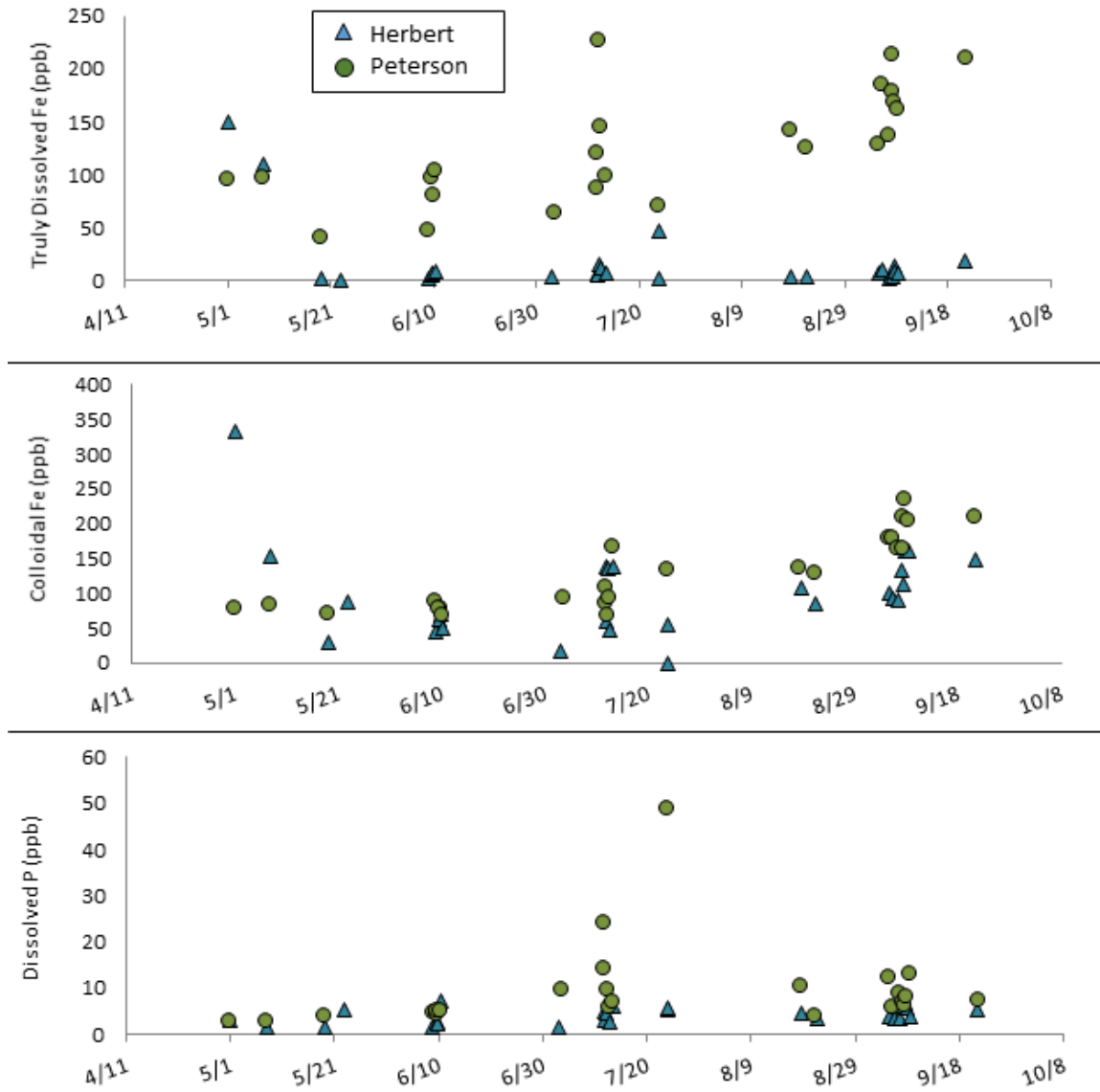


Figure 8. Time series trends in truly dissolved Fe (top), colloidal Fe (middle), and dissolved P (bottom) for both watersheds.

**Appendix A: Supporting Information for the
Biogeochemistry Manuscript**

Supporting Information for

**Coupling of reactive riverine phosphorus and iron during high flow events: impacts
of land cover and seasonality**

Braden D. Rosenberg^{1,2}, Andrew W. Schroth¹

Contents of this file:
Figures S1 to S4
Tables S1 and S2

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Introduction

This supplement includes additional plots to accompany the primary manuscript. The figures included here show: size distributions of Fe and Mn, and correlation matrices for soluble P and metals relationships. The tables included summarize all soluble and suspended P, Fe, and Mn concentrations for all land covers and seasons.

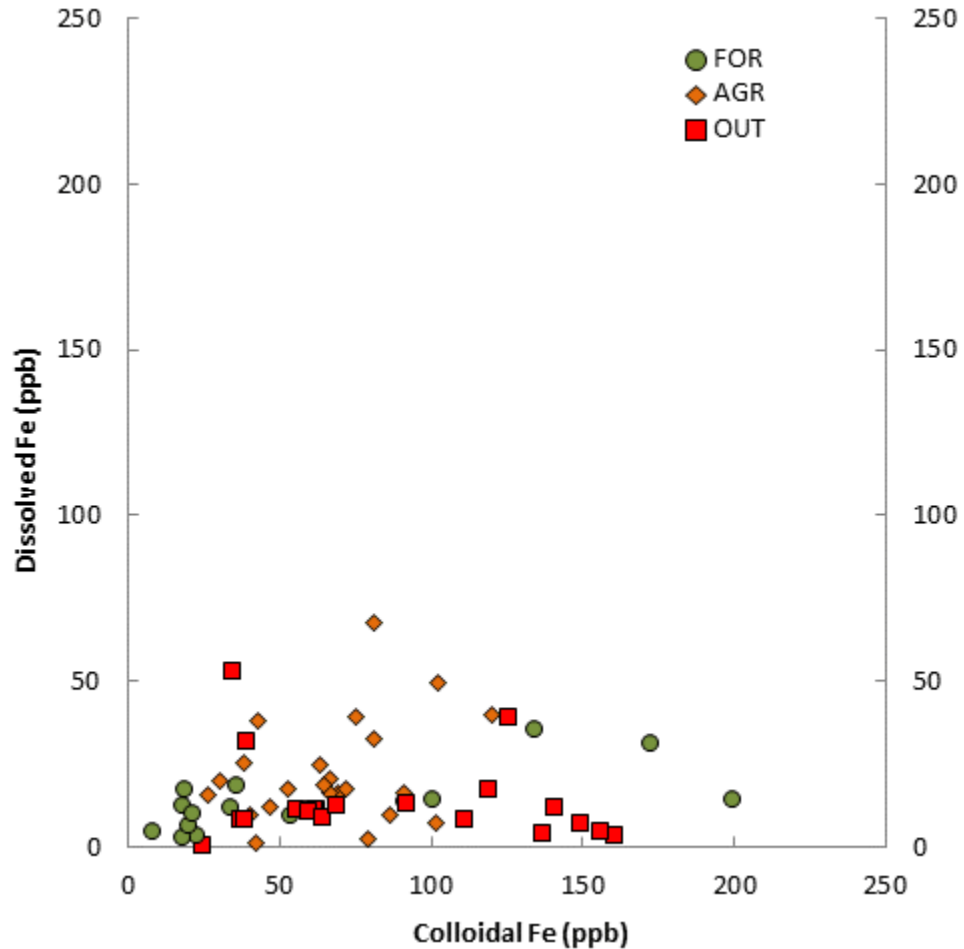


Figure S1. Distribution scatterplot showing the relative abundance of dissolved and colloidal Fe for all sample sites. No distinction is made between spring runoff and summer samples, as the distribution of Fe size fractions did not change significantly by season.

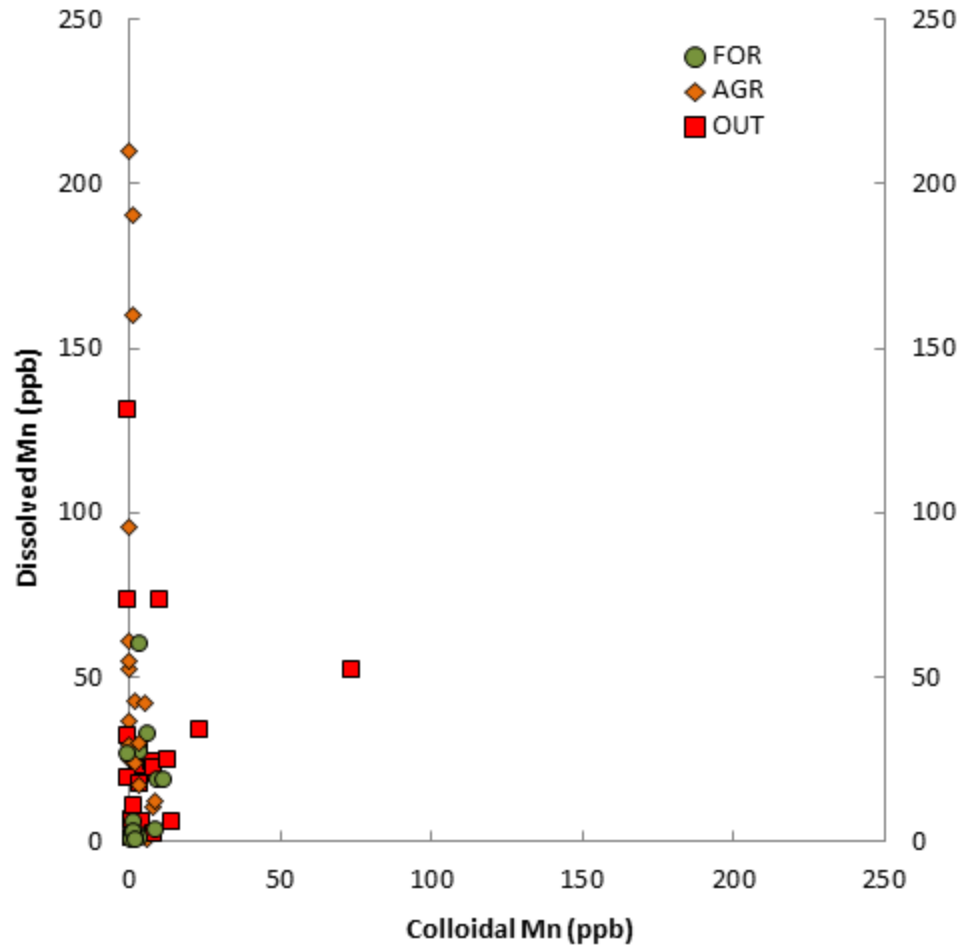


Figure S2. Distribution scatterplot showing the relative abundance of dissolved and colloidal Mn for all sample sites. No distinction is made between spring runoff and summer samples, as the distribution of Mn size fractions did not change significantly by season. Samples with negative colloidal Mn values (common in AGR) were given a value of 0 for ease of viewing.

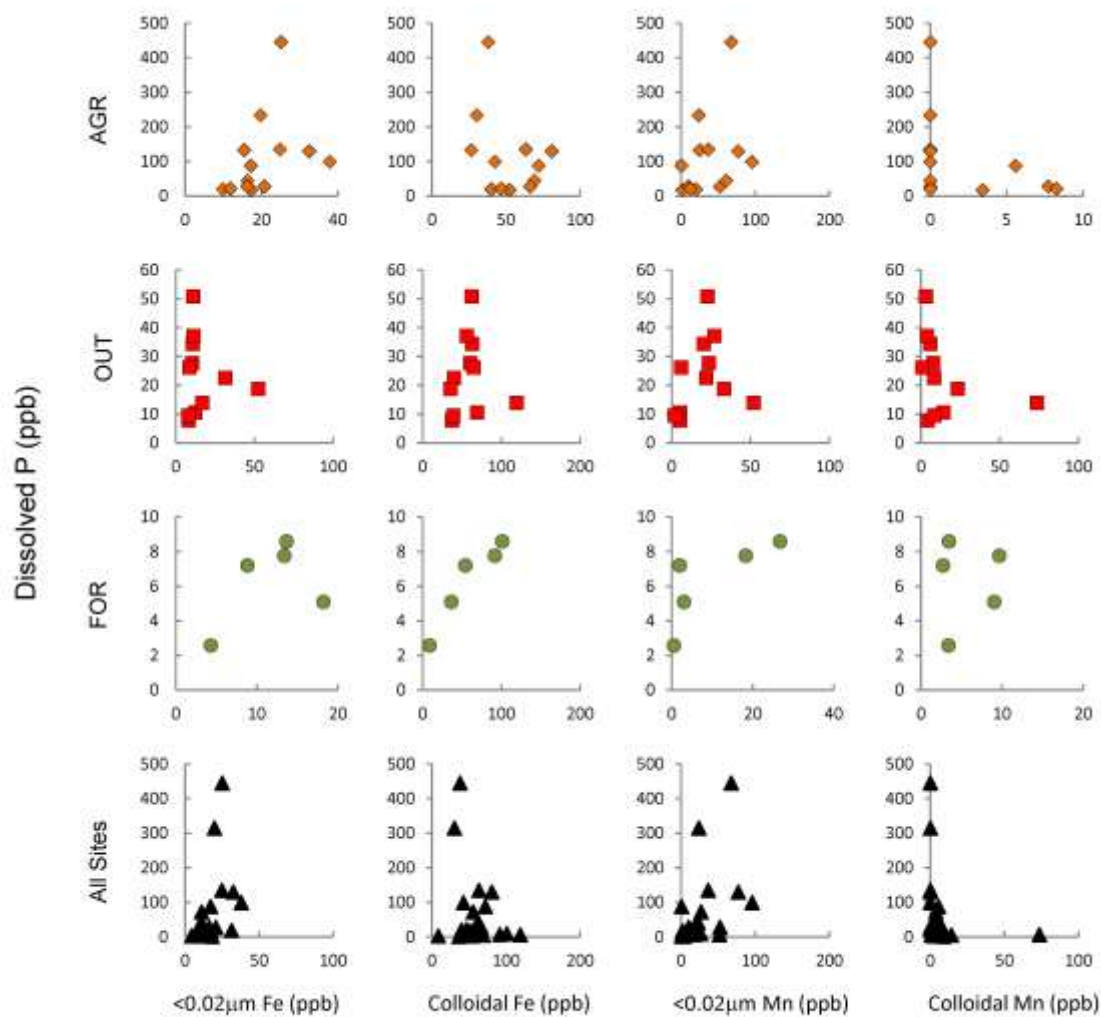


Figure S3. Scatterplot matrix showing the relationship between phosphorus (y-axis for all plots) and the different Fe and Mn size fractions. These plots show only spring runoff samples. Negative colloidal Mn values were given a concentration of 0 to allow plotting.

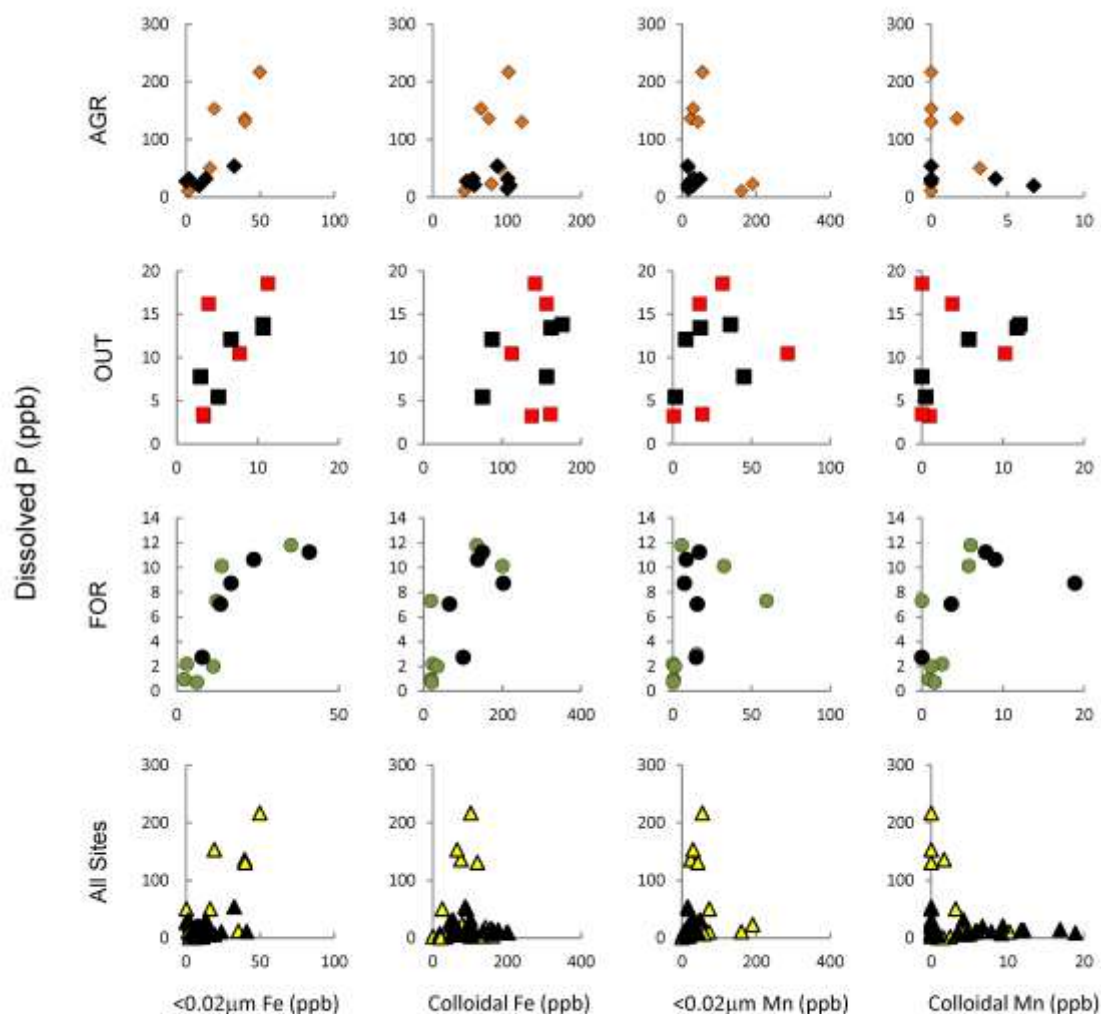


Figure S4. Scatterplot matrix showing the relationship between phosphorus (y-axis for all plots) and the different Fe and Mn size fractions. All samples shown here were collected during the summer. For the top 3 panels (AGR, OUT, and FOR), black markers identify samples collected during 2013. In the bottom panel, the 2013 samples are shown in yellow.

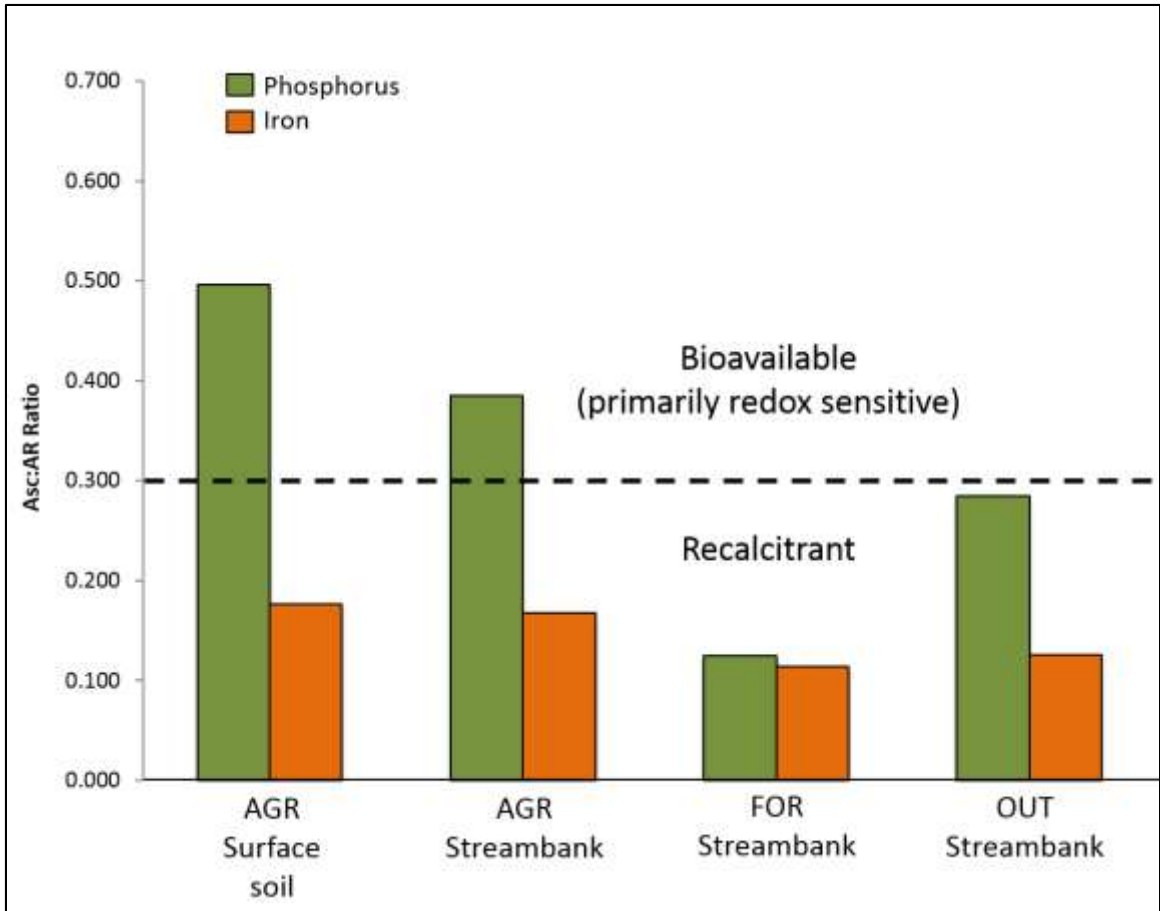


Figure S5. Parent material samples from the Missisquoi basin. Streambank samples were collected just upstream of water sampling sites; agricultural soil sample was collected further upstream from farmland adjacent to Hungerford Brook. This sample was a mix of recently applied manure and soil. All parent material was extracted and digested using the same methods as suspended sediment analysis.

Reducible (Asc)										
	SITE NAME	P Min	P Max	P Mean	Fe Min	Fe Max	Fe Mean	Mn Min	Mn Max	Mn Mean
SPRING RUNOFF	AGR	0.02	0.30	0.11	0.09	2.82	0.90	0.01	0.21	0.08
	OUT	0.02	0.13	0.05	0.16	1.71	0.58	0.01	0.17	0.06
	FOR	0.02	0.05	0.03	0.27	0.99	0.63	0.05	0.20	0.12
SUMMER	AGR	0.04	0.10	0.06	0.29	0.37	0.47	0.03	0.13	0.06
	OUT	0.01	0.02	0.01	0.07	0.41	0.24	0.02	0.08	0.04
	FOR	0.01	0.03	0.01	0.13	0.53	0.26	0.01	0.08	0.03
ANNUAL	AGR	0.02	0.30	0.10	0.09	2.82	0.75	0.01	0.21	0.07
	OUT	0.01	0.13	0.04	0.07	1.71	0.47	0.01	0.17	0.05
	FOR	0.01	0.05	0.02	0.13	0.99	0.38	0.01	0.20	0.06

Digestible (AR)										
	SITE NAME	P Min	P Max	P Mean	Fe Min	Fe Max	Fe Mean	Mn Min	Mn Max	Mn Mean
SPRING RUNOFF	AGR	0.05	0.77	0.27	0.46	19.36	6.04	0.01	0.44	0.15
	OUT	0.04	0.38	0.15	0.84	13.06	4.97	0.02	0.39	0.17
	FOR	0.06	0.19	0.12	1.90	7.86	4.88	0.07	0.34	0.21
SUMMER	AGR	0.10	0.17	0.14	0.93	2.53	1.70	0.04	0.09	0.07
	OUT	0.02	0.06	0.04	0.47	1.68	1.00	0.04	0.11	0.06
	FOR	0.01	0.06	0.03	0.44	1.99	1.12	0.03	0.12	0.06
ANNUAL	AGR	0.05	0.77	0.24	0.46	19.36	5.04	0.03	0.44	0.13
	OUT	0.02	0.38	0.12	0.47	13.06	3.78	0.02	0.39	0.14
	FOR	0.01	0.19	0.07	0.44	7.86	2.62	0.03	0.34	0.12

Table S1. Min, max, and mean spring thaw, summer, and annual concentrations of suspended sediment phase P, Fe, and Mn. All values are in mg/L (ppm).

	SITE NAME	Dissolved P			Truly Dissolved Fe (<0.02µm)			Colloidal Fe (0.02-0.45µm)			Truly Dissolved Mn (<0.02µm)			Colloidal Mn (0.02-0.45µm)		
		P Min	P Max	P Mean	Fe Min	Fe Max	Fe Mean	Fe Min	Fe Max	Fe Mean	Mn Min	Mn Max	Mn Mean	Mn Min	Mn Max	Mn Mean
SPRING RUNOFF	AGR	17.14	445.05	102.77	9.88	37.88	20.39	26.51	80.84	53.39	0.57	95.79	37.28	0.00	8.25	1.92
	OUT	3.41	72.03	20.77	7.84	52.32	16.38	35.11	119.16	58.58	1.72	51.90	19.87	0.72	73.60	13.93
	FOR	2.43	8.59	5.61	4.31	18.21	11.68	8.73	100.99	58.38	0.48	26.70	10.07	2.71	9.65	5.64
SUMMER	AGR	10.86	216.82	86.10	1.41	49.70	23.98	42.42	119.94	82.03	17.22	190.59	74.07	0.00	3.19	0.70
	OUT	3.24	50.51	13.56	0.16	11.21	4.93	25.03	160.85	122.00	0.69	73.10	35.68	0.00	10.26	2.49
	FOR	0.71	11.81	4.76	2.31	35.18	12.00	18.19	199.83	64.10	0.17	59.45	14.37	0.00	6.00	2.56
ANNUAL	AGR	10.86	445.05	95.44	1.41	49.70	21.65	26.51	119.94	63.41	0.57	190.59	50.15	0.00	8.25	1.49
	OUT	6.54	72.03	18.14	0.16	52.32	12.34	25.04	160.86	80.97	0.69	73.10	25.45	0.00	73.60	9.90
	FOR	0.71	11.81	5.13	2.31	35.18	11.87	8.73	199.83	61.71	0.17	59.45	12.71	0.00	9.65	3.84

Table S2. Min, max, and mean spring thaw, summer, and annual concentrations of suspended sediment phase P, Fe, and Mn. All values are in mg/L (ppm).