Impact of the Kenow wildfire on the form and mobility of particulate phosphorus in gravel-bed rivers at large basin scales: Implications for downstream propagation

by

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Author’s Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

This thesis consists in part of two manuscripts prepared as refereed papers that have not yet been submitted for publication (Chapters 3 and 4). Chapters 1, 2 and 5 were not written with the intent of publication.

Research presented in Chapter 3:
This research was conducted at the University of Waterloo by Mia Tullio under the supervision of Dr. Micheal Stone. Sediment sample collection was conducted by members of the Southern Rockies Watershed Project and geochemical analyses of samples were conducted at a commercial laboratory (Actlabs). Mia Tullio compiled and interpreted all data, completed statistical analyses, produced all figures and tables, as well as a draft manuscript, with edits made by Dr. Micheal Stone and Dr. Helen Jarvie.

Research presented in Chapter 4:
This research was conducted at the University of Waterloo by Mia Tullio under the supervision of Dr. Micheal Stone. Water and sediment samples were collected by members of the Southern Rockies Watershed Project. Unpublished water chemistry data was provided by Dr. Uldis Silins of the University of Alberta. Mia Tullio completed laboratory analysis of samples, compiled and interpreted all data, completed all statistical analyses, constructed all figures and tables and drafted the manuscript, with edits made by Dr. Micheal Stone and Dr. Helen Jarvie.

Abstract

Landscape disturbance by wildfire in forested source water regions can significantly accelerate fine sediment transport from hillslopes to receiving streams. The mobilization of fine sediment and associated nutrients, such as phosphorus (P) into high quality surface waters, which can drastically increase primary production and cause eutrophication, which can severely degrade water quality for ecosystem and human use. In the present study, abiotic controls on the form and mobility of particulate phosphorus (PP) in fine suspended and ingressed river sediment were examined in several oligotrophic gravel-bed rivers in Alberta, Canada, following the 2017 Kenow wildfire. Suspended sediment samples from seven (burned) study sites within Waterton Lakes National Park and three nearby reference rivers draining unburned watersheds were examined from 2018 to 2020 during environmentally sensitive flow conditions, in addition to ingressed sediment samples from burned sites one year post-fire. A sequential extraction scheme and batch equilibrium experiments were conducted to assess the immediate influence of severe wildfire on the form (non-apatite inorganic P, apatite P, organic P) and mobility (equilibrium phosphorus concentration, EPC_0) of PP in these systems, respectively. Sediment geochemistry and particle size characteristics were also investigated. Results of the study show that total concentrations of PP and concentrations of bioavailable PP (NAIP) were significantly higher in sediment from rivers draining burned watersheds compared to sediment from rivers in reference watersheds. Elevated bioavailable PP concentrations in burned river sediment were highly correlated with elevated Mn concentrations, which may have been a significant component of pyrogenic material following wildfire. While there were no significant differences in PP mobility between burned and reference river sediment, maximum mean EPC_0 values were observed two years after the wildfire, highlighting the potential legacy effect of wildfire disturbance on this key nutrient within rivers. Sediment from both burned and unburned rivers displayed the potential to act as a source of soluble reactive phosphorus (SRP) to the overlying water column, particularly during low flow conditions. Differences in PP form and mobility between burned and reference river sediment were likely influenced by catchment characteristics and in-stream biogeochemical processes. This thesis provides new insights regarding the impact of wildfire and site-specific abiotic processes on the form and mobility of PP in gravel-bed rivers in high quality source water regions.

Keywords: wildfire, gravel-bed rivers, fine sediment, particulate phosphorus fractionation, particulate phosphorus mobility

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List of Abbreviations

AP – apatite phosphorus

BD-RP – bicarbonate-dithionite reactive phosphorus

EPC_0 – equilibrium phosphorus concentration

NAIP – non-apatite inorganic phosphorus

NaOH-RP – sodium hydroxide reactive phosphorus

NH_4Cl-RP – ammonium chloride reactive phosphorus

OP – organic phosphorus

P – phosphorus

PP – particulate phosphorus

SRP – soluble reactive phosphorus

SWP – source water protection

TDP – total dissolved phosphorus

TP – total phosphorus

TPP – total particulate phosphorus

WLNP – Waterton Lakes National Park

Chapter 1
Problem statement and thesis organization

1.1. Problem Statement

The natural storage and filtration of water by global forests is valued at ~$4 trillion per year and these regions supply high quality source water to most of Canada's largest urban centers and many Indigenous and remote northern communities (Costanza et al., 1997; Emelko and Sham, 2014). Approximately 85% of drinking water supplies for Albertan communities originate in the forested slopes of the eastern Rocky Mountains (Emelko et al., 2011) and this region provides headwaters for many large rivers that represent significant freshwater resources in Canada (Hauer et al. 1997). Climate change-exacerbated severe landscape disturbances such as wildfire threaten these supplies, as they can deliver significant amounts of sediment and associated nutrients to receiving waters (Bladon et al., 2008; Emelko et al., 2016). These impacts can propagate downstream and last for decades, leading to more variable water quality and cascading impacts on stream ecology, river biodiversity and water security (Bladon et al., 2008; Emelko et al., 2016; Stone et al., 2011; Vörösmarty, 2010). The resulting deterioration and greater variability in source water quality can challenge water treatment operations and increase treatment costs (Emelko and Sham, 2014). The consensus by the wildfire science community is that wildfire severity and extent burned will continue to increase in many parts of the world, including western Canada (Flannigan et al., 2005). Within the current literature, reports describing wildfire effects on fine sediment and ash transport in receiving streams and rivers are scant and the associated implications of this research on water quality, especially treatability, are also poorly understood. Accordingly, the downstream effects of wildfire on water quality and treatability are of increasing concern to drinking water utility managers globally (Emelko and Sham, 2014).

Fine sediment (<63µm) comprises a small fraction (<10%) of the sediment mass transported in many rivers, but it can convey upwards of 90% of the adsorbed contaminants, including phosphorus that can promote algal blooms in reservoirs (Wentworth, 1922; Crouch et al., 2006). Fine sediment is a vector for nutrient transport because of several properties (physical, geochemical and biological), that preferentially bind and transport PP. Some of these properties include large specific surface areas and metal oxyhydroxide surfaces, as well as environmental factors such as redox conditions (Stone and Mudroch, 1989; Stone and English, 1993; Withers and Jarvie, 2008; Emelko et al., 2016). Further, ingressed fine sediment in gravel bed rivers can represent a significant, long-term source of bioavailable PP, due to the entrapment of associated nutrients (Emelko et al., 2016; Wilkes et al., 2018); however, its influence on phosphorus mobility in a range of riverine environments undergoing landscape pressures requires further understanding (Karna et al., 2014). While gravel-bed rivers can typically have relatively high biotic uptake of phosphorus (Lottig and Stanley, 2007), these processes are often subject to change after severe landscape disturbances such as wildfire, which introduce large amounts of sediment and other debris into aquatic systems and alter hydrologic regimes (McDowell et al., 2002; Owens and Walling, 2002; Silins et al., 2009; Silins et al., 2014). The extent to which wildfire transforms the phosphorus characteristics of pyrogenic materials and how these materials influence nutrient dynamics in rivers at large basin scales is a research area of increasing importance, as the impacts of fire-generated materials on drinking water treatability related to reservoir water quality and ecological response are not well understood in high quality forested source water regions across the globe. Recent studies report that wildfire-derived fine sediment and associated bioavailable P can represent legacy nutrients that are released to the water column in rivers draining burned watersheds (Watt et al., 2021), even at larger basin scales (Emelko et al., 2016; Stone et al., 2021).

The goal of this study is to examine the effects of the 2017 Kenow wildfire in Waterton Lakes National Park (WNLP) on the form and mobility of sediment-associated P within forested rivers at large basin scales. Since this research is the first of its kind globally to examine immediate post-fire impacts on the form and mobility of P, the results of this research provide new insights regarding relationships between the form and mobility of sediment-associated P and the physical and geochemical composition of suspended and ingressed solids in wildfire-impacted gravel-bed rivers over large basin scales.

1.2. Research Objectives

The overarching goal of this work is to characterize the abiotic controls on wildfire-impacted fine sediment and associated phosphorus in forested rivers at a large basin scale. Specific objectives of this research are to:

1. Evaluate the form of sediment-associated phosphorus (NAIP, AP, OP) in wildfire-impacted rivers and unburned reference rivers.
2. Examine relationships between particulate phosphorus forms and the physical and geochemical properties of riverine sediment (e.g., particle size, Fe, Al, and Mn).
3. Evaluate the mobility (EPC_0) of fine sediment-associated phosphorus wildfire-impacted and reference rivers.
4. Discuss the implications of wildfire-related enhanced fine sediment and nutrient inputs on water quality and water treatability.

1.3. Tasks

To address the thesis objectives, two sets of bench-scale experiments were conducted. Objectives 1 and 2 were achieved by investigating PP forms using a sequential extraction scheme developed by Pettersson and Istvánovics (1988) and characterizing the physical and geochemical composition of fine suspended solids collected with Phillips samplers deployed in rivers across the study area. Objective 3 was achieved using batch experiments to determine the equilibrium phosphate concentration (EPC_0) of fine sediment according to the methods described by Froelich (1988). Objective 4 was addressed through a synthesis of the literature and discussion of the data regarding the implications for water quality in Waterton Lakes National Park.

1.4. Thesis Organization

This thesis is written in manuscript format. Chapter 2 is a comprehensive literature review and discussion of existing knowledge gaps. Chapter 3 focuses on the results of the phosphorus speciation and sediment geochemistry experiments and Chapter 4 focuses on the results of the phosphorus mobility experiments. Chapter 5 provides a synthesis of the results in the context of the literature.

Chapter 2
Wildfire on sediment-associated phosphorus in forested river systems

2.1. Literature Review

The following is a review of the scientific literature currently available on sediment-associated phosphorus in forested rivers and how its spatial and temporal distribution and chemical composition are influenced by enhanced climate change and associated natural disasters such as wildfire. Knowledge gaps within the literature are identified and the relation of this research area to drinking water quality and treatability is highlighted.

2.1.1. Influence of enhanced climate change on freshwater resources

Forested landscapes are valuable source water regions that provide high quality drinking water for many communities across North America by regulating surface and groundwater flow that naturally purify water supplies (Emelko and Sham, 2014). Increasing climate change-exacerbated landscape disturbances threaten the “green infrastructure” present in forested landscapes that provide high quality supplies of freshwater for human consumption (Emelko et al., 2016). High quality freshwater resources emanating from forested source water regions are especially vulnerable to the effects of climate change due to their relative geographic isolation, their sensitivity to temperature fluctuations and the fact that these systems are also often subject to anthropogenic stresses (Woodward et al., 2010). The effects of climate change are expected to decrease the quantity and quality of freshwater supplies and increase the global demand for this resource, which will have significant environmental and economic consequences (Hall et al., 2008). With enhanced climate warming, freshwater resources are subject to greater variability in regional precipitation patterns, more frequent extreme precipitation events and greater vulnerability to drought (Hall et al., 2008; Kundzewicz et al., 2008). Reduced snowpack volumes, reduced soil moisture and increased evapotranspiration are also associated with climate change-driven temperatures increases and these processes reduce stream inflow to reservoirs, as well as potentially increase river salinity, challenging treatment processes of freshwater supplies (Hall et al. 2008). As a result of altered hydroclimatic conditions, the quality of freshwater resources is likely to be negatively impacted through enhanced rates of diffuse-source contaminant entry into waters from increased runoff, as well as the malfunctioning of water infrastructure and the overloading of water treatment facilities due to enhanced precipitation leading to floods (Kundzewicz et al., 2008). Further, enhanced climate change threatens valuable freshwater supplies through the increased likelihood of extreme landscape disturbances, such as wildfire, which can influence the form, mobility and transport of sediment and associated contaminants entering freshwater bodies (Son et al., 2015; Emelko et al., 2016).

2.1.2. Influence of wildfire on fluvial sediment and associated nutrients

The current trend of enhanced climate warming has contributed to increases in both wildfire severity and frequency across the globe within recent decades, leading to increased focus on this topic within the literature (Flannigan et al., 2005). The "mega-fire," is a recent concept that has been introduced in the literature and describes less than 1% of wildfires, but accounts for 90-95% of the annual area burned across the globe, with recent mega-fires having occurred in locations such as North America, Greece, Russia, and Australia (Williams, 2013). Flannigan et al., (2005) report that by the end of the century, the length of wildfire season, wildfire severity and total area burned in Canadian forests will increase between 74-118%, with similar trends also predicted for the United States. Factors that have contributed to significant change in the pattern and intensity of wildfires across western North America in recent decades include the trends of warming climate, altered timing of precipitation events, increased availability of fuels and the expansion of the interface between wildland and urban development (Schoennagel et al., 2017). Historically, the influence of anthropogenic disturbance, (particularly harvesting, urban development and agriculture) on sediment-associated P form and mobility within rivers has been emphasized in the literature (Owens and Walling, 2002, McDowell et al., 2002), with the role of climate-change exacerbated extreme landscape disturbances such as wildfire more recently receiving increased recognition (Emelko et al., 2016; Son et al., 2015; Watt et al., 2021).

There is increasing recognition that large-scale landscape disturbance by wildfire can alter the physical characteristics of rivers and related ecosystem services (Allin et al., 2012). Wildfire can exert strong influence on the quality and quantity of water in headwater streams by drastically decreasing the amount of water loss to interception and evaporation through removal of vegetation, increasing moisture content of soils and increasing hillslope runoff generation, which can lead to enhanced storm runoff (DeBano et al., 1998; Emelko et al., 2011; Neary et al., 2003). Increased post-wildfire erosion rates and runoff generation can increase fluxes of sediment and associated nutrients, potentially leading to nutrient enrichment of reservoirs and proliferation of cyanobacteria, challenging water treatment (Emelko et al., 2011; Smith et al., 2011). Erodibility and chemical composition of sediment have also been shown to be influenced by wildfire, as fire-modified sediments may be more erosion-resistant and have lower settling velocities due to greater porosity and organic content, which can require higher critical shear stress for erosion due to biostabilization in fire-impacted streams (Stone et al., 2011). The increased post-fire delivery of fine sediment to receiving streams is detrimental to the health of aquatic ecosystems and can pose a serious threat to the quality of forested source water systems (Harper et al., 2017; Wilkes et al., 2018.). Some negative effects associated with increased fine sediment content in rivers includes clogged streambeds, greater instability of river channels and channel morphology and altered river temperatures, which can have drastic impacts on aquatic ecosystems (Bladon et al., 2014).

Landscape change by wildfire can mobilize large amounts of sediment (Silins et al., 2009) and associated nutrients, such as P, from terrestrial surfaces to inland water bodies (Blake et al., 2010; Emelko et al., 2016; Watt et al., 2021) and notably, dissolved and particulate P concentrations in river sediment increase after wildfire (See Table 2.1.2). Wildfire can mobilize inorganic phosphorus by desorbing it from soil organic matter and subsequently releasing it in rivers during runoff (Bennett et al., 2001; Emelko et al., 2011; Lane et al., 2011). It has been demonstrated that high nutrient concentrations following wildfires can be long-lasting, and in some cases persist up to decades after the disturbance (Emelko et al., 2016). Phosphorus exports from catchments can vary considerably depending on factors such as the burn area and intensity, local erosion dynamics, delivery processes to streams, soil type and vegetation characteristics (Smith et al., 2011). The timing and intensity of precipitation events following landscape disturbances, such as wildfire, are key drivers of changes in water quality that challenge prediction of effects (Emelko and Sham, 2014). Since forested source water regions are particularly vulnerable to sediment and contaminant influxes associated with mobile post-wildfire ash, further research focussing on the composition, transport and mobility of wildfire-generated pyrogenic materials in forested regions will have important implications for the protection of drinking water supplies and development of water treatment strategies (Emelko et al., 2011; Emelko and Sham, 2014; Silins et al., 2009; Silins et al., 2014; Stone et al., 2011).

Table 2.1.2. – Summary of current research on P concentrations in forested river sediment following wildfire in Alberta, Canada.

Location	Year of wildfire	Years of monitoring	Maximum post-fire P concentration	P species	Source
Castle River Basin, AB	2003	2009-2010	667.7 μg g^{-1}	TPP	Emelko et al., 2016
Crowsnest River Basin, AB	2003	2003-2010	386 μg g^{-1}	NAIP	Allin et al., 2012
	2003	2009-2010	758.7 μg g^{-1}	TPP	Emelko et al., 2016
	2003	2016-2017	734.1 μg g^{-1}	TPP	Watt et al., 2021

2.1.3. Enhanced post-fire phosphorus fluxes into rivers and implications for water treatability

Water security lies at the intersection of ecosystem and human health and requires knowledge on both fronts to implement effective treatment options for source water supplies (Emelko et al., 2011). Water treatability refers to any process that improves water quality to a level that can be safely used for a specific function, such as human consumption (Emelko and Sham, 2014). Landscape disturbances such as wildfire are capable of imparting severe and long-lasting physical, biological, and chemical impacts on downstream river reaches, which in turn necessitate specific design, operation and cost adjustments to effectively treat drinking water supplies (Emelko et al., 2011). Following wildfire, the downstream propagation of sediment and associated contaminants could drastically alter in-stream biogeochemical processes, which in turn can modify existing ecological assemblages and degrade water quality (Wood and Armitage, 1997). Notably, deteriorated quality of drinking water supplies ma last for timescales ranging from months to years, with extreme cases lasting up to decades (Emelko and Sham, 2014).

Due to its high volatization temperature compared to other nutrients such as nitrogen, phosphorus is a nutrient of particular concern in rivers following wildfire (Son et al., 2015).

Phosphorus content in rivers is intrinsically related to water treatability, as elevated P concentrations may proliferate the growth of cyanobacteria in source water supplies, such as reservoirs (Emelko et al., 2011; Juhna et al., 2007; Makris et al., 2004). Critical “trigger” ranges of P concentrations for varying river water quality classes have been defined by the Canadian Council of Ministers of the Environment (CCME) and aquatic systems with total phosphorus (TP) concentrations between 4 and 10 μg/L TP are considered oligotrophic, low productivity waters (CCME 2004, See Table 2.1.3). Due to the dynamic nature P transport in rivers, as well as potential historical inputs and the ability of riverbed sediments to retain nutrients, the effects of enhanced P concentrations are difficult constrain in areas with multiple disturbances (Collins and Walling, 2002). Additionally, elevated post-fire sediment-associated P fluxes within watersheds typically increase with severity of disturbance (Wohl, 2015). Accordingly, to effectively manage valuable water supplies, it is necessary to improve the understanding of the source and transport of sediment and associated P in areas affected by landscape disturbance (Withers et al., 2014).

Phosphorus is the limiting nutrient in determining the biological productivity of aquatic plants, algae and cyanobacteria in freshwater bodies (Schindler, 1977; Bennett et al., 2001; McDowell, 2015) and this is due to the role it plays in binding carbon in living organic matter (Spivakov et al., 1999). In aquatic ecosystems, even small changes in P concentrations can have significant impacts (Bennett et al., 2001; Bowes et al., 2003; CCME, 2004; Dodds and Smith, 2016; Keup, 1968; Lehtola et al., 2002; Mainstone and Parr, 2002; Miettenen et al., 1997; Smith et al., 2011; Spivakov et al., 1999). Elevated P concentrations in rivers following wildfire disturbance may lead to several negative environmental effects, of which a primary concern is eutrophication, which is a state of nutrient enrichment in aquatic ecosystems from diffuse and point sources that results in algal overgrowth (Correll et al., 1998). Flowing bodies of water are particularly vulnerable to eutrophication, since they are often subject to additional disturbance such as proximity to urban zones and are regularly exploited for natural resources (Withers and Jarvie, 2008). Phosphorus has long been considered the primary nutrient responsible for causing eutrophication, though it has recently been shown that the combined effect of increased phosphorus and nitrogen loads into receiving waters carries a higher risk for stimulating eutrophication that increases in either nutrient alone (Paerl et al., 2016). Eutrophication is associated with an increased risk of harmful algae blooms (HABs), which can disrupt ecosystem dynamics, as well as affect the taste, colour and odour of drinking water (Drewry et al., 2006;

Mainstone and Parr, 2002; NHMRC, 2004). In oligotrophic waters, increased nutrient loads related to disturbance by fire have the potential to stimulate primary production in downstream reaches, demonstrating how the effects of fire can propagate great distances (Hauer and Spencer, 1998). Since wildfires are capable of releasing and mobilizing phosphorus in river systems where only small additions of bioavailable phosphorus are needed to stimulate significant microbial growth, this topic is of growing concern for forested drinking water supplies (Miettenen et al., 1997; Lehtola et al. 2002). The relationship between enhanced riverine P concentrations and proliferation of primary producers is important to understand, as the removal of pathogens is always a top priority in terms of water treatment (Silins et al., 2014). Predicting the delivery of contaminants to stream networks represents a major issue in water quality management (Lane et al., 2011). With enhanced understanding of the biogeochemical processes responsible for the transfer of P between riverine sediments and water, catchment specific responses to landscape disturbance can be used to make better informed management decisions regarding valuable forested water supplies.

Table 2.1.3. – Canadian Council of Ministers of the Environment (CCME) guidelines for P concentrations in freshwater rivers and lakes in Canada.

Trophic Status	**Canadian TP Trigger Ranges (µg/L)**
Ultra-oligotrophic	<4
Oligotrophic	4-10
Mesotrophic	10-20
Meso-eutrophic	20-35
Eutrophic	35-100
Hyper-eutrophic	>100

2.1.4. Particulate phosphorus forms and relations to sediment geochemistry

Phosphorus exists in rivers in a variety of both particulate and dissolved phases (Drewry et al., 2006; Jarvie et al., 2002) and transformations between these phases have been attributed to changes in pH, temperature and dissolved oxygen content (Wilkes et al., 2018). Dissolved reactive, or soluble reactive phosphorus (DRP or SRP, respectively) is an operationally defined P form that is able to pass through 0.45 µm filters and is generally more bioavailable. In contrast, particulate phosphorus (PP), which too large to pass through 0.45 µm filters, is capable of adsorbing and releasing SRP (Froelich, 1988). SRP is an important source of bioavailable phosphorus within lakes and rivers (House and Denison, 2002). Generally, dissolved P species include orthophosphates, and inorganic condensed phosphates, while particulate P species consist of phosphorus-enriched minerals or mixed phases that contain sorbed phosphorus (Jarvie et al., 2002; Spivakov et al., 1999). Key particulate phosphorus fractions have been defined based on their relative bioavailabilities based on the pioneering work of Chang and Jackson (1953). These fractions are characterized using operationally-defined sequential extraction schemes for sediments with Al, Fe and Mn-oxides and hydroxides, Ca and organic/humic components (e.g. Psenner et al., 1984; Pettersson and Istvánovics, 1988). Non-apatite inorganic phosphorus (NAIP) is the most bioavailable form and is associated with particles with metal-hydroxide surfaces (Emelko et al., 2016). NAIP is the sum of 3 leaches; NH_4Cl (1.0M) is used to remove the most easily desorbable P, BD (0.11M, 40°C) is used to remove Fe-bound, reductant-soluble P and NaOH (1.0 M) is used to remove reactive P bound to Ca and Mg metal-oxides (Pettersson and Istvánovics, 1988, Stone and English, 1993). Apatite phosphorus (AP) is removed using HCl (0.5M), and this form is geochemically stable. AP consists of phosphate minerals (typically Ca, Mg and Fe minerals found in sedimentary environments) that are typically not available for biotic use (Pettersson and Istvánovics, 1988; Stone and English, 1993). Finally, organic phosphorus (OP), which may exist in both dissolved and particulate forms is removed using NaOH (1.0M, 85°C) and is generally considered unavailable for biological use (De Pinto et al., 1981; Jarvie et al., 2002; Pettersson et al., 1988), although it may become bioavailable through hydrolysis (Golterman, 1995). Operationally defined phosphorus fractions in freshwater environments are a combination of species and include total dissolved (or soluble) phosphorus (TDP) and total particulate phosphorus (TPP), which are distinguished by filtration through a 0.45μm membrane. Total phosphorus (TP) is the sum of TDP and TPP (Jarvie et al., 2002).

Table 2.1.4. – Particulate phosphorus forms and their significance (after Spivakov et al., 1999).

Form	**Significance**
Total Phosphorus	Indicates total phosphorus burden
Non-Apatite Inorganic Phosphorus	Most bioavailable form
NH_4Cl-Reactive Phosphorus	Most easily desorbable form
BD-Reactive Phosphorus	Reductant-soluble, bound to Fe
NaOH-Reactive Phosphorus	Reactive, bound to Ca and Mg metal-oxides
Apatite Phosphorus	Mineral-bound, geochemically stable, not bioavailable
Organic Phosphorus	Unreactive, predominantly not bioavailable

The majority of P in freshwater exists as dissolved, colloidal and particulate P in both organic and inorganic fractions (CCME, 2004 and sources therein). The availability of P in freshwater systems is largely influenced by geochemical controls (Boström et al., 1988). Relationships between P concentrations and major element sediment geochemistry are well documented, since P is often bound to or transported by fine sediment fractions, such as clays and ash, which often have Fe, Al, Mn or organic coatings (Evans et al., 2004, McDowell et al., 2002; House and Denison, 2002). Accordingly, there is often a negative correlation between grain size and P concentration, as well as between P and elements such as Si, Ca and Mg, which are key components of resistant minerals within ingressed sediments (eg. Stone and Mudroch, 1989). Elements such as Al, Fe and Mn bound to mineral surfaces or organic matter are often influenced by redox conditions (Lijklema, 1993; Borch et al., 2010) and these elements are generally positively correlated with P concentrations (Stone and Mudroch, 1989). Phosphate ions have high a negative charge density and oxy-hydroxides and other metals often act as electron acceptors, resulting in the phosphate ion sorbing to the metal complexes (Klotz, 1991). The availability of metal oxyhydroxides within an environment will therefore influence the binding of P to metal coatings on sediment (Golterman, 2004). Further, transformations of these metals could influence the availability of P, as well as contribute to P fluxes (Klotz, 1991). The interactions of PP forms and sediment geochemistry are further influenced by the presence or absence of oxygen within an aquatic environment. In oxygen-depleted environments, SRP can precipitate with Fe and calcite to form P minerals that are relatively stable (Golterman, 1995). As well, under oxygen-depleted conditions, Fe oxy-hydroxides may undergo reduction, and OP may undergo hydrolysis, increasing potential bioavailability (Golterman, 1995; Jensen et al., 1992). Alternatively, in oxygenated environments, metals, calcite and OC availability can be influenced by chemical gradients that result from the presence of biofilms (Boano et al., 2014) and P co-precipitation with calcite may be enabled via photosynthesis (Neal, 2001). Often, an interplay between abiotic and biotic controls on sediment geochemistry will influence the form and availability of PP in aquatic environments (See Figure 2.1.4).

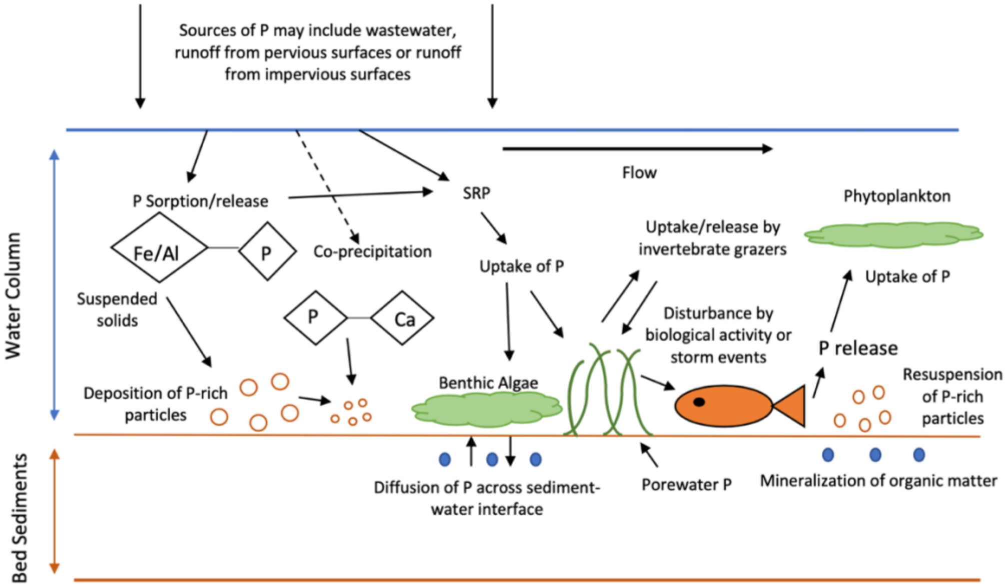

Figure 2.1.4. – Conceptual model of in-stream processes influencing P concentrations in rivers (after Withers and Jarvie, 2008).

2.1.5. Phosphorus cycling and mobility

Models of phosphorus sorption (e.g. Langmuir, Freudlich, and Temkin) are commonly used to determine the ability of sediment to buffer P from overlying water. Sediments can adsorb or desorb P from solution and the maximum adsorption capacity of sediment corresponds to the solution concentration at which neither adsorption or desorption occurs, termed the 'zero equilibrium concentration,' or EPC_0 (Froelich, 1988) (See Figure 2.1.5). To determine the EPC_0 of sediment, a standard amount of sediment is combined with a standard amount of a series of SRP solutions of known concentrations, which are then mixed for an adequate amount of time to assume equilibrium between the sediment and solution has been reached (Golterman, 2004). The amount of P adsorbed or desorbed by sediment is calculated by finding the difference between the initial and final measured concentrations of SRP, multiplying this value by the amount of solution added, and dividing this value by the weight of sediment used during analysis. The calculated amount of P adsorbed or desorbed is then plotted against initial SRP solution concentrations to create the sediment buffer diagram. Buffer diagrams are used examine the mechanistic behaviour of sediments and the slopes of these diagrams represent adsorption coefficients, with steeper slopes demonstrating greater ability to buffer P (Froelich, 1988). It is important to note that sorption characteristics can be influenced by several factors, some of which include pH, temperature, chemistry and ionic strength of solutions, as well as the ratio of sediment to solution (Lucci et al., 2010; Bhadha et al., 2012). Due to this, sorption isotherms simulated in laboratory settings cannot be considered completely accurate representations of ecosystem conditions, but rather relative proxies (Barrow et al., 1980).

Generally, in freshwater environments if P concentrations in the water column are elevated relative to the sediment EPC_0, this may lead to P uptake by sediment, whereas if P concentrations in the water column are low, and sediments are P-saturated, this may lead to a flux of P from the sediments into the water (Froelich, 1988). The abiotic uptake and release of riverine P is largely controlled by sorption and desorption reactions, as well as precipitation and dissolution reactions (Withers and Jarvie, 2008) and the transfer of phosphorus to and from sediments initially occurs rapidly and is then followed by slower-paced solid-state diffusion (Froelich, 1988; Reddy et al., 1999). However, the mobility, transport and ultimate fate of river sediment and associated P can be influenced by natural and anthropogenic landscape disturbances, which modify hydrological and biogeochemical processes, the effects of which last varying time scales depending on the geology, hydroclimatic conditions and vegetation within a watershed (Son et al., 2015; Emelko et al., 2016). The historical loading of PP into receiving waters has also been shown to create a legacy effect (Sharpley et al. 2013), with sediments releasing P during periods of reduced external P loading (Sondergaard et al., 2001). For instance, following a storm event agitation of rivers may remobilize riverbed sediment and associated PP, allowing for propagation great distances downstream (Koski-Vähälä and Hartikainen, 2001; Evans et al, 2004). Notably, the internal loading of P in the form of bioavailable orthophosphates is often the main source of P entering lakes and reservoirs during environmentally sensitive conditions in summer (Nürnberg, 2009).

The concept of internal loading of aquatic systems due to the release of P from sediment has been evaluated by determining the EPC_0 in freshwater bodies affected by various landscape disturbance (Froelich, 1988). Although the majority of these studies have focused on anthropogenic landscape disturbances, such as agriculture, urbanization and sewage treatment, among others, as opposed to natural landscape disturbances, such as wildfire. The EPC_0 of riverbed sediments vary greatly across a range of aquatic systems and in some cases, display large ranges even within the same location. For example, Son et al., (2015) analyzed the effects of wildfire on the Cache la Poudre River in Colorado, and found sediment EPC_0 to range from 300 – 1200 μg P

L^{-1}. In contrast, another study analyzing the wildfire-impacted Crowsnest River in southern Alberta reported maximum EPC$_0$ values to be 213.5 µg P L^{-1} (Emelko et al., 2016). Factors that can be used to explain the variability in EPC$_0$ of riverbed sediments include compounding land-use effects, the complexities of P sorption to particulate matter, varying sediment sources, and sediment geochemistry, among others (Stone and English, 1993; Stutter and Lumsden, 2008).

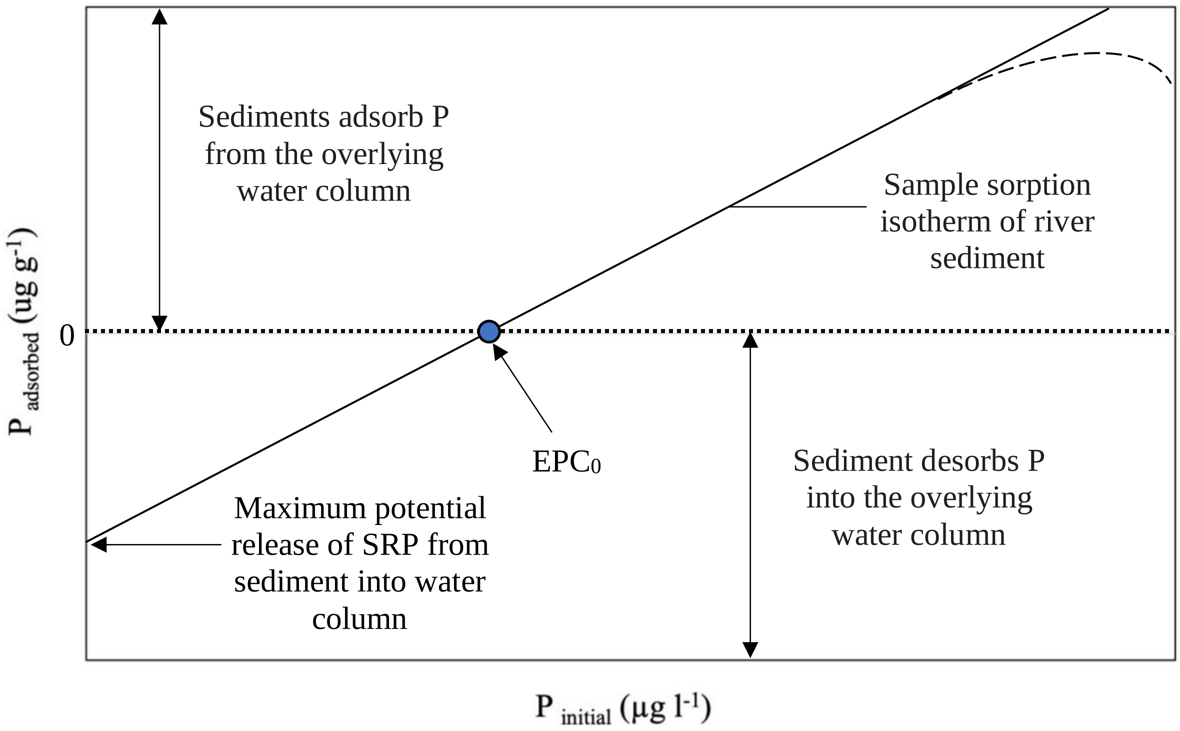

Figure 2.1.5. – Sample sorption profile of riverine sediment, where x=0 (dotted line) represents equilibrium conditions between river sediments and the overlying water column.

2.2. Current Knowledge Gaps

While the impacts of wildfire on sediment-associated P in forested rivers have received increased focus in the literature in recent years, several key research gaps remain. For instance, while it has been reported that post-fire impacts on forested water supplies can propagate downstream and last up to decades in large basins (Allin et al., 2012; Emelko et al., 2016; Silins et al., 2009; Stone et al., 2011; Stone et al., 2014), the immediate effects of high intensity wildfire on high quality gravel-bed rivers that drain glaciated mountain landscapes are poorly documented.

In particular, there is a paucity of studies on the immediate influence of wildfire on particulate phosphorus forms (NAIP, AP, OP). Further research on the storage of fine sediment in gravel-bed rivers is necessary (Karna et al., 2014). More specifically, the transport dynamics and sediment ingress rates of fire-impacted sediment in gravel bed rivers have not been documented, though these dynamics have been evaluated in flume experiments (Krishnappan and Engel, 2006). Existing research on wildfire-generated pyrogenic materials has focussed largely on hillslope environments and small-scale river channels, with some attention also focussed on runoff, erosion and water yield-related processed within catchments (Moody et al., 2013). Recent literature has also concentrated on the composition of these pyrogenic materials and its implications for downstream water quality (Bodí et al., 2014; Silins et al., 2009; Stone et al., 2014), but few studies have focussed on how the composition of pyrogenic materials vary during downstream transport and the effects this may have on water quality. While GIS models estimating spatial distribution of ash following wildfire have been developed (Chuvieco et al. 2010), they exist at a coarse resolution and do not provide insight on the transport mechanisms or fate of ash in these riverine systems, particularly at the basin-scale.

To date, one of the most significant gaps in the literature is the lack of comprehensive understanding of post-fire impacts on drinking water treatability. The ability to predict the impacts of climate change on freshwater bodies requires enhanced understanding of modelling, bench scale experiments and in-situ analysis at multiple scales (Woodward et al., 2010). Enhanced understanding of the relationship between sediment-associated P following wildfire and proliferation of toxin-forming cyanobacteria in reservoirs is also necessary, though the role of sediment as a vector for P transport and its internal loading processes in reservoirs has been more thoroughly studied (Schindler, 1977; Stone and Mudroch, 1989; Stone and English 1993). Enhanced understanding of the role of riverbeds as potential P sinks/sources would be useful to inform water management decisions in these environments (Withers and Jarvie, 2008). As environmental pressures from urbanization, agriculture and climate change-related disasters mount, there is a strong need for increased research on the interacting influences of disturbance, sediment source and composition and P propagation in freshwater systems (Sharpley et al., 2013; Stone et al., 2014)

Chapter 3

Phosphorus speciation and sediment geochemistry of fine sediment in forested gravel-bed rivers following wildfire

3.1. Abstract

Fine sediment plays an important role in influencing the form and bioavailability of phosphorus (P) within forested river systems. While many studies have analyzed particulate phosphorus (PP) dynamics in rivers affected by anthropogenic impacts, much less is known about P dynamics in forested source water regions subjected to severe natural landscape disturbance, such as wildfire. Additionally, relatively few studies have examined abiotic controls of fine sediment on PP form and concentration within gravel-bed streams in this setting. This study examines the spatial and temporal distribution of PP form (non-apatite inorganic P, apatite P, organic P, total particulate P) and major elements (Al, Fe, Mn, Mg, Ca, Na) within suspended and ingressed riverbed sediment in gravel-bed rivers following severe wildfire. River sediment from nine sites in Waterton Lakes National Park, AB and reference, (unburned) watersheds that vary in slope, connectivity and sediment source were examined following the 2017 Kenow wildfire. Sample collection occurred during environmentally sensitive summer and fall flow periods for three years immediately after the fire. Results show that NAIP and TPP concentrations were both significantly higher in burned rivers compared to unburned reference rivers and within burned rivers these concentrations were greatest in suspended sediment fractions. Elevated NAIP enrichment did not change significantly over the three years of study and was significantly higher in rivers draining burned watersheds than reference watersheds, highlighting the potential of sediment-associated PP generated from burned landscapes to have legacy effects in oligotrophic river systems. Elevated Mn concentrations were highly correlated with elevated bioavailable PP concentrations in burned sediment, which could be explained by the composition of atmospherically deposited pyrogenic materials and previous fire activity in the watershed, Differences in PP form between burned and reference sites were attributed to differences in sediment source, catchment slope and connectivity, in-stream biogeochemical processing of sediment and geochemical composition of sediment.

Keywords: wildfire, forested watersheds, gravel-bed rivers, fine sediment, particulate phosphorus form, major element sediment geochemistry

3.2 Introduction

Forests cover approximately four billion hectares of total global landmass (FAO, 2020). These landscapes are significant source water regions that supply high-quality drinking water for domestic, agricultural, industrial and ecological needs. This is largely due to the ability of forests to naturally store and filter water supplies, as well as the fact that they are often situated in regions with high annual precipitation and can produce large amounts of runoff with relatively low sediment and associated contaminant concentrations (Bladon et al., 2014). The value of the natural storage and filtration of water supplies in forests is estimated to be over $4 trillion annually (Costanza et al., 1997) and the naturally high quality of these water supplies significantly reduces the costs of additional water treatment and infrastructure (Bladon et al., 2014). Due to the high quality of these water supplies, forested landscapes are particularly vulnerable to the effects of both anthropogenic and natural disturbance. In many forested areas, wildfire is the dominant landscape disturbance (Weber and Flannigan, 1997) and the frequency and severity of wildfire occurrence will increase due to climate change in many areas across the globe (Flannigan et al., 2005). While wildfire is a naturally occurring phenomenon necessary for the maintenance of forested watersheds and associated aquatic ecosystems (Bladon et al., 2014), severe wildfires can have devastating and potentially long-lasting effects on these systems (Emelko et al., 2016). Severe landscape disturbance by wildfire, can drastically reshape valuable forested source water regions by modifying regional hydrologic regimes and accelerating inputs of pyrogenic solids and associated contaminant fluxes to receiving waters (Silins et al., 2009; Emelko et al., 2011; Bladon et al., 2014).

There is increasing awareness of the effects of wildfire on nutrient loading to surface waters in a range of landscapes across the globe (Smith et al., 2011). Nutrients such as phosphorus are predominantly bound to and transported by fine sediment (McDowell and Sharpley, 2001). After wildfire, mobilization of fine sediment during runoff can accelerate transport from hillslopes to receiving waters (Stone and English; 1993; Evans et al., 2004). Many studies have reported the enrichment ratio (ER) of P on fine sediment to be high (Stone and English, 1993; Stone et al., 1995; Stutter and Lumsden, 2008; Lane et al., 2011) and this has been attributed to the greater specific surface area and metal oxyhydroxide coatings typically associated with this fine sediment fraction (Evans et al., 2004; Stone and English., 1993; Stone and Mudroch, 1989). Inorganic forms of phosphorus tend to strongly interact with the surfaces of solids, particularly those containing metal oxyhydroxides of Al, Fe and Mn within their complexes (House et al., 1995). The geochemical controls on the form and availability of sediment-associated P can vary between catchments and environmental conditions such as redox (Records et al., 2016). Redox conditions largely drive the binding of P to Fe and Mn (Evans et al., 2004), though in alkaline systems, Ca and Mg have been shown to be more significant drivers of P binding to sediment (House and Denison, 2000). The chemical composition and mineralogy of sediment are two of the main controls on the ability of phosphate to adsorb to particles (Stone and Mudroch, 1989) and in gravel-bed streams, more research is necessary to further understand abiotic controls on the regulation of PP form by fine sediment.

The amount of particulate phosphorus (PP) in aquatic systems is controlled by factors such as regional geology and geomorphology, varying sediment sources, water chemistry and transformations of PP forms in downstream reaches (Stone and Mudroch, 1989; Withers and Jarvie, 2008; Records et al., 2016). Phosphorus inputs from point and nonpoint sources may accumulate in several locations in the land-freshwater continuum, where they may then be remobilized or recycled (McDowell et al., 2002; Sharpley et al., 2013). Since fine sediment has a low settling velocity, P bound to these particles can be transported large distances downstream in rivers (Haralampides et al., 2003), though due to the dynamic nature of sediment geochemistry, the availability of PP has been shown to fluctuate during transport (Withers and Jarvie, 2008). For instance, bedload transport is a significant mode of P transport in rivers (Keup, 1968) and riverbed sediment plays an important role in regulating soluble reactive phosphorus (SRP) concentrations in the water column, especially during low flow conditions (Froelich, 1988; Stone and Mudroch, 1989; Jarvie et al., 2005). Fine sediment may also become ingressed within gravel riverbeds (Karna et al., 2014), potentially acting as legacy sources of P (Jarvie et al., 2005; Emelko et al., 2016). When these rivers experience high flow events, sufficient bed shear stresses can mobilize the gravel-bed armour layer and release fine sediment and PP into the water column (Evans et al., 2004). Release of SRP by desorption from ingressed sediment stored in gravel-bed rivers is an important mechanism for increasing P bioavailability, particularly at large river basin scales where increased channel bed area can provide increased fine sediment storage in the riverbed (Emelko et al., 2016). In rivers with less flashy hydrologic regimes, increased in-stream processing and longer retention and residence times of PP may occur (Basu et al., 2011), demonstrating the highly dynamic nature of sediment and PP regimes within river systems.

Phosphorus is the limiting nutrient for primary productivity in freshwater systems and is integral to the health of river ecosystems (Schindler, 1977; Bennett et al., 2001; McDowell, 2015). Changes in the form, concentration and availability of PP in these systems has implications for eutrophication; a condition of excess nutrient concentrations that leads to nuisance algal blooms (Correll, 1998; Withers and Jarvie, 2008). Eutrophication is one of the most widespread water quality issues affecting surface freshwater bodies in North America (Smith and Schindler, 2009). Eutrophic waterbodies typically experience a shift toward cyanobacterial dominance (Pick, 2006; Skei et al., 2000; Smith et al., 2011) and this is associated with increased risk of harmful algal blooms (HABs), which are cyanobacterial blooms containing toxic microcystins (Heisler et al., 2008). In addition to challenges to water security and treatability of valuable source water supplies, HABs may result in altered aquatic community structures, changes in dominant species and losses of biodiversity (Anderson et al., 2002). Eutrophication is of particular concern in oligotrophic rivers, since these high-quality systems are especially vulnerable to altered nutrient concentrations and biotic uptake, particularly following disturbance by wildfire (Bladon et al., 2014).

Within the existing phosphorus speciation literature, emphasis has been directed towards quantifying anthropogenic impacts, such as agriculture, sewage inputs and urbanization. While multiple studies have reported the effects of wildfire on river systems (e.g. Beaty, 1994; Hauer and Spencer, 1998; Earl and Blinn, 2003; Spencer et al., 2003; Townsend and Douglas, 2004; Burke et al., 2005; Mast and Chow, 2008; Blake et al., 2010; Noske et al., 2010; Santos et al., 2015; Son et al., 2015) and additionally some studies have focussed on the effects of wildfire on high quality river systems in southern Alberta (Stone et al., 2011; Allin et al., 2012; Bladon et al., 2014; Stone et al., 2014; Emelko et al., 2016, Watt et al., 2021), most studies occur several years after the occurrence of wildfire and cover relatively small geographic areas. The present study examined phosphorus fractionation, sediment geochemistry and particle size in burned and unburned gravel-bed river sediment following the 2017 Kenow wildfire. Based on the results of earlier work (e.g. Emelko et al., 2016; Watt et al., 2021), it was hypothesized that forested rivers systems subjected to wildfire would contain elevated concentrations of fine sediment-associated PP, particularly bioavailable PP forms (NAIP), compared to unburned reference rivers. Moreover, it was also expected that these bioavailable PP forms would correlate with physical and geochemical properties of river sediment, such as particle size and Fe, Al, and Mn concentrations (Stone and Mudroch, 1989; Stone and English, 1993; Owens et al., 2005). Finally, it was hypothesized that upstream sites would have higher concentrations of PP than downstream sites due to connectivity with burned landscapes and that lower PP concentrations would be a function of distance from burn, as well as time since the burn. Accordingly, the primary goal of this research was to examine abiotic controls on fine sediment-associated PP forms in the critical forested source water region located in Waterton Lakes National Park, AB, Canada.

Specific objectives of this study include:

1. Evaluate the spatial and temporal variation of sediment-associated PP forms (NAIP, AP, OP) in reference and wildfire-impacted rivers.
2. Evaluate relationships between PP form and the physical and geochemical properties of river sediment following wildfire.
3. Discuss the implications of wildfire-related fine sediment and nutrient inputs on water quality and water treatability.

3.3. Methods

3.3.1. Site Description

Waterton Lakes National Park (WLNP) has an area of 505km^2 and is located on the eastern slopes of the Rocky Mountains, on the borders of southwestern Alberta, southeastern British Colombia and northern Montana. The park is located within the Crown of the Continent biosphere, and contains 4 distinct ecoregions; Foothills Parkland, Montane, Subalpine and Alpine, which are characterized by variable altitudes and dominant plant communities (Parks Canada, 2018a). The Foothills Parkland and Montane ecoregions are distinguished by their highly productive and biotically diverse stream valleys and riparian woodlands, which are also highly sensitive to disturbance (Parks Canada, 2018a). There are forty-five types of vegetation identified within the WLNP, 16 of which have been classified as rare or threatened (Parks Canada, 2018a).

The climate in this region is continental and generally moist, mild and windy (Coen and Holland, 1976; Parks Canada 2018a). Chinooks, or prevailing warm, westerly winds are common in this area of southern Alberta (Coen and Holland, 1976). WLNP has the highest average annual precipitation in Alberta at 1072mm, most of which falls as snow (Parks Canada, 2018a). Peak monthly precipitation in the park has historically occurred in June (Coen and Holland, 1976). The abundant rain and snowmelt that falls east of the continental divide flows east through two main watersheds within WLNP (Parks Canada, 2018c).

Land surface within WLNP is highly variable, and includes outwash plains, alluvial fans and mountain ranges, with elevations that range from 985 – 3150 m (Coen and Holland, 1976; Parks Canada 2018b). The underlying geology of the area is predominantly marine Purcell Supergroup sediment (1.5Ma), which consists of argillite, carbonate and dolomite formations with minor stromatolite-bearing sections (Parks Canada, 2018b). Mountain building in the area occurred through the overlapping of tilted thrust sheets and resulted in the Lewis overthrust, which is a single overlap that laterally placed Proterozoic sediments atop Cretaceous schists (Parks Canada, 2018b). This process was followed by glaciation, the most recent of which was the Wisconsin glaciation, which reached maximum extent in North America 25,000 – 21,000 years before present. The current landscape of the park includes glacial features such as hanging valleys, arêtes, glacial troughs, cirques, eskers, kames and kettles, among others (Hauer et al., 1997; Parks Canada, 2018b). Glacial-derived surface deposits include sands, silts, clays and gravels (Parks Canada, 2018b). The soils of the park form above porous glacial till and this along with the relatively steep topography of area allow for relatively good drainage throughout most of the park (Coen and Holland, 1976; Parks Canada, 2018b).

The Waterton Lakes Chain is comprised of over 100 km of rivers and streams, as well as nearly 80 lakes and ponds, including the Upper, Lower and Middle Waterton Lakes and the Maskinonge Lake, which together represent nearly two thirds of the total water surface area in WLNP (Parks Canada, 2018c). This chain empties into the Waterton River, which drains a significant portion of the park and which along with the Belly River eventually flows through the Boreal Forests and into Hudson’s Bay (Parks Canada, 2018c). Waters draining mountains within the park are typically oxygen-rich and nutrient-poor, with average temperatures below 15^{o}C (Parks Canada, 2018c). These conditions result in rivers within the park having low abundance of aquatic plant life, but relatively high aquatic diversity, with many species of bacteria, insects, plankton and fish having been observed (Parks Canada, 2018c).

2017 Kenow Wildfire

The Kenow wildfire was caused by lightning during a storm on August 30th, 2017, approximately 10km west of WLNP (Parks Canada, 2019). The fire moved rapidly due to dry, hot weather conditions and strong winds and entered WLNP on September 11th. The fire moved northeast along the Cameron Valley, until it was controlled on October 3rd, 2017 (Parks Canada, 2019). The Kenow wildfire was extremely severe, burning a nearly contiguous area of over 35,000 ha, 9,000 ha of which was within WLNP, representing 38% of park surface area. The drainage networks of the Cameron and Blakiston rivers were severely affected by the Kenow Wildfire, with extensive areas of soil and pyrogenic materials in near-stream riparian areas being exposed post-fire.

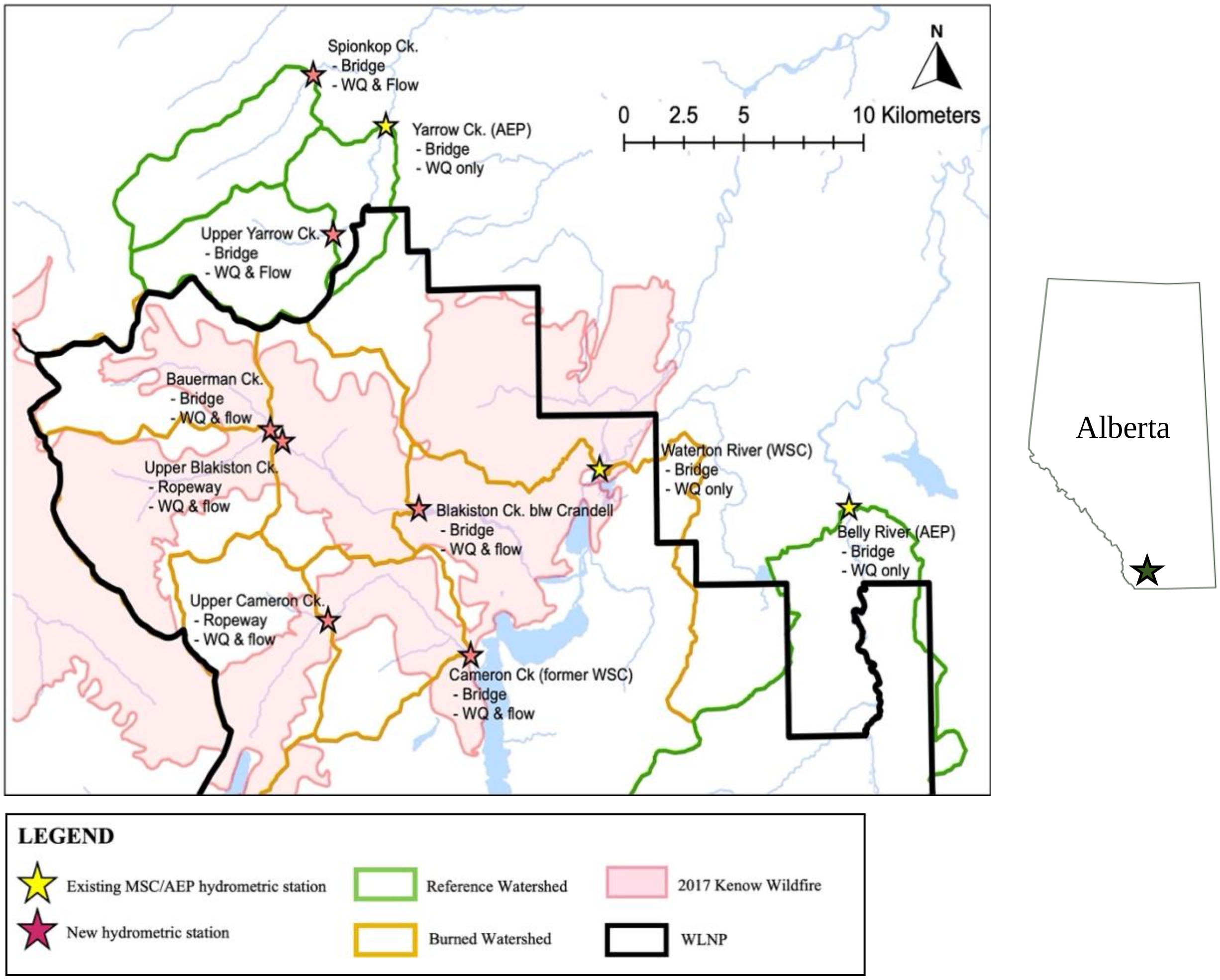

Figure 3.3.1. – Map of study area (Modified from Dr. U. Silins of the University of Alberta).

3.3.2. Sampling Design

The goal of this research was to collect and characterize fine sediment in burned rivers in WLNP (Blakiston River, Bauerman River, Cameron River and Waterton River) and unburned reference rivers in surrounding areas (Yarrow River, Spionkop River and Belly River) (Tables 3.3.2a and 3.3.2b) in the three years immediately following the 2017 Kenow wildfire. Of the four burned rivers, two were analyzed at upstream and downstream segments to better understand the spatial effects of wildfire (Cameron River and Blakiston River). Within the park, two major river continuums were analyzed, the first of which originates at the Bauerman and Upper Blakiston Rivers, flows through the lower Blakiston River and empties into lower Waterton Lake. The second continuum extends from the upper to the lower Cameron River before emptying into upper

Waterton Lake. Both continuums flow through the Waterton Lakes chain and into the Waterton River, which along the Belly River represent the two main outflow sources in the park. All river sites in the study displayed varying characteristics in terms of slope, landscape-stream connectivity and vegetation (Table 3.3.2c).

Table 3.3.2a. – Characteristics of burned sampling sites.

Basin Scale	Station Status	Station Type	Area (km^2)			% Burned
			Unburned	Burned	Total	
Small						
Bauerman	New	Bridge	23.9	15.5	39.4	39.4
Upper Blakiston	New	Ropeway	12.9	36.1	49.1	73.6
Upper Cameron	New	Ropeway	26.8	19.3	46.2	41.9
Medium						
Blakiston	New	Bridge	50.3	84.6	135.0	62.7
Cameron	New	Bridge	43.3	36.1	79.4	45.5
Large						
Waterton R.	Existing	Bridge	448.3	163.9	612.2	26.8

Table 3.3.2b. – Characteristics of reference sampling sites.

Basin Scale	Station Status	Station Type	Area (km^2)
Small			
Upper Yarrow	New	Bridge	29.2
Spionkop	New	Bridge	26.0
Yarrow	Existing	Bridge	46.8
Large			
Belly River	Existing	Bridge	325.7

Table 3.3.2c. – Sampling site descriptions.

Site ID	**River**	**Characteristics**
UC	Upper Cameron River	Within 'V"-shaped valley, riparian zones extend directly to banks, close proximity to mountains
LC	Lower Cameron River	Within 'V"-shaped valley, more deeply incised than upstream section, riparian zones extend directly to banks, close proximity to mountains
UB	Upper Blakiston River	Within "U"-shaped valley, large gravelly floodplains and large mid-channel sediment bars, close proximity to vegetation
LB	Lower Blakiston River	Within "U"-shaped valley, more deeply incised than upstream section, large gravelly floodplains and close proximity to vegetation
Ba	Bauerman River	Northernmost burned river, riparian zone extends directly to very shallowly incised banks, large mid-channel boulders
W	Waterton River	Most downstream burned river, low sinuosity, shallowly incised banks, some sediment bars
Y*	Yarrow River	~30km north of WLNP, collects drainage from northern slopes of mountains near northern edge of park boundary, moderate sinuosity
S*	Spionkop River	~30km north of WLNP, pastureland for cattle and bison
B*	Belly River	~20km east of WLNP, within Blood Tribe First Nations Reserve, ~20m in width, relatively low sinuosity, variable incision of banks

Suspended sediment samples were collected with Phillips samplers, which represent a passive form of time-integrated sediment sampling that is commonly used to characterize fine sediment-associated contaminants and is a useful methodology for collection within remote areas (Phillips et al., 2000) (Figure 2.2.1). Phillips samplers were deployed in the upstream and downstream reaches of the Cameron and Blakiston rivers and a single Phillips sampler was deployed in accessible portions of the Bauerman and Waterton rivers, as well as the unburned reference rivers (Yarrow, Spionkop and Belly rivers) (Tables 3.3.2b and 3.3.2c). Sample collection occurred each year during summer and fall low flow conditions (July-August and October-November, respectively) from 2018 to 2020, with a final round of sampling scheduled to occur in May-June 2021. Suspended sediment samples were emptied into clean plastic containers where the fines were left to settle for two days. Following this, the supernatant water was siphoned off and the sediment slurry was transferred to Ziplock bags, which were then frozen and shipped to the University of Waterloo, where they remained frozen in storage until analysis.

Samples of ingressed sediment were also collected from burned river sites in triplicate during the fall 2018 sampling campaign using the Lambert and Walling, 1988 technique, which utilizes a cylinder that is randomly inserted into the gravel-bed river. Fine sediments were manually suspended by disturbing the ingressed materials contained within the cylinder with a plastic rod. A bilge pump was then used to collect the sediment-water mixture and transfer it into a clean container, which was left undisturbed to settle for two days before the overlying water was siphoned out. The remaining mixture was transferred to Ziplock bags, frozen and shipped to the University of Waterloo. Samples were sieved and the fine sediment fraction (< 250 μm) was stored for phosphorus speciation and geochemical analysis.

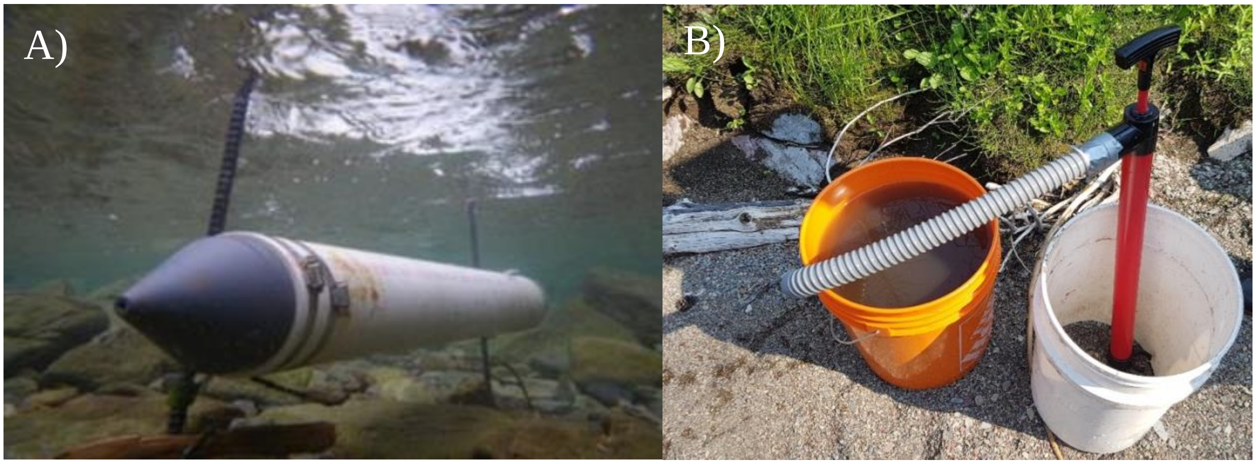

Figure 3.3.2. – Phillips sampler for the collection of suspended solids (A) and the Lambert and Walling, 1988 technique for the collection of ingressed solids (B) (Source: Dr. M. Stone).

3.3.3. Laboratory Analysis

Particulate phosphorus fractionation

Particulate phosphorus fractionation was characterized using a commonly utilized sequential extraction scheme (Pettersson and Istvánovics, 1988; Stone and English, 1993) which involves removing phosphorus fractions from sediment in order of decreasing bioavailability using various extractants. The most bioavailable PP form, non-apatite inorganic P (NAIP) is removed first using 3 extractants; 25mL of 1.0M NH_4Cl to remove the most easily desorbable phosphorus over two periods of two hours, 25mL of 0.1M bicarbonate-dithionite (DB) to remove reductant-soluble phosphorus that is bound to iron over thirty minutes at 40ºC, and lastly 25mL of 1.0M NaOH to remove reactive phosphorus that is bound to calcium and magnesium metal-oxides over sixteen hours (Stone and English, 1993). Total NAIP is the sum of these three NAIP constituents and this form is most bioavailable due to the ability of phosphate (PO_4^{3-}) to desorb readily from the surface of sediment into the overlying water column (DePinto et al., 1981; Jarvie et al., 2002; House, 2003). Apatite P (AP), or mineral-bound P is then removed using 25mL of 0.5M HCl over twenty-four hours (Stone and English, 1993). Organic P (OP) is unreactive or refractory P and is measured last using 25mL of 1.0M NaOH over twenty-four hours at 85ºC (Stone and English, 1993). Total particulate phosphorus (TPP) is calculated by summing NAIP, AP and OP and the enrichment factor of NAIP is found by dividing NAIP by TPP.

Geochemistry and physical characteristics of sediment

Major element sediment geochemistry (Al, Fe, Mn, Mg, Ca, Na and K) was measured using inductively coupled plasma-optical emission spectrometry (ICP-OES) and reported as percent dry weight. Quality control was ensured through random duplicate analysis of samples (See Appendix B). The particle size characteristics and geochemical composition of suspended and ingressed river sediment were evaluated at a commercial laboratory (Act Labs, Hamilton, ON) using standard methods. A Malvern Mastersizer 2000 was used to measure particle size distributions (D_{10} and D_{90}, which represent grain diameters of which 10% and 90% of particles are smaller than, respectively), median diameter (D_{50},), and specific surface area (SSA), assuming spherical particles.

3.3.4. Statistical Analyses

SPSS (SPSS 21, IBM Corp., 2012) was used to sort and analyze the data by site (including upstream and downstream portions of the same river), year, watershed and status (burned versus unburned). Results of P-P and Q-Q plots, as well as Shapiro Wilks normality tests indicated that the data failed to meet the assumptions for normality ($p > 0.05$) in all cases, though normality of residuals was achieved when splitting the file by status. Due to the failure of the data to meet assumptions of normality, non-parametric tests Kruskal-Wallace rank sum tests and Mann-Whitney rank sum tests were conducted to determine if differences in PP form, sediment geochemistry and particle size characteristics of sediment were significantly different across and within river sites, year of sampling, watershed and status, as well as between suspended versus ingressed sediment for 2018 samples from burned sites.

Stepwise linear regression was conducted in SPSS to examine geochemical controls on PP form in WLNP and reference rivers. Stepwise regression is an iterative regression model that successively adds and removes explanatory variables from a model, testing for statistical significance with each alteration. To conduct stepwise regression, PP forms and major elements were standardized to determine relative importance of parameters (beta values). A variation inflation factor (VIF, 1/(1 -R)) was used to distinguish variables that lacked multicollinearity, which would be included in the model. While different acceptable VIF thresholds have been reported in the literature, VIF values < 10 are generally used to indicate acceptable levels of multicollinearity (Graham, 2003). All variables included in the model had VIF values < 2. Linear Discriminant Analysis (LDA) was also conducted in SPSS to analyze the differences between PP forms between the two burned watersheds in the study, as well as to determine the number of dimensions that could explain these differences. All variables included in the model had VIF values < 2.5. Finally, non-parametric Spearman's rank correlation coefficients were calculated to examine relationships between concentrations of PP forms and major elements, as well as aid in interpretation of regressions with reduced parameters. For all statistical analyses conducted in this study, results were deemed to be statistically significant if $p < 0.05$.

3.4. Results

3.4.1. Spatial variation in riverine phosphorus following wildfire

The spatial variation of PP in river sediment following the Kenow wildfire is illustrated in Figure 3.4.1a. While there was no statistically significant difference in OP concentrations between sites, the most bioavailable P fraction, NAIP, was significantly higher in burned sites compared to reference sites ($H (1) =10.80$, $p = 0.001$). TPP concentrations were also significantly higher in burned sites than reference sites (H (1) = 4.31, pp = 0.038). The highest TPP concentration was measured at the Upper Blakiston site (949.5 $\mu g/g_{sediment}$ ± 117.7 $\mu g/g_{sediment}$), while the lowest TPP concentration was recorded at the Yarrow River site (386.7 $\mu g/g_{sediment}$ ± 179.4 $\mu g/g_{sediment}$), both within the suspended sediment fractions. Conversely, AP concentrations were significantly higher in reference sites than burned sites (H (1) = 7.33, p = 0.007). PP concentrations were also compared at the upstream and downstream reaches of the Cameron and Blakiston rivers. Over the three years of study, there were no significant differences in mean concentrations of any PP form between upper and lower reaches of the Cameron River, though TPP concentrations were found to be significantly higher at the upper Cameron site (H (1) = 3.01, p = 0.083). No significant differences in PP concentrations were observed between the upper and lower reaches of the Blakiston rivers, though AP concentrations were observed to be significantly higher in the Blakiston watershed (H (1) = 4.59, p = 0.032) compared to the Cameron watershed. When comparing the two reference watersheds, NAIP and TPP concentrations were both significantly higher in the northern reference watershed than the eastern watershed (H (1) = 5.55, p = 0.019 and H (1) = 3.40, p = 0.065, respectively).

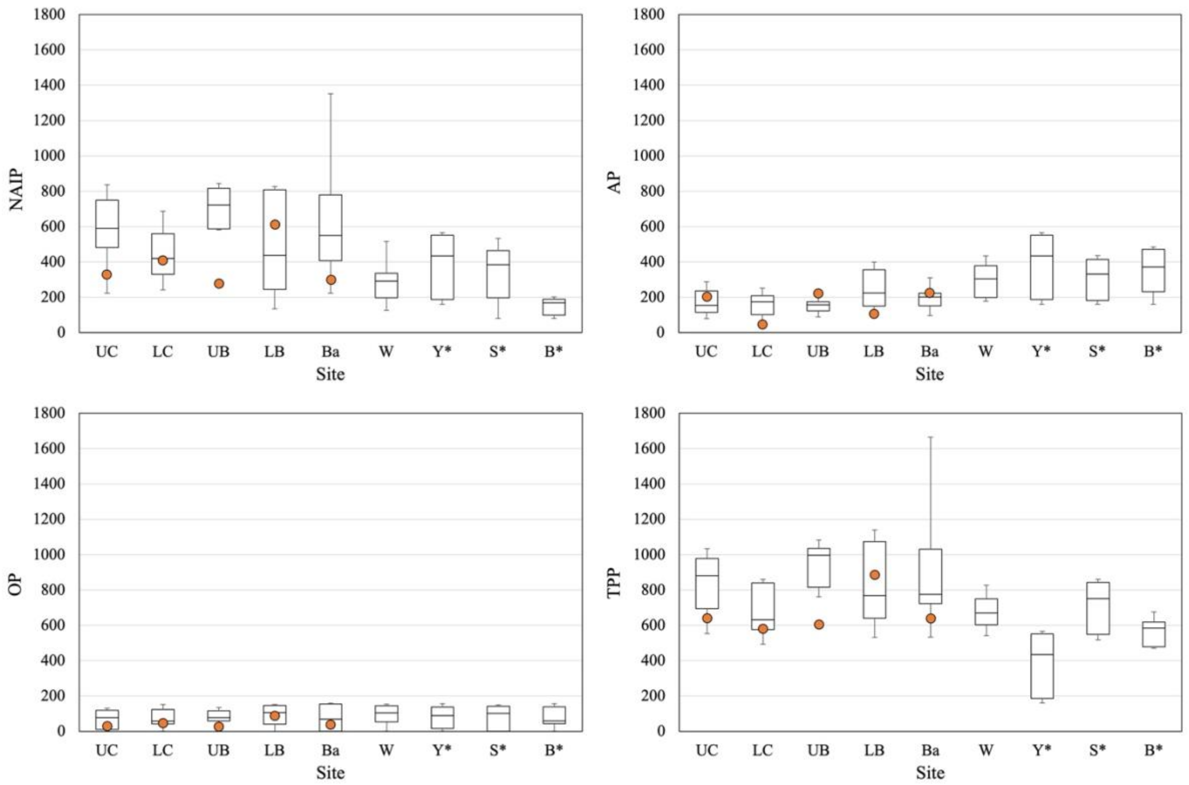

Figure 3.4.1a. – Boxplots of PP forms in suspended sediment (n=8 for UC, n=6 for LC, n=7 for UB, n=6 for LB, n=7 for B, n=10 for W, n=8 for Y*, n=7 for S*, n=7 for Y*) with mean PP forms in deposited sediment (n=1 per site, in triplicate) values represented by orange circles for 2018 to 2020.

The spatial variation of mean PP in suspended and ingressed river sediments following the Kenow wildfire are presented in Table 3.4.1a. There were statistically significant differences in all major PP forms between suspended and ingressed sediment. NAIP and TPP were both significantly higher suspended sediment (H (1) = 11.90, p = 0.001 and H (1) = 11.15, p = 0.001, respectively), while AP and OP were significantly higher in ingressed sediment (H (1) = 6.21, p = 0.013 and H (1) = 16.00, $p < 0.001$, respectively). NAIP enrichment factors were calculated (Appendix A, tables A2a a-c) and NAIP enrichment was higher in suspended sediment across all sites, except the Lower Cameron and Lower Blakiston sites, where they were similar. The highest NAIP enrichment was observed at the Upper Cameron, Upper Blakiston and Bauerman sites.

The spatial variation of mean NAIP concentrations in suspended and ingressed river sediments following the Kenow wildfire are presented in Table 3.4.1b. No significant differences were found among NAIP fractions and in nearly all sites in both suspended and ingressed sediment fractions, NaOH-RP concentrations were highest and NH_4Cl-RP concentrations were lowest. The exception to this was the suspended sediment fraction at the Waterton River site, where BD-RP concentrations were highest and NH_4Cl-RP concentrations were lowest.

Table 3.4.1a. – Spatial distribution of mean (± standard deviation) of particulate phosphorus forms ($\mu g/g_{sediment}$) in suspended and bed sediment fractions from Waterton Lakes National Park study rivers and nearby reference rivers from 2018-2020. Reference rivers are indicated with *.

	Site	**NAIP**	**AP**	**OP**	**TPP**
Suspended Sediment	UC n=8	593.14 ±193.18	173.24 ±71.99	70.76 ±52.48	837.13 ±169.45
	LC n=6	441.20 ±152.19	161.65 ±66.81	72.86 ±52.91	675.71 ±142.33
	UB n=7	719.20 ±102.60	151.09 ±37.18	79.22 ±44.55	949.51 ±117.70
	LB n=6	486.52 ±279.87	242.60 ±111.49	94.01 ±60.02	823.13 ±232.39
	Ba n=7	623.30 ±362.81	195.97 ±66.82	82.12 ±68.16	901.39 ±367.92
	W n=10	281.03 ±111.57	295.10 ±95.92	94.51 ±59.51	670.64 ±91.73
	Y* n=8	386.73 ±179.36	386.73 ±179.36	84.11 ±61.33	386.73 ±179.36
	S* n=7	329.60 ±164.50	304.86 ±110.81	81.75 ±61.58	716.21 ±135.64
	B* n=7	149.47 ±46.07	338.86 ±124.31	81.91 ±56.88	570.24 ±73.56
Ingressed Sediment (n=1)	UC	358.27	242.00	60.80	661.07
	LC	436.00	89.95	77.05	603.00
	UB	308.37	260.00	57.53	625.90
	LB	633.30	148.00	118.00	899.30
	Ba	328.45	262.00	68.75	659.20

Table 3.4.1b. – Spatial distribution of mean (± standard deviation) of particulate NAIP forms ($\mu g/g_{sediment}$) in suspended and bed sediment fractions from Waterton Lakes National Park study rivers and nearby reference rivers from 2018-2020. Reference rivers are indicated with *.

	Site	**NH_4Cl-RP**	**BD-RP**	**NaOH-RP**
Suspended Sediment	UC n=8	39.64 ±31.71	136.24 ±82.80	432.13 ±114.01
	LC n=6	17.55 ±4.31	133.85 ±52.96	301.50 ±103.63
	UB n=7	52.20 ±38.27	239.29 ±72.97	427.71 ±55.72
	LB n=6	24.60 ±8.35	229.35 ±172.14	244.87 ±113.58
	Ba n=7	56.87 ±34.15	198.21 ±80.38	400.71 ±273.23
	W n=10	52.55 ±25.39	148.24 ±71.30	122.28 ±32.69
	Y* n=8	44.93 ±29.61	103.40 ±55.51	249.63 ±113.37
	S* n=7	44.83 ±37.26	97.47 ±44.53	206.51 ±96.33
	B* n=7	23.70	57.13 ±22.52	88.96 ±31.12
Ingressed Sediment (n=1)	UC	0.00	100.27	258.00
	LC	13.00	136.50	293.00
	UB	0.00	96.63	211.73
	LB	20.30	222.00	391.00
	Ba	19.40	118.25	200.50

Linear discriminant analysis (LDA) was conducted to determine which PP forms best explained the variance observed among the different watersheds within the study area across the three years of study (Figure 3.4.1b and Table 3.4.1c). Two river continuums were examined, including the river reach extending from the upper Blakiston and Bauerman River sites to the Waterton River site (Figure 3.3.1 and Table 3.2.3c) and the river reach extending from the upper Cameron to the lower Cameron River site. The results of this analysis for the Blakiston River continuum show that ~98% of variance between sampling sites was explained by the standardized function 1.29*OP + 1.18*AP – 0.42*NAIP and therefore most variance was captured by OP and

AP. An LDA for the Cameron River watershed was also conducted, the results of which determined that 100% of variance in PP form within this watershed was explained by the standardized function 1.45*NAIP + 1.46*OP – 0.08*AP, demonstrating the majority of the variance within this watershed was captured by NAIP and OP. The prevalence of OP in capturing variance in both river continuums may demonstrate the important role of atmospheric pyrogenic materials in burned watersheds following wildfire.

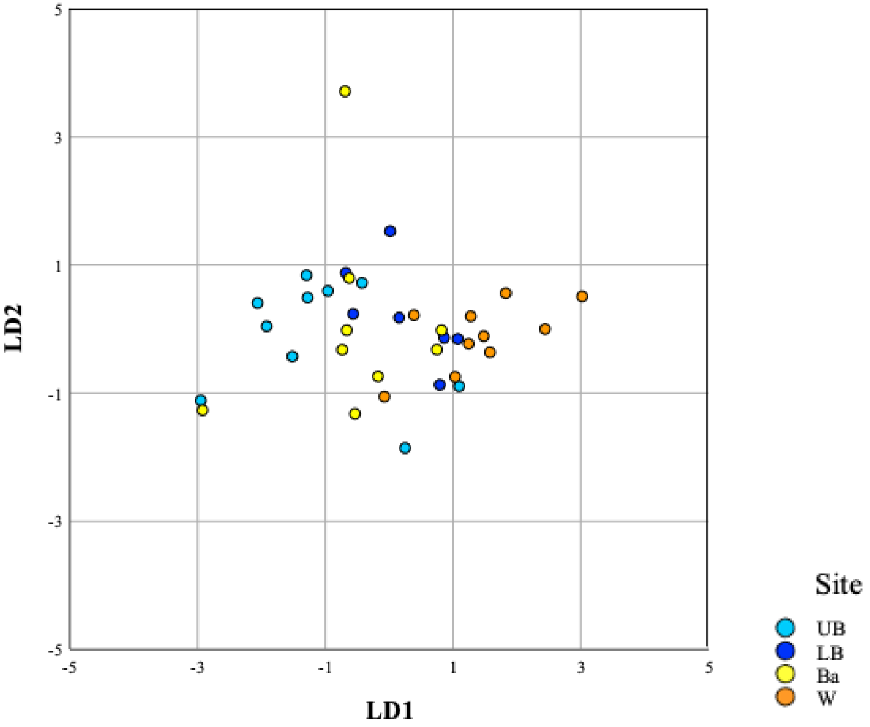

Figure 3.4.1b. – First two components of LDA of suspended and ingressed sediment from UB, LB, Ba and W rivers from 2018-2020 (n=36) with all PP variables satisfying a VIF threshold of < 2.5 to avoid issues of multicollinearity.

Table 3.4.1c. – Linear discriminant components of suspended and ingressed sediment from the Blakiston river watershed (UB, LB, Ba, W) from 2018-2020 (n=36). PP variables included in the model satisfied a VIF < 2.5 to minimize issues of multicollinearity.

	LD1	**LD2**	**LD3**
NAIP	-0.42	1.05	0.77
AP	1.18	0.82	0.93
OP	1.29	0.65	-0.50
% Variance Explained	97.9	1.9	0.2
Cumulative % Variance Explained	97.9	99.8	100

3.4.2. Temporal variation in riverine phosphorus following wildfire

The temporal variation in mean PP of river sediments across all sites are presented in Figure 3.4.2a. All PP forms analyzed were found to have varied significantly between the three years of sampling. While TPP concentrations were not significantly different from 2018 to 2019, they were significantly higher in 2019 than 2020 (H (1) = 9.42, p = 0.002). AP concentrations were significantly higher in 2019 than 2018 (H (1) = 15.98, p < 0.001), though no significant differences were observed from 2019 to 2020. OP concentrations were significantly higher in 2019 compared to 2018 and 2020 (H (1) = 21.93, p < 0.001 and H (1) = 25.45, p < 0.001, respectively). By 2020, OP concentrations were essentially negligible in all rivers. No significant differences in NAIP concentrations were observed between 2018 and 2019 or 2019 and 2020. While differences were not statistically significant, mean NAIP and TPP concentrations across all sites decreased from 2018 to 2020.

The temporal variation of mean NAIP concentrations of river sediments across all sites are presented in Figure 3.4.2b. While there were no statistically significant differences from 2018 to 2020, some patterns did emerge. Across nearly all sites in all three years of analysis, NaOH-RP concentrations were highest and NH_4Cl-RP concentrations were lowest. The exception to this was the Waterton River site in 2018 and 2019, where BD-RP concentrations were highest and NH_4Cl-RP concentrations were lowest. NH_4Cl-RP concentrations across all sites decreased from 2018 to 2019 and further decreased from 2019 to 2020, when concentrations were essentially negligible in all sediment.

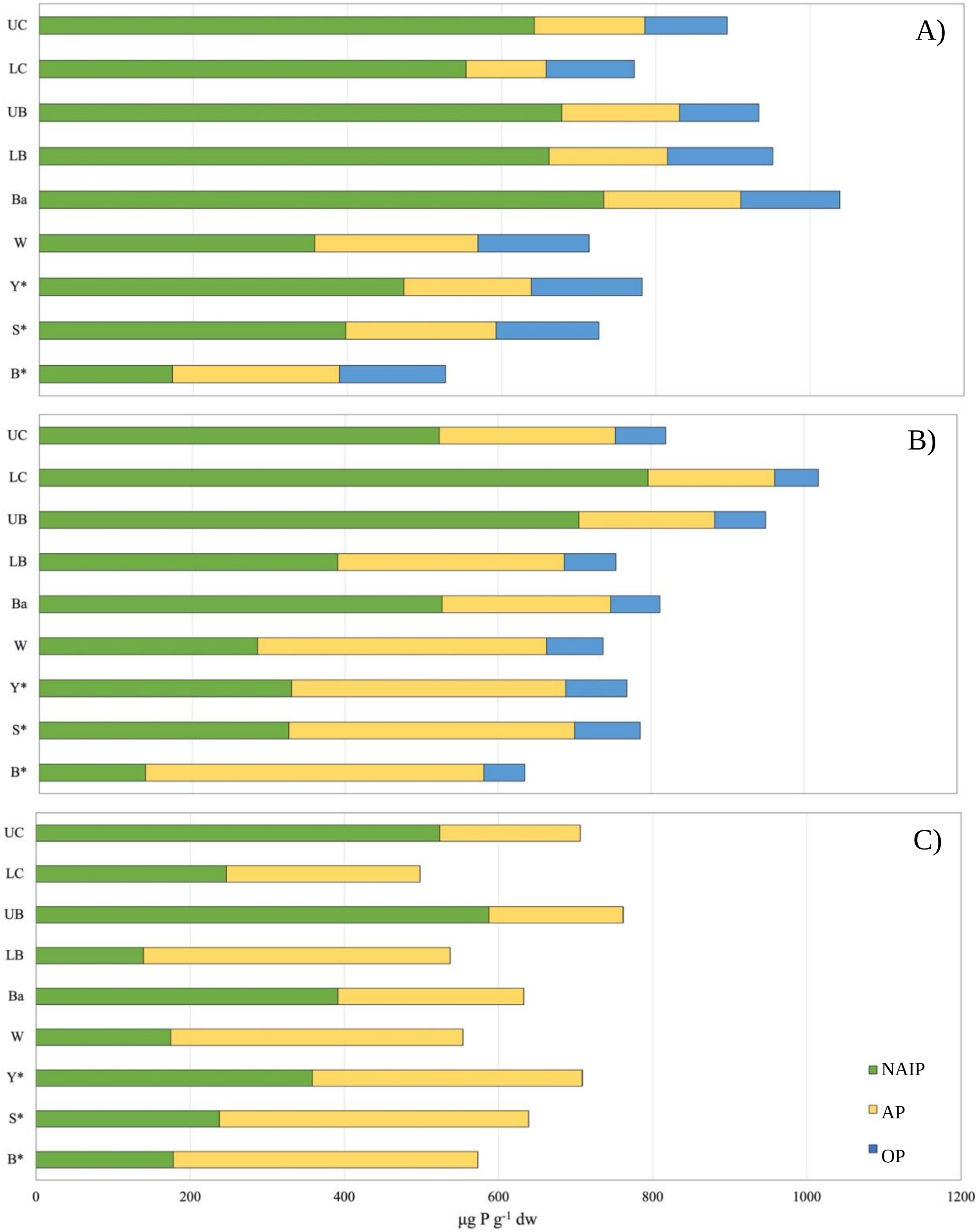

Figure 3.4.2a. – Comparison of sediment-associated PP forms in burned WLNP rivers and unburned reference rivers A) 2018 B) 2019 and C) 2020. Data are composite mean values that include all sampling periods during each year for both suspended and ingressed sediment.

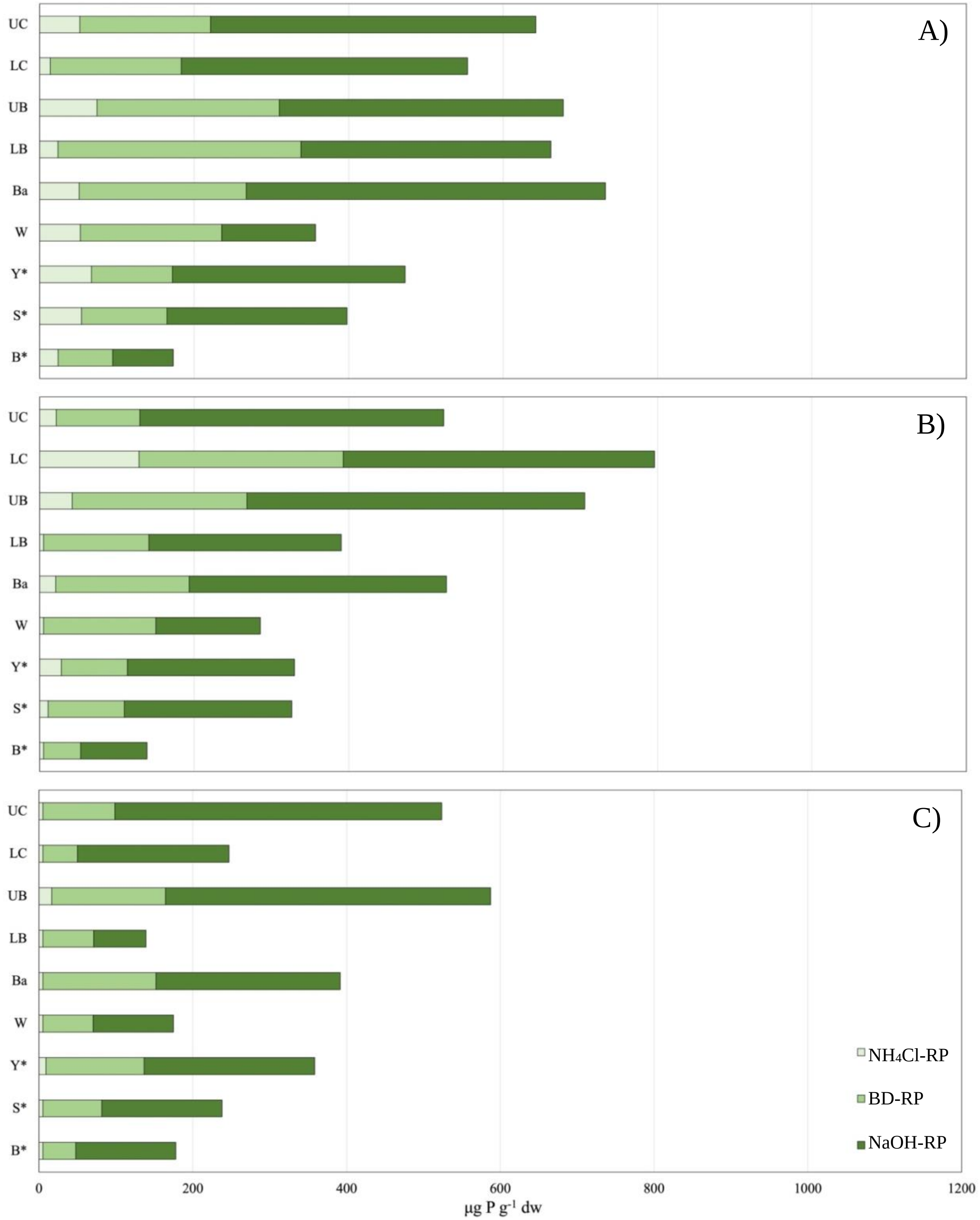

Figure 3.4.2b. – Comparison of sediment-associated NAIP forms in burned WLNP rivers and unburned reference rivers A) 2018, B) 2019 and C) 2020. Data are composite mean values that include all sampling periods during each year for both suspended and ingressed sediment.

The seasonal variation of mean PP concentrations of river sediment is presented in Figure 3.4.2c. NAIP had the highest median values in summer and fall in burned river sediment, as well in reference river sediment in the fall. Median AP values were highest during summer in unburned river sediment. NAIP and TPP concentrations displayed the highest variability for both seasons in burned and unburned river sediment. The highest and lowest median TPP values were recorded in burned river sediment during summer and fall, respectively.

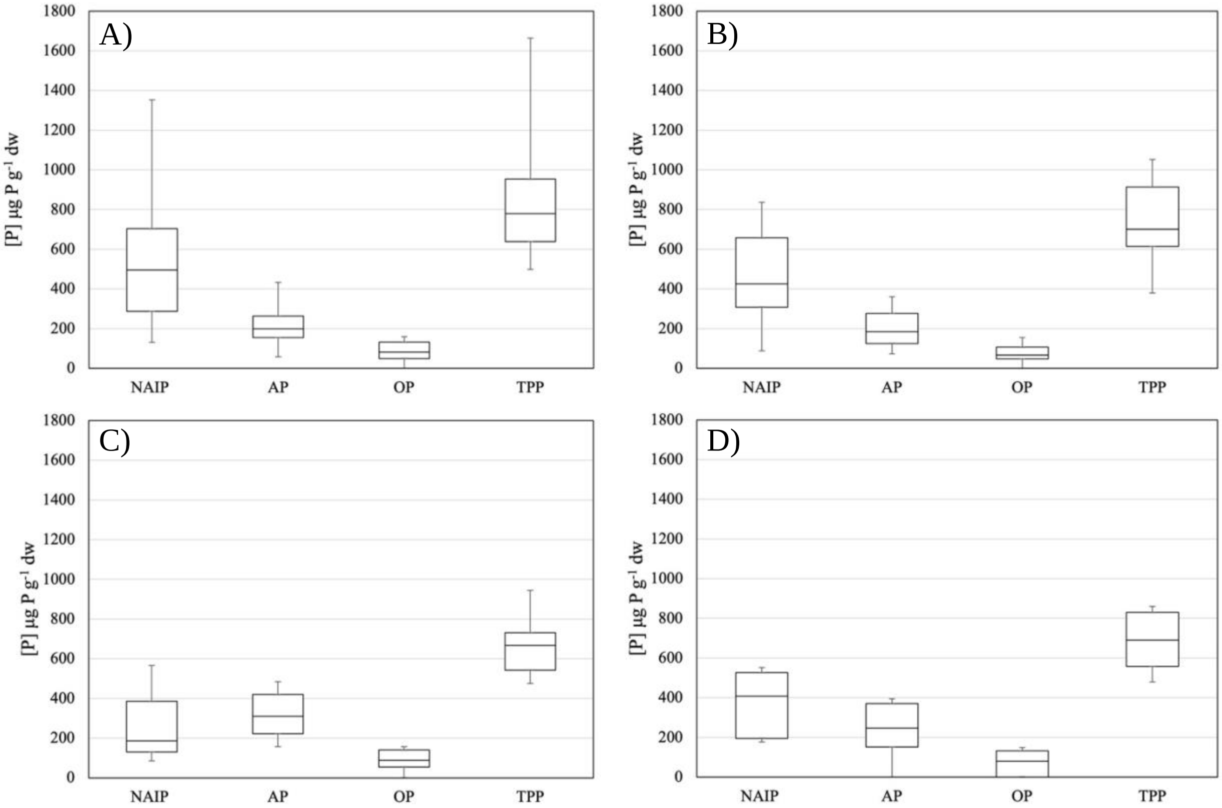

Figure 3.4.2c. – Seasonal variation of PP species where A) burned rivers during summer sampling (n=29), B) burned rivers during fall sampling (n=26), C) unburned reference rivers during summer sampling (n=14) and D) unburned reference rivers during fall sampling (n=8). Data are composite mean values that include both suspended and ingressed sediment.

3.4.3. Physical and geochemical properties of riverine sediment following wildfire

Physical Properties of riverine sediment following wildfire

Particle size characteristics of suspended and ingressed river sediment from 2018 to 2020 are presented in Appendix A (Tables A1a, A1b and A1c). There were no significant differences in

SSA, D_{50} or D_{90} between burned and unburned river sediments or between ingressed and suspended sediment fractions within burned river sediment. Temporally, there were significant differences in SSA, D_{50} and D_{90} among the three years of study, with largest mean particle size occurring in 2019 (Figures 3.4.3a and 3.4.3b). While SSA was higher in 2018 than 2019 ($H(1) = 17.10$, $p < 0.001$), d_{50} and d_{90} increased from 2018 to 2019 ($H(1) = 18.18$, $p < 0.001$ and $H(1) = 7.10$, $p = 0.008$, respectively). While there was no significant difference in SSA from 2019 to 2020 among sites, d_{50} and d_{90} were both higher in 2019 than 2020 ($H(1) = 3.42$, $p = 0.064$ and $H(1) = 9.30$, $p = 0.002$, respectively).

There were no significant differences in particle size characteristics between the upper and lower reaches of the Cameron River from 2018 to 2020. When comparing the upper and lower reaches of the Blakiston River, it was found that D_{50} and SSA were both significantly higher in upper reach of the Blakiston River ($H(1) = 3.19$, $p = 0.074$ and $H(1) = 3.78$, $p = 0.052$, respectively). When comparing the burned watersheds within the study, no significant differences in grain size were found between the Cameron and Blakiston river continuums. Alternatively, when analyzing the two unburned watersheds, SSA was significantly higher in the eastern reference watershed compared to the northern reference watershed ($H(1) = 3.01$, $p = 0.083$).

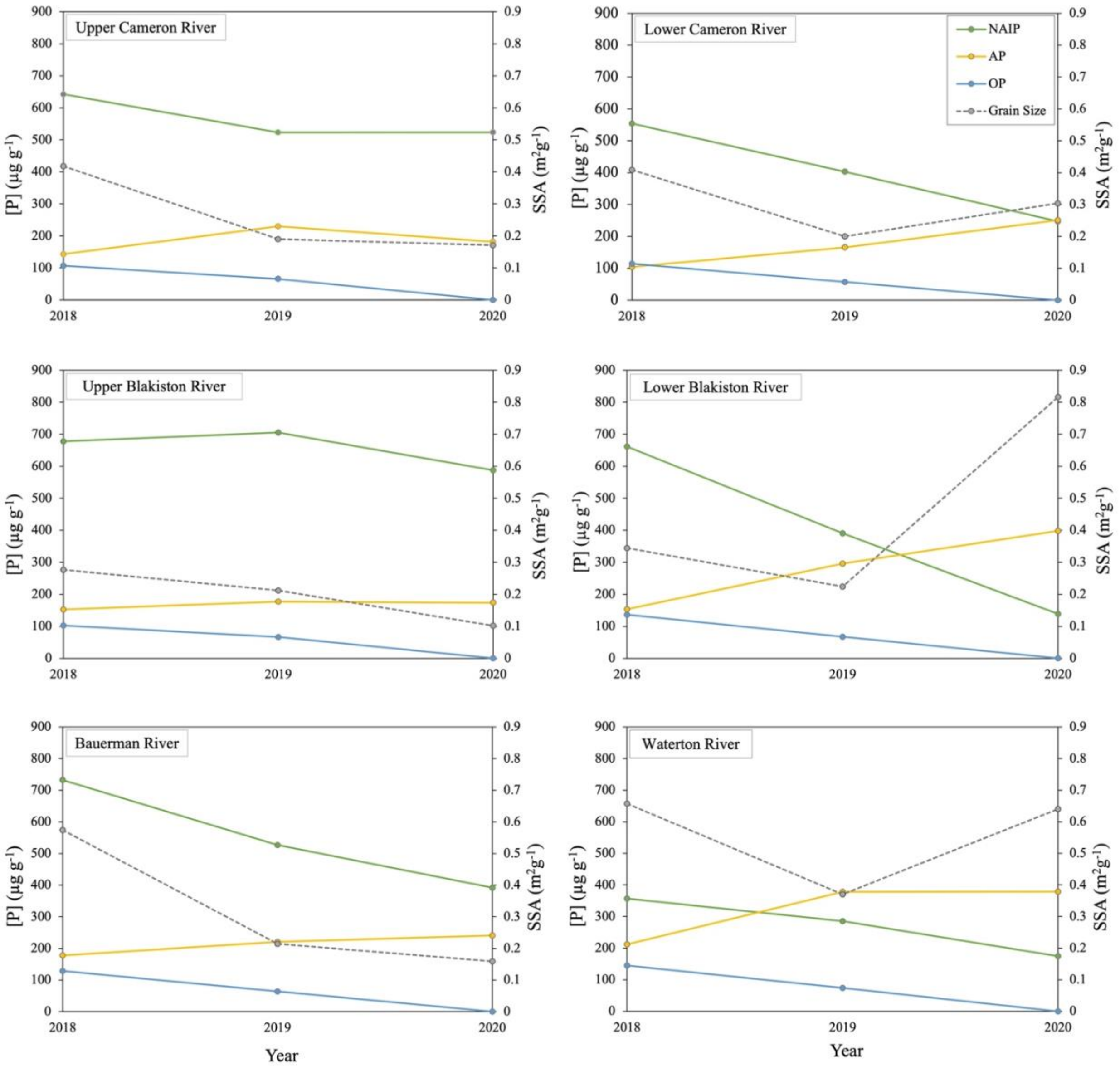

Figure 3.4.3a. – Concentrations of particulate phosphorus species and specific surface area of suspended and ingressed river sediment from unburned reference rivers in areas surrounding WLNP from 2018 to 2020

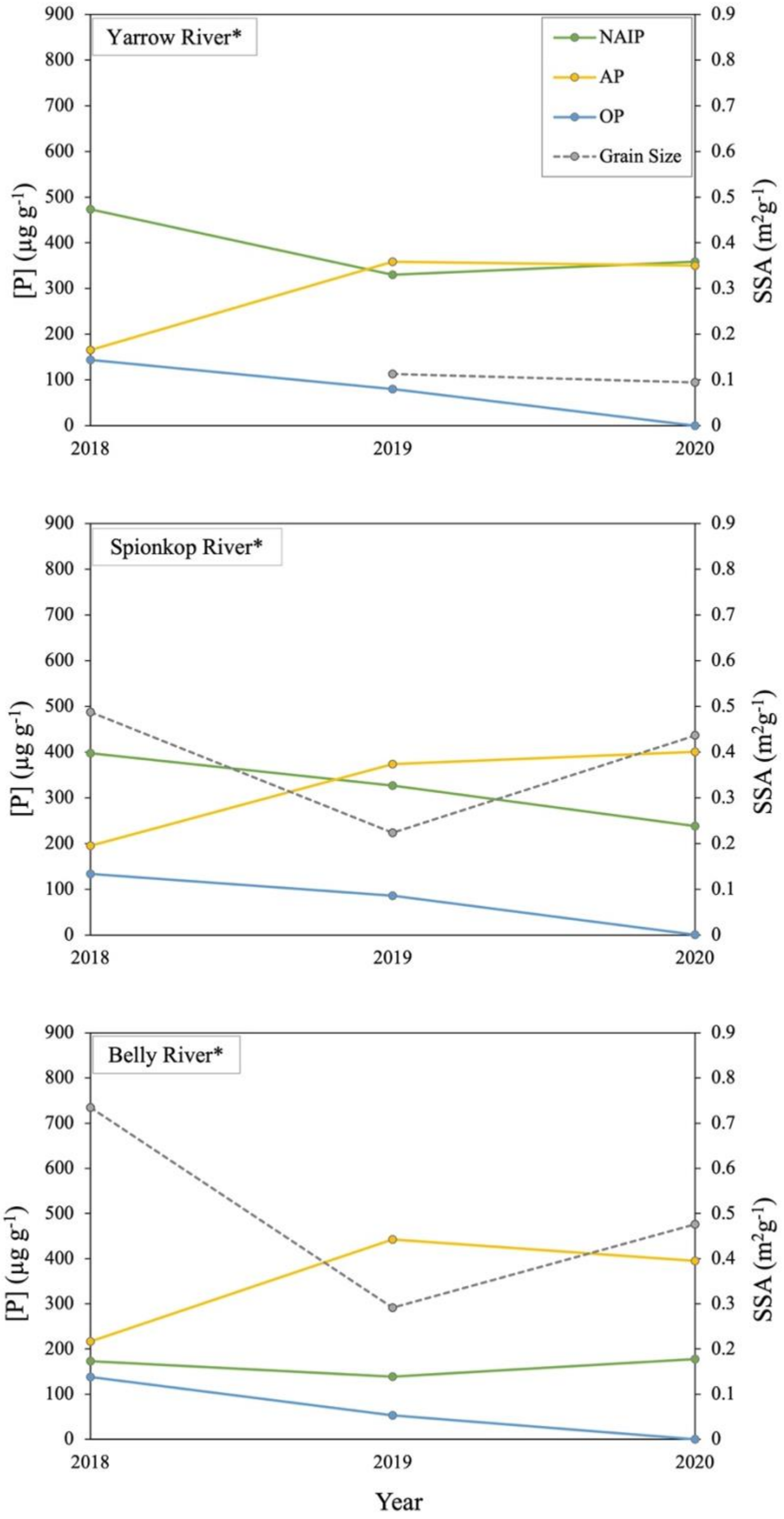

Figure 3.4.3b. – Concentrations of particulate phosphorus species and specific surface area of suspended and ingressed river sediment from unburned reference rivers in areas surrounding WLNP from 2018 to 2020.

Geochemical Properties of riverine sediment following wildfire

Inter- and intra-site variability in the geochemical composition of riverbed and suspended sediment in WLNP and surrounding areas are illustrated in Figure 3.4.3c. Burned river sediment contained significantly higher concentrations of Mg (H (1) = 9.70, p = 0.002), while unburned reference river sediment contained significantly higher concentrations of Fe and K (H (1) = 4.25, p = 0.039 and H (1) = 5.79, p = 0.016, respectively). The suspended solids fraction contained significantly higher concentrations of Al (H (1) = 4.11, p = 0.043), Mn (H (1) = 9.62, p = 0.002) and K (H (1) = 2.93, p = 0.087), while the ingressed fraction contained significantly higher concentrations of Fe (H (1) = 8.07, p = 0.005), Mg (H (1) = 8.74, p = 0.003) and Ca (H (1) = 8.56, p = 0.003). Major elements that displayed greatest inter and intra- site variability included Mn, Mg and Ca and the highest variability was observed at the Lower Blakiston, Bauerman and Waterton river sites. Most chemical constituents in river sediment did not vary temporally over the three years of study, but concentrations of Na and K, were significantly different among the three years of sampling. Peak concentrations of these elements were measured in 2019 (H (2) = 7.45, p = 0.024 and H (2) = 8.20, p = 0.017, respectively).

When comparing upstream and downstream reaches of the Blakiston and Cameron rivers, differences in chemical composition of river sediment were observed. Over the three-year study period, Mg and Ca concentrations were significantly higher in the lower reach of the Cameron River (H (1) = 5.24, p = 0.022 and H (1) = 4.87, p = 0.027, respectively), while the lower reach of the Blakiston river had significantly higher concentrations of Al and K (H (1) = 4.69, p = 0.030 and H (1) = 4.02, p = 0.045, respectively). River sediment in the Blakiston watershed had significantly higher concentrations of several chemical constituents compared to the Cameron River watershed. These elements included Mn (H (1) = 5.19, p = 0.023), Mg (H (1) = 3.86, p = 0.05), Ca (H (1) = 9.60, p = 0.002) and K (H (1) = 4.86, p = 0.027). There were no significant differences in river sediment geochemistry between the northern and eastern reference watersheds.

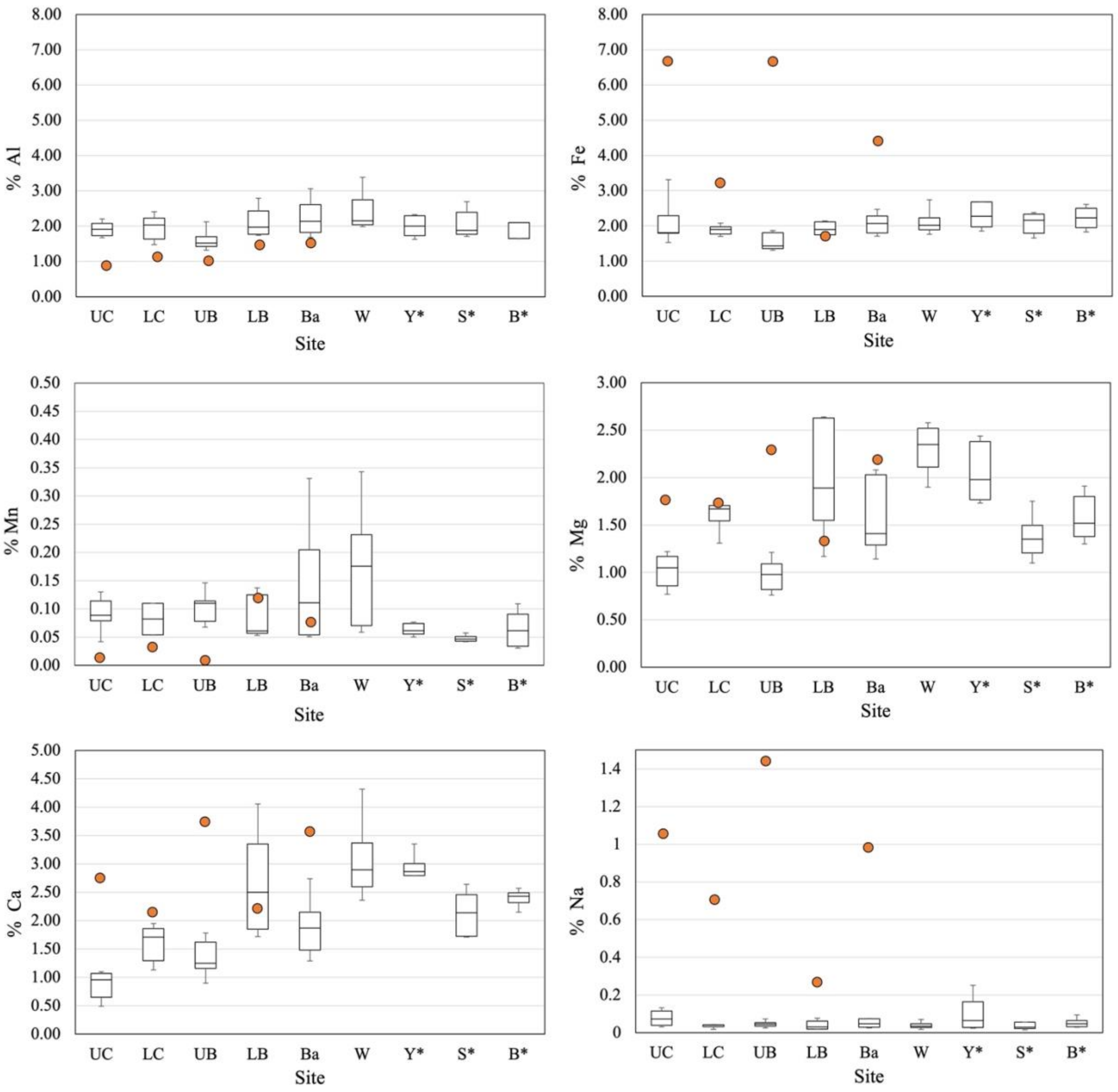

Figure 3.4.3c. – Boxplots of mean major element geochemistry of suspended sediment (n=7 for UC, n=6 for LC, n=7 for UB, n=7 for LB, n=7 for B, n=10 for W, n=6 for Y*, n=6 for S*, n=7 for Y*) with ingressed sediment (n=1 per site, in triplicate) values represented by orange circles, for 2018 to 2020. Note the different y-axis values.

Several statistically significant correlations were observed between PP forms and major elements within sediment (Table 3.4.3a). There was strong negative correlation between NAIP and TPP and Mg, Fe and Ca concentrations and strong positive correlation between NAIP and TPP and Mn concentrations. OP and Al and Mn concentrations were also significantly positively correlated, as were AP and Fe, Mg and Ca concentrations. Stepwise linear regression was also conducted to determine whether sediment geochemistry could be used to predict PP distribution in river sediment from WLNP and reference rivers (Table 3.4.3b). The results of this analysis demonstrate that both NAIP and TPP content within the study area can be modeled predominantly by Mg and Mn and to a lesser degree, Fe (R^2 adj =0.58, $p < 0.001$ and R^2 adj =0.54, $p < 0.001$, respectively).

Table 3.4.3a. – Spearman Rank correlation coefficients between particulate phosphorus form, major element geochemistry (n=54) and particle size (n=41) for burned suspended and ingressed sediments from WLNP 2018-2020.

	NAIP	**AP**	**OP**	**TPP**
Al			0.454**	
Fe	-0.377**	0.392**		-0.324*
Mn	0.314*		0.533**	0.429**
Mg	-0.773**	0.610**		-0.631**
Ca	-0.467**	0.432**		-0.316*
Na_2	0.393**			0.368**
K	-0.314*	0.313*		
SSA	-0.275		0.300	

Unmarked $p < 0.1$, * $p < 0.05$, ** $p < 0.01$

Table 3.4.3b. – Step-wise multiple regressions for standardized particulate P form (n=55) using standardized major element data of suspended and ingressed river sediment in burned rivers from 2018-2020.

Predictor Variable	**Formula**	**Adjusted R Square**	**p**
NAIP	687.09 – 0.69*Mg + 0.53*Mn + 0.36*Fe	0.582	$1.49*10^{-10}$
AP	78.11 + 0.43*Mg	0.171	$8.98*10^{-4}$
OP	52.26 + 0.39*Mn	0.138	$3.00*10^{-3}$
TPP	895.12 – 0.61*Mg + 0.57*Mn + 0.36*Fe	0.535	$2.3531*10^{-9}$

3.5. Discussion

3.5.1. Spatial and temporal patterns in particulate phosphorus forms

NAIP and TPP concentrations were both significantly higher in sediment collected from rivers draining burned watersheds than those draining unburned watersheds. There was high intra- and inter-site variability of NAIP and TPP, while AP and OP concentrations displayed low intra and inter-site variability. In most undisturbed forested environments, the losses of phosphorus in runoff are low (Burke et al., 2005). However, elevated concentrations of bioavailable PP have previously been reported in rivers affected by wildfire (Allin et al., 2012; Emelko et al., 2016). Smith et al., (2011) reported P concentrations in streams following wildfire 0.3 to > 5 times greater than unburned conditions. In this study, mean NAIP enrichment in river sediment from burned sites measured 65% in 2018, 59% in 2019 and 53% in 2020, whereas NAIP enrichment measured 49%, 35% and 45% from 2018 to 2020, respectively, in sediment from unburned sites (See Appendix A, Tables A2a a-c). The sites with the highest NAIP and TPP concentrations included the upper and lower Blakiston River and Bauerman River. While the upper and lower Blakiston River sites were the two rivers most spatially affected by wildfire in the study (79.6% and 62.7% of surface area burned, respectively, see Table 3.3.2a), the Bauerman River was only moderately affected by the wildfire compared to other sites (39.4% of surface area burned). This may point to the importance of other coincident controls that influence spatial distribution of PP form and concentration in fine river sediment.

In addition to burn severity, other factors may explain the spatial distribution of PP. The spatial variability in PP form and concentration in riverine sediments has been attributed to differences in the physiographic characteristics of catchments, hydroclimatic conditions, regional geology, soil type and landscape disturbance (Owens and Walling, 2002). For instance, the lower Blakiston River had the highest NAIP and TPP values in the study and this site is situated within a "U"-shaped valley with an extensive floodplain (See Appendix A, Figure A1). The deposition, storage and subsequent remobilization of fine sediment within floodplains and channel beds is an important factor in controlling the routing, transport and fate of PP within river basins (Owens and Walling, 2002) and this may explain the elevated PP levels recorded in sediment at this site. Alternatively, the Cameron River is situated within a "V"-shaped valley, which may also have implications for sediment dynamics, as upstream segments of highly incised rivers may have higher concentrations of water quality constituents, including PP than downstream segments, which could undergo sediment fining due to in-stream trapping of particles. These data contradict the results of Emelko et al., (2016), who found that PP concentrations increase in downstream reaches of rivers in the Crowsnest and Castle River basins of Alberta due to cumulative effects of wildfire disturbance. In contrast, no significant differences in PP concentration were found between upper and lower reaches of the Cameron and Blakiston rivers and this may be due to the significantly smaller study area (reaches were within ~10km of each other), which may not be a sufficient distance for cumulative effects or significant sediment fining to occur. The small distance between sites may also explain the elevated TPP concentrations recorded in some reference river sediment. Sediment from the Spionkop River had median TPP concentrations higher than that of sediment from some burned sites. Due to the proximity of this reference watershed to the area burned by the Kenow wildfire, atmospheric deposition of pyrogenic materials from the wildfire and previous historical prescribed fire activity may represent two possible sources of TPP in this watershed. Ultimately, the spatial variation of PP in this study is likely a function of several factors, some of which may include varying sediment sources and in-stream biogeochemical processes.

There were significant differences in both the form and concentration of PP across the three years of study. Peak TPP concentrations across sites occurred 2 years post-fire, which may point to the legacy effect of PP within gravel-bed rivers observed in studies carried out over longer time scales following wildfire (e.g. Emelko et al., 2016; Watt et al., 2021). NAIP was not significantly different between 2018 and 2020, although the NH_4Cl-RP fraction of NAIP was essentially negligible by 2020, which was mostly likely desorbed from sediment into the water column, in these oligotrophic streams. OP concentrations were also very low across all rivers in 2020 and this may be due to the decreased delivery of pyrogenic solids into the river systems in years following wildfire. These temporal differences in PP concentrations may also be a function of enhanced climate change altering regional hydrologic regimes. Generally, the hydrology of the Rocky Mountains region is characterized by winter snowpack accumulation, spring snowmelt and autumnal baseflow. During spring runoff, rivers discharge > 70% of their annual water budget and instantaneous discharges 10-100 times greater than mean low flow can occur (Hauer et al., 1997). Within areas surrounding the Rocky Mountains, runoff from snowmelt has typically occurred around March-April, with annual peak discharge reached between May and June, before returning to baseflow conditions in July or August (Hauer et al., 1997). Shifts in winter precipitation from snow to rain because of climate change effects on temperature, as well as extreme climate events such as wildfire have resulted in changes in streamflow peaks in many mountain regions, including WLNP (Kundzewicz et al., 2008). This has been demonstrated in years since the Kenow wildfire, as peak discharge has shifted to early May (See Appendix A, Figure A3). This may have implications for measurements of PP forms, as time-integrated Phillips samplers were used to collect suspended sediment within the study areas, and these devices were typically left installed within rivers from three weeks to a month at a time. It should also be noted that the temporal distribution of all PP forms were not normally distributed, and this may be due to the highly dynamic hydroclimatic conditions that exist at large river basin scales, such as those of WLNP, which could lead to variable spatial extent and duration of effects of the 2017 Kenow wildfire on sediment-associated PP (Emelko et al., 2016).

3.5.2. Physical and geochemical factors influencing particulate phosphorus forms

Multiple physical and geochemical factors can influence PP forms within aquatic environments, including redox conditions, temperature, particle size and sediment geochemistry (e.g. Owens and Walling, 2002; Stone and Mudroch, 1989; Stone and English, 1993). In the present study, grain size differences were not significantly different when comparing sediment from burned and unburned rivers, or when comparing suspended and ingressed sediment within burned rivers. This observation contrasts the findings of other studies, such as that by Owens and Walling (2002), who found higher TPP content within suspended sediment in the Rivers Aire and Swale, UK were associated with smaller particle size fractions. Additionally, in a study assessing PP form in the Garonne River of Southern France, Vervier et al., (2009) found TPP concentrations to be greatest in fine sediment fractions. The lack of grain size differences observed in the present study may be a function of methods used for sediment collection, as Phillips samplers preferentially collect fine materials (< 100 µm) (Phillips et al., 2000). Additionally, sediment was sampled during low flow conditions in summer and fall, which could skew the grain size distributions toward dominance of smaller particles. Like the spatial differences in PP form observed in this study, the lack of grain size differences may be a function of the relatively small geographic area covered in the study site, which could result in rivers having the same or similar sediment sources. The average grain size of particles across sites was largest in 2019, which corresponded to the year of study with the highest TPP concentrations across sites (Figures 3.5.2a and 3.5.2b). The lack of grain size differences observed in this study may point to the potential importance of geochemical controls on PP form.

The geochemical composition of sediment can influence the ability of P to bind to sediment, as well as the bioavailability of PP within aquatic environments (Stone and English, 1993). For instance, NaOH-RP was the dominant NAIP species at all sites excluding Waterton River, and this may demonstrate the prevalence of Ca and Mn-oxides within the regional geology of WLNP and surrounding areas. Multiple differences in major element composition were observed for fine river sediment at sites within WLNP and surrounding areas. Sediment from rivers draining burned watersheds displayed significantly higher Mn concentrations than sediment from rivers draining reference watersheds, which displayed higher Fe and K concentrations. Within burned rivers, suspended sediment had significantly higher Mn and K concentrations, while ingressed sediment displayed significantly higher Fe, Mg and Ca concentrations. Most major element concentrations examined in river sediment did not vary significantly over the three years of study, which may point to the lasting effect of pyrogenic-derived materials within wildfire-affected systems. Major elements with the greatest variability in concentration within and between sites included Mn, Mg and Ca and the highest intra-site variability was observed at the Lower Blakiston, Bauerman and Waterton River sites. This may be a function of the effect of surficial geology on sediment source within the study area and the materials collected may represent the geochemical composition of solids in these watersheds.

Phosphorus is primarily bound to and transported in associated with fine sediment that includes clays with Fe, Mn, Al and organic coatings (Stone and Mudroch, 1989). It follows that a negative correlation between PP concentration and particle size, as well as elements such as Ca, Mg and Si, which are associated with more resistant minerals might be expected. Additionally, positive correlations between PP concentrations and Fe, Mn, and Al concentrations would be expected (Stone and Mudroch, 1989; Evans et al., 2004). In the present study, there was a significant negative correlation between NAIP and TPP and Mg, Ca and Fe concentrations and strong positive correlation between NAIP and TPP and Mn concentrations. There was also a significant positive correlation between OP and Mn concentrations (Table 3.4.3a). These correlations are likely a function of wildfire ash chemistry, as well as sediment geochemistry in a previously glaciated landscape with high clay content. These correlations differ from those observed in studies by Stone and English, (1993) where NAIP was positively correlated with Al, Mn, K, and organic C and negatively correlated with Si and Na in sediment from two Lake Erie tributaries and by Watt et al., (2021), where NAIP positively correlated with Al and Mn in a reach of the Crowsnest River, AB. Emelko et al., (2016) also reported correlations between OC and NAIP in the Crowsnest River.

The results of a stepwise linear regression (Table 3.4.3b) demonstrated that both NAIP and TPP content within the study area can be modeled predominantly by Mg and Mn and to a lesser extent, Fe. This points to PP forms in sediment being strongly influenced by metal oxy-hydroxides, which aligns with the work of Agudelo et al., (2011), who found that PP form and mobility in rivers two agriculturally-impacted rivers in Arkansas were governed by redox-sensitive metal oxy-hydroxides. Alternatively, AP and OP content were modelled by Mg and Mn concentrations, respectively, although these relationships were less significant. These findings were very different from the work of Watt et al., (2021), who demonstrated that less bioavailable PP forms (AP and OP) in the Crowsnest River, AB were influenced by complex interactions between many major elements and P. An explanation for this difference in findings may be that while the study of Watt et al., (2021) in the Crowsnest River was affected by compounding natural and anthropogenic impacts, the present study focused predominantly on the effects of wildfire over several rivers with varying catchment characteristics, vegetation and hydrologic regimes. While sediment geochemistry provided insight into the distribution of sediment-associated P forms in this study, the response of sediment to landscape disturbance will vary depending on the biogeochemical processes at play in a particular environment.

3.5.3. Comparison of particulate phosphorus forms in suspended and ingressed sediment

There is a paucity of studies in the literature comparing differences in PP form and concentration between suspended and ingressed river sediments (House et al., 1995, Owens and Walling, 2002). In the present study, significant differences between suspended and ingressed sediment existed for all PP forms analysed, with higher NAIP and TPP concentrations measured in suspended sediment and higher AP and OP concentrations in ingressed sediment. These findings are comparable to those of Kerr et al., 2011, who reported higher AP and OP content in ingressed sediment and higher NAIP content in riverbed sediment in the Upper Brisbane River, Australia. They attributed this trend to selective erosion and transport of fine materials. While there were no significant differences in grain size distribution between suspended and ingressed sediment fractions in the present work, suspended sediment fractions had larger mean particle size in the upper Cameron, upper Blakiston and Bauerman sampling sites, while ingressed sediment displayed larger grain size in the lower Cameron and lower Blakiston sites (See Appendix A, Table A1a). This could be a function of increased channel width moving from upper to lower reaches of study sites, which would correspond to weaker flow, allowing larger particles to settle out and potentially increased fine sediment ingress in the stream bed. Additionally, since sediment sampling occurred during summer and fall, low flow in channels may have allowed for the transport of larger particles greater distances downstream than would be possible under weaker flow conditions. This low flow may also have created an environment in which in-stream biogeochemical processes were more influential on sediment dynamics than local hydrologic processes, which could also explain differences PP form between suspended and ingressed sediment. Since grain size has been demonstrated to be controlling factor for major element composition and PP form in river sediments, (Stone and Mudroch, 1989; Stone and English, 1993) the absence of grain size differences between suspended and ingressed sediment must point to the importance of other controlling factors present in WLNP and nearby study areas.

It is likely that differences in fine sediment dynamics between study sites in WLNP and surrounding areas are a function several interconnected factors, some of which include varying types and degree of landscape disturbance, sediment sources, connectivity from source to channel, biogeochemical processes and sediment-water interactions. The amount and type of sediment that can potentially enter a river channel is controlled several natural and anthropogenic factors, which in turn depend on delivery pathways from sources to the river (Wilkes et al., 2018). Within rivers, the transport of fine sediment and associated nutrients is attributed to a complex interplay between particle resuspension and deposition (Stone and English, 1993) and particles may become temporarily stored in bed surface materials or become ingressed within riverbeds over longer time periods (Wilkes et al., 2018). It has been demonstrated that suspended and ingressed material behave differently in terms of ability to adsorb P (House et al., 1995; Owens and Walling, 2002). For instance, while Allin et al., (2012), reported that PP forms in suspended sediment in southern

Alberta rivers varied as a function of season, this was not observed in the current work. Ultimately, understanding the transport of fine sediment-associated P within rivers where grain size, associated chemistry and particle dynamics including settling rates, stability and flocculation are not fully understood is inherently complicated (Stone et al., 1995). It should also be taken into consideration that in the present study, the Lambert and Walling, (1988) technique was used to collect ingressed sediment fractions and this method only allows for collection of sediment contained within the uppermost ~10cm of a riverbed and provides no information on riverbed stratification or depth of sediment storage. In future works, it is recommended to pair collection of ingressed sediment with freeze core sampling, as this would provide more context for sediment dynamics within the riverbed (Lambert and Walling, 1988). While the present study showed that suspended sediment contained overall higher PP concentrations and higher concentrations of the most bioavailable PP form, more work is needed to understand the different controls on suspended and ingressed sediment dynamics within forested rivers.

3.5.4. Implications of wildfire on particulate phosphorus forms

Wildfire can be a strong factor in influencing the form of PP and the present study examined the effects of the 2017 Kenow wildfire on the form, concentration and availability of sediment-associated P within forested rivers in WLNP. It was found that the most bioavailable form of PP (NAIP) and TPP were both significantly higher in rivers directly affected by wildfire and within these rivers, most P was associated with suspended sediment. Due to the large quantities and high quality of water supplies in typically oligotrophic forested rivers, such as those of WLNP, these areas are particularly vulnerable to the effects wildfire (Bladon et al., 2014). When examining the effects of landscape disturbance on PP form and concentration in rivers, is important to recognize the influence of confounding factors. In many locations throughout the Rocky Mountains, anthropogenic disturbance could obscure the influence of climate change on enhanced river nutrient concentrations, some of which include deforestation, urbanization, mining, and agriculture (Hauer et al., 1997). This was demonstrated in the present study, as some unburned rivers in nearby catchments that were analyzed for background conditions also displayed elevated PP concentrations. Specifically, sediment from the Spionkop River displayed TPP concentrations ranging from 639.1 $\mu g/g_{sediment}$ – 786.0 $\mu g/g_{sediment}$. For reference, the burned site with highest mean

TPP concentration was the upper Blakiston site and values ranged from 761.6 $\mu g/g_{sediment}$ – 949.8 $\mu g/g_{sediment}$. Elevated PP concentrations in reference sites may be attributed to the proximity of sites to the burn and therefore susceptibility to atmospheric deposition of P-rich pyrogenic materials. Additionally, land uses in the area, such as pasture and grazing land for bison could have contributed to elevated nutrient concentrations. Comparing results across catchments or within a single catchment with varying geology, mineralogical makeup of sediment and soil types also presents challenges (Records et al., 2016). Within WLNP study rivers, varying geology, slope and connectivity could all contribute to differences in the form and concentrations of PP measured. Micro-scale processes and sub-surface processes may also contribute to variability within sites and further work in this area could enhance understanding of PP cycling within rivers.

Following wildfire, enhanced sediment and associated nutrient inputs entering forested rivers can pose numerous challenges to water quality and water treatability. Since P has a tendency to be bound to fine sediment fractions, a challenge to water treatability is suspended sediment input after wildfire, which can affect the colour and turbidity of water, interfere with the detection of bacteria and viruses and hinder the effectiveness of disinfection treatments (Smith et al., 2011). Predicting the delivery of contaminants to stream networks represents a major issue in water quality management (Lane et al., 2011). Currently, common treatment processes for the removal of sediment-associated P from water supplies include coagulation, flocculation or sedimentation (Emelko et al., 2011; Emelko and Sham, 2014). A challenge to water treatment resulting from post-fire increased PP concentrations includes increased dependence on solids and dissolved organic carbon (DOC) removal processes (Emelko et al., 2011). Since the removal of pathogens is always a priority in terms of water treatment, the relationship between enhanced riverine P concentrations following wildfire and proliferation of primary producers is important to understand (Silins et al., 2014). Heightened bioavailable P in waters following wildfire may lead to exponential microbial growth and the growth of microbial communities related to enhanced P in drinking water supplies is commonly controlled by disinfecting agents, some of which include chlorine, hypochlorite and ozone (Miettenen et al., 1997). With enhanced understanding of the biogeochemical processes responsible for the transfer of P between riverine sediments and water, catchment specific responses to landscape disturbance can be used to make better informed management decisions regarding valuable water supplies in regions vulnerable to wildfire disturbance, such as WLNP. For effective remediation of these affected systems to occur, both the location and management of potential P inputs in a landscape and the behaviour of P within river systems must be considered (McDowell and Sharpley, 2003).

3.6. Conclusions

This study aimed to evaluate abiotic controls on fine sediment-associated PP forms in gravel-bed streams affected by severe wildfire, as well as associations of PP forms to major element sediment geochemistry in WLNP, AB. Conclusions of this study include:

1. Mean TPP and NAIP concentrations were significantly higher in sediment from rivers draining burned areas, which demonstrates the potential of wildfire to severely degrade water quality in source water systems.
2. There were no significant differences in PP concentrations between upstream and downstream reached of fire-impacted rivers, which may be due to close physical proximity of sites.
3. While NAIP and TPP concentrations decreased over the three years of study, elevated post-fire NAIP enrichment did not change significantly and ranged from 65% to 53%, demonstrating the legacy effect of this bioavailable nutrient in oligotrophic river systems.
4. Within burned rivers, suspended sediment displayed significantly higher mean NAIP and TPP concentrations compared to ingressed sediment, demonstrating the highly dynamic hydrologic regimes at play at in at large basin scales.
5. There were no significant differences in particle size characteristics of river sediment impacted by wildfire, which points to the importance of sediment geochemistry in influencing PP form.
6. Bioavailable PP forms were strongly negatively correlated with Fe, Mg and Ca concentrations and strongly positively correlated with Mn concentrations, which could be a function of wildfire ash chemistry, as well as sediment geochemistry in a previously glaciated landscape with high clay content.

Chapter 4
Particulate phosphorus sorption and water quality in forested gravel-bed rivers following wildfire

4.1 Abstract

There is increasing evidence that climate change-exacerbated natural landscape disturbance by wildfire is increasing in frequency and severity in forested source water regions across the globe. These often catastrophic events strongly influence the availability and transport of sediment-associated nutrients from hillslopes to receiving streams in forested watersheds. Accordingly, there is a critical need to understand the mobility of pyrogenic sediment-bound phosphorus in streams, as it can be released from sediment and impact the health of aquatic ecosystems and challenge water treatability. This work examines the spatial and temporal variability in mobility of particulate phosphorus (PP) in gravel-bed rivers affected by severe wildfire and nearby reference sites during environmentally sensitive summer and fall flow periods for three years post fire. Fine suspended sediment samples were collected with Phillips samplers deployed at nine study sites in rivers draining burned and unburned watersheds in Waterton Lakes National Park (WLNP), AB and nearby areas. The phosphorus release potential of both fine suspended and ingressed river sediment was examined using batch experiments and construction of sediment buffer diagrams after Froelich, 1988 to determine the equilibrium phosphorus concentration (EPC_0). There was no statistically significant difference in EPC_0 across burned and unburned sites and this was attributed to the close proximity of reference sites to the burn, allowing for wet and dry atmospheric deposition of pyrogenic materials, as well as land use impacts within the reference sites. There were also no significant differences in EPC when considering distance from burn or time since burn occurrence. Peak EPC_0 concentrations occurred two years post-wildfire disturbance, demonstrating potential legacy effects of nutrient-enriched fine sediment within river systems. The data suggest that fine sediment originating from both burned and unburned landscapes that has been delivered to streams may act as a source of SRP for the overlying water column. This study provides insight into the potential of fine sediment within gravel-bed rivers to regulate PP mobility following disturbance by wildfire.

Keywords: wildfire, forested watersheds gravel-bed rivers, fine sediment, particulate phosphorus equilibrium phosphorus concentration, sorption

4.2 Introduction

The current trend of enhanced climate change has increased the frequency and severity of climate change-exacerbated landscape disturbances, including wildfire (Stone et al., 2011; Silins et al., 2014) and wildfire is the dominant natural landscape disturbance in many forested environments, including much of western North America (Weber and Flannigan, 1997). A landscape that is particularly vulnerable to the effects of enhanced climate change-exacerbated landscape disturbance includes forested rivers (Emelko et al., 2016). Following wildfire, forested rivers can experience shifts in physical, chemical and biological landscape processes that may result in increased sediment, nutrient and heavy metal inputs to downstream environments, (Emelko and Sham, 2014) though direct impacts on a landscape are variable and depend on factors such as fuel load, slope angle and the behaviour of the fire spread (Otero et al., 2015). Wildfire can strongly influence the mobility and transport of sediment from hillslopes to receiving waters and this sediment is often associated with various nutrients, including particulate phosphorus (PP) (Emelko et al., 2016). Since phosphorus is the limiting nutrient for productivity in freshwater environments, (Schindler, 1977; Bennett et al., 2001; McDowell, 2015) the issue of enhanced P inputs following wildfire is particularly relevant in terms of increased risk of cyanobacteria blooms, or eutrophication of drinking water supplies, which is one of the biggest threats to drinking water supplies in Canada and globally (Bladon et al., 2014). Forested areas provide drinking water for approximately two thirds of municipalities in the United States and approximately one third of the largest cities in the world (CHIFM, 2008). Therefore, better understanding of the implications of wildfire in these environments, particularly in terms of increased sediment-associated nutrient loads is needed to ensure long-term security of drinking water.

Within rivers, the advective flow of fine sediment (<63 μm) downstream is the primary vector for PP transport (Lijklema, 1993; Reddy et al., 1999; Owens et al., 2005). This is attributed to properties of fine sediment such as low settling velocities, (Haralampides et al., 2003), large surface area (Horowitz and Elrick, 1987) and charged surfaces to which PP tends to adhere (Stone and Mudroch, 1989). Nearly 84% of the external phosphorus loads entering aquatic surface waters originate from non-point sources, including forests (Carpenter et al., 1998). Forest fires have been shown to mobilize nutrients such as PP within the forest floor litter and mineral soil layers both directly through oxidation and volatization reactions and indirectly though leaching and the transport of ash by wind or water erosion (Bodí et al., 2014). These non-point sources of PP entering river systems can present challenges, as historically they are harder to target and associated elevated concentrations of nutrients may persist for long time periods (Agudelo et al., 2011; McDowell, 2015). The storage of fine sediment within gravel riverbeds can influence the fate of PP (Reddy et al., 1999) and the physical and geochemical properties of sediment can influence the degree to which P will sorb to riverbed sediment (Froelich, 1988, Lottig and Stanley, 2007). A particular challenge within forested rivers is that the deposition of fine sediment and associated nutrients from upstream sources may have legacy impacts and create lags in ecosystem recovery following disturbance (Meals et al., 2010; Sharpley et al., 2013). There are multiple challenges associated with assessing internal P loads, some of which include inexact definitions, uncertainties about origins of sediment-released P, unclear modelling and distinguishing internal from external loads (Nürnberg, 2009). The transport of PP across the sediment-water interface, as well as within the sediment profile itself also has important implications for ecosystem productivity and water quality and is conducted through mechanisms such as dispersion, diffusion, seepage, resuspension, sedimentation and bioturbation (Lijklema, 1993). Riverbeds are important sources of sediment and associated bioavailable SRP, particularly during low flow conditions within impacted systems (Jarvie et al., 2005). The availability of sediment-associated P within rivers is dynamic and depends on hydrologic, chemical and biological processes (Machensky et al., 2010). Through a combination of abiotic and biotic processes, river sediments may act as a source or sink of PP (Reddy et al., 1999; McDowell, 2015) and retention by sediment can lead to large quantities of PP accumulating in river systems (Agudelo et al., 2011).

The equilibrium phosphate concentration (EPC_0) is defined as the cumulative effect of abiotic processes influencing sediment in rivers and represents a state of net zero sorption or desorption of P by sediments (Koski-Vähälä and Hartikainen, 2001; McDowell, 2015). Conditions between river sediment and overlying water can be considered in equilibrium if water column SRP concentrations and sediment EPC_0 values are within 20% of each other (Jarvie et al., 2005). The EPC_0 indicates the critical concentration of P above or below which sediment will release or adsorb P respectively, and therefore describes the risk of P loading in river systems (Koski-Vähälä and Hartikainen, 2001). A recent meta-analysis of EPC_0 research across the globe found that in 83% of studies, sediments displayed the potential to remove or release P into streamwater, indicating equilibrium between sediment and the overlying water column is rare (Simpson et al., 2021). The transfer of PP between sediments and water occurs in a two-step process beginning with a rapid phase of initial surface retention, followed by a slower phase of diffusion into a solid phase (Froelich, 1988; Reddy et al., 1999). Existing research has shown that the potential for P exchange between sediment and streamwater is influenced by both stream and sediment characteristics, such as stream pH, sorption affinity, exchangeable P concentrations and particle sizes (Simpson et al., 2021). The EPC_0 of river sediment is highly variable due to several compounding factors, such as regional hydrologic regimes, land management in surrounding areas and the form and availability of PP within the sediment (Withers and Jarvie, 2008). Particle size and the geochemical composition of sediment including the presence of iron oxides, as well as redox conditions also exert a major control on adsorption/desorption processes (Lijklema, 1993; Stone and Mudroch, 1989; House and Denison, 2002). The EPC_0 is widely used as an indicator of the response of sediment to SRP in a solution (House and Dennison, 2000) and provides insight into whether river sediments are a source or sink of PP (McDowell, 2015).

Much of the existing research on phosphorus sorption in rivers has focussed on agriculture-impacted areas (e.g. Reddy et al., 1995; McDowell and Sharpley, 2003; Jarvie et al., 2005; Ekka et al., 2006; Hoffman et al., 2009; Machesky et al., 2010, Agudelo et al., 2011) as well as wastewater treatment plants (WWTPs) (e.g. House and Dennison, 2002; Wang and Pant, 2010; Ekka et al., 2016). More recently, attention has been directed to regions affected by climate change-exacerbated landscape disturbance by wildfire, as nutrient-enriched sediment transported from these landscapes is a key driver of nutrient enrichment in receiving waters (Son et al., 2015; Watt et al., 2021). The potential impact of wildfire on water treatability is also increasingly being reported (Emelko et al., 2016). Due to the logistical and financial difficulty of monitoring immediate post-fire effects on sediment-associated nutrients in rivers, many studies often report disturbance effect several years after the wildfire occurred. There is a critical lack of data on the immediate post-fire effects on sediment properties and nutrient dynamics in receiving streams. To address this gap, the objective of this study was to quantify the mobility of PP in oligotrophic gravel-bed rivers in Waterton Lakes National Park, AB, Canada. Batch experiments were conducted to determine the EPC_0 of suspended and ingressed solids across several burned and reference (unburned) streams during ice-free conditions for three years after the Kenow wildfire. It was hypothesized that sediment from rivers draining burned watersheds would display higher EPC_0 values than those draining unburned watersheds.

Specific objectives of this study include:

1. Evaluate the spatial and temporal variation of sorption characteristics (EPC_0, maximum potential release of SRP from sediment) of river sediment in reference and wildfire-impacted rivers.
2. Evaluate variation in sorption dynamics between suspended and ingressed sediment fractions.
3. Determine whether fine sediment in wildfire-impacted rivers may act as a sink or source of SRP to the overlying water column.

4.3. Methods

4.3.1. Site Description

Waterton Lakes National Park is located on the forested slopes of the eastern Rocky Mountains in southwestern Alberta, and this area of the province provides high quality sources of drinking water to a significant portion of the provincial population (Hauer et al., 1997). Rivers within the park and surrounding areas are typically oligotrophic and oxygen-rich, with low abundance of aquatic plant life but high aquatic diversity (Parks Canada, 2018c). These rivers display varying characteristics in terms of slope, connectivity and vegetation. For a more detailed study site description and information on the 2017 Kenow wildfire, which affected 38% of the surface area of WLNP, refer to section 3.3.1. in Chapter 3.

4.3.2. Sampling Design

In this study, fine river sediment from seven rivers in WLNP and unburned surrounding areas were examined following the 2017 Kenow wildfire, with sample collection occurring during the three years immediately after fire occurrence. Four of the rivers were situated within the burned portion of the park (Cameron River, Blakiston River, Bauerman River, Waterton River), while the remaining three rivers located in unburned watersheds were located outside the park boundaries (Yarrow River, Spionkop River, Belly River). Of the four burned rivers, two were analyzed at upstream and downstream sections in order to compare spatial changes in P release (Cameron River and Blakiston River). Sediment samples were collected multiple times a year during summer and fall flow conditions (July-August and October-November, respectively). Time-integrated Phillips samplers were deployed to collect suspended solids using standard techniques and storage protocols described by Phillips et al., 2000 (See Figure 2.2.1). To compare the mobility of PP in suspended and ingressed sediment, interstitial sediment was collected during fall of 2018 following the method of Lambert and Walling (1988). For a more detailed study sampling design description, refer to section 3.3.2. in Chapter 3.

4.3.3. Equilibrium phosphorus concentration experiments

Batch equilibrium experiments were conducted to quantify the EPC_0 of pyrogenic materials, (Emelko et al., 2016) which were compared with soluble reactive phosphorus (SRP) concentrations in the overlying water column to determine the potential for P retention or release. Calculations of EPC_0 were carried out using the method reported by Froelich (1988), though it is important to note that there is no standard method in place to measure EPC_0 (Simpson et al., 2021). Sample preparation involved measuring 0.25 g of dry sediment through the cone and quarter method (when the mass of sediment was sufficient) and combining the sediment with 25 mL of deionized (DI) water, as well as 25, 50, 100, 200, 400 and 800 µg P L^{-1} solutions in polypropylene tubes in triplicate. These tubes were then put on a shaker table for a standard of 18 hours at 100 rpm at room temperature to ensure thorough mixing. Following this, samples were filtered with 0.45 µm polypropylene syringe filters into scintillation vials. SRP concentrations were measured on the Technicon Autoanalyzer using the ammonium molybdate/stannous chloride method, which has a method detection limit of 1 µg P/L (Froelich, 1988; Stone and Mudroch, 1989; Stone and English, 1993).

The amount of phosphorus adsorbed to or released from river sediments was calculated using equation 4.3.3.,

$$P_{ads} = \frac{[(P_{initial} - P_{final}) * 0.025L]}{wt_{sed}} \qquad \text{eqn. 4.3.3}$$

where P_{ads} = P adsorbed by sediment (µg P g^{-1} dry weight sediment), $P_{initial}$ = initial phosphate concentration of solution (µg P L^{-1}), P_{final} = final phosphate concentration (µg P L^{-1}), wt_{sed} = weight of dry sediment (g). P_{ads} was then plotted against $P_{initial}$ to create sediment buffer diagrams, the x-intercept of which corresponded to the EPC_0 of sediment. EPC_0 values greater than 1 indicate that sediments are adsorbing phosphorus from the overlying water column, whereas EPC_0 values less than 1 indicate that sediment is desorbing phosphorus into the overlying water column (Froelich, 1988). The y-intercept of the sediment buffer diagram corresponds to the maximum potential release of SRP by sediment into the overlying water column.

All chemicals, including phosphorus standards were of high purity and stored under recommended conditions when not in use. All glassware used in storing, testing and analyzing samples for SRP were triple rinsed with 10% Extran ® 300 Liquid Detergent for Manual Washing to remove residual sediment, type 2 DI water and 20% sulfuric acid solution to remove residual phosphorus before being triple rinsed in DI a final time and left to air dry.

4.3.4. Statistical analysis

All statistics were performed with SPSS (SPSS 21, IBM Corp., 2012). Normality of data was determined using descriptive statistics splitting the file by site, year, watershed, status (burned versus unburned) and sediment type (suspended versus ingressed). Results of P-P and Q-Q plots, as well as Shapiro Wilks normality tests indicated that the data failed to meet the assumptions for normality ($p > 0.05$) in all cases. Since the data to meet assumptions of normality, non-parametric Mann-Whitney Rank Sum Tests were used to determine if differences in PP sorption behaviour were significant across river sites, year of sampling, watershed and status, as well as between suspended and ingressed sediment from burned river sites.

4.4. Results

4.4.1. Spatial variation in particulate phosphorus sorption dynamics

EPC_0 in both burned and reference river sediment displayed inter- and intra-site variability and are presented in Figure 4.4.1 and Table 4.4.1b. The median EPC_0 was greatest for Waterton River sediment (>1000 μg P L^{-1}) and lowest at the upper and lower reaches of the Cameron and Belly rivers (<500 μg P L^{-1}). The lower Cameron River had the lowest EPC_0 across all sites. Intermediate median EPC_0 values (500 μg P L^{-1} – 1000 μg P L^{-1}) were measured at the upper and lower reaches of Blakiston River, as well as the Bauerman, Yarrow and Spionkop rivers. EPC_0 was least variable for Bauerman and Waterton River sediment. Across the three years of study, the mean EPC_0 of burned river sediment (795 μg P L^{-1}) was higher but not statistically different than mean EPC_0 of unburned reference sediment (737 μg P L^{-1}). Unexpectedly, the mean EPC_0 of sediment in reference streams (Yarrow and Spionkop) were higher than some burned rivers, such as the upper and lower Cameron and Blakiston rivers.

There was no significant difference in EPC_0 between upstream and downstream reaches of the Cameron and Blakiston rivers. Within the Blakiston watershed, median values in the upper Blakiston and Bauerman rivers were relatively similar, but gradually decreased downstream in the lower Blakiston River, before increasing more noticeably at the Waterton River. Within the Cameron watershed, median EPC_0 values decreased moving from the upper to lower Cameron River, though variability in EPC_0 also increased in the downstream direction.

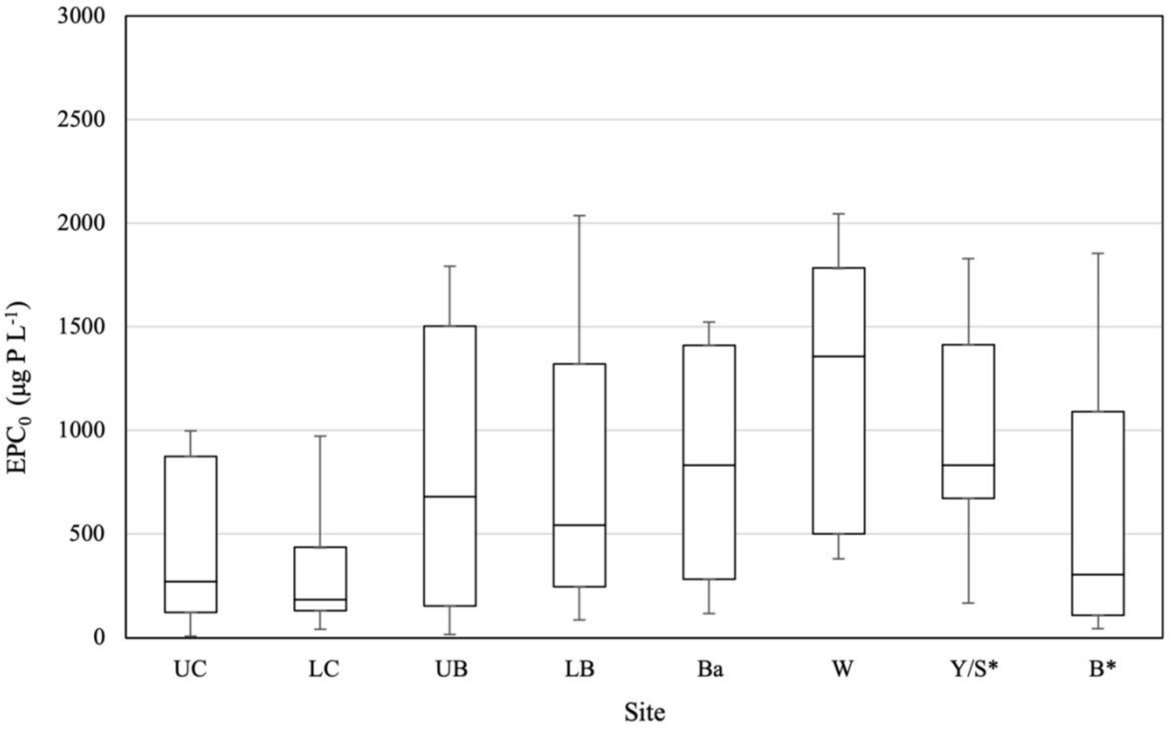

Figure 4.4.1a. – EPC₀ values of suspended and ingressed sediment for burned and unburned reference river sites (n=6 for UC, n=8 for LC, n=8 for UB, n=8 for LB, n=8 for Ba, n=9 for W, n=8 for Y/S* and n=6 for B) from 2018-2020. Reference rivers are indicated with *.

Table 4.4.1a. – Spatial distribution of mean (± standard deviation) EPC₀ values (µg P L^{-1}) of suspended and ingressed sediment for burned and unburned reference river sites from 2018-2020.

UC	LC	UB	LB	Ba	W	Y	S	B
423 ±400	309 ±300	809 ±671	751 ±680	837 ±550	1161 ±659	752	1024 ±594	579 ±687

The maximum SRP release potential from sediment in the study can be found in Appendix A, Table A4. The maximum SRP release potential data were highly variable within and between sites and there were no statistically significant differences between burned and unburned reference sediment. When comparing composite mean values of SRP maximum release potentials, the highest values were recorded in Yarrow River sediment (152 µg P L^{-1}), Spionkop River sediment (120 µg P L^{-1}) and upper Blakiston River sediment (120 µg P L^{-1}). Sediment from the lower Blakiston River, Bauerman River and Waterton Rivers displayed mean release values ranging from ~55 µg P L^{-1} to ~85 µg P L^{-1}, and the Belly River, and upper and lower Cameron River had mean release values under 35 µg P L^{-1}, with the lowest mean value measuring 24 µg P L^{-1} within lower

Cameron sediment. Unpublished water chemistry data provided by Dr. Silins of the University of Alberta indicated that median SRP concentrations in rivers in WLNP and surrounding areas were low, ranging from 2 µg P L^{-1} -3.5 µg P L^{-1} (Table 4.4.1b). When considering the EPC_0 of sediment relative to SRP concentrations in overlying water, sediment from all river sites across the three years of study displayed potential to release SRP into the overlying water column. In 2018, maximum potential SRP release from river sediment to water ranged from 15 µg P $g_{sediment}^{-1}$ in the upper and lower Cameron River to 233 µg P $g_{sediment}^{-1}$ in the Yarrow river. In 2019 maximum SRP release values of sediment ranged from 7 µg P $g_{sediment}^{-1}$ in the Belly River to 169 µg P $g_{sediment}^{-1}$ in the Spionkop River and in 2020 values ranged from 14 µg P $g_{sediment}^{-1}$ in the lower Cameron River to 127 µg P $g_{sediment}^{-1}$ in the upper Blakiston River. EPC_0 was plotted against the ambient SRP concentrations in the overlying water for all study sites (Figure 4.4.1b). The data were clustered above the 1:1 line, which indicates equilibrium between phosphorus concentrations in sediment and overlying water. Accordingly, the data show maximum SRP release potential increased with increases in EPC_0 values and therefore suspended solids in both burned and unburned reference rivers are sources of P to the overlying water column via the release of P from sediment.

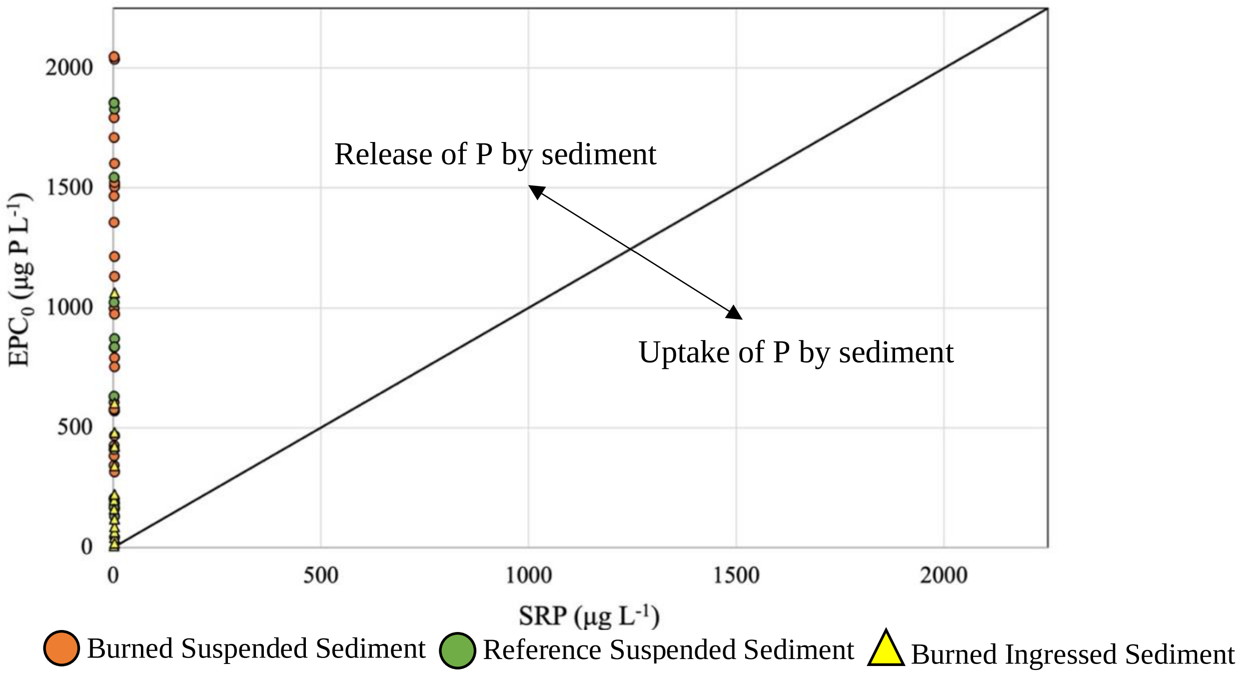

Figure 4.4.1b. – The relationship between SRP concentrations of river water and sediment EPC_0 for suspended solids (circles) and ingressed solids (triangles) in burned and unburned reference rivers from 2018-2020 (n=46), after Stutter and Lumdson, 2008. The 1:1 line represents equilibrium conditions between P in riverine sediment and the overlying water column.

Table 4.4.1b. – Median values of SRP concentrations of water (μg L^{-1}), EPC_0 of suspended and ingressed sediment (μg P L^{-1}) and estimated maximum potential SRP release of sediment (μg P $g_{sediment}^{-1}$) for all sites from 2018 to 2020.

		UC	**LC**	**UB**	**LB**	**Ba**	**W**	**Y**	**S**	**B**
2018	SRP_{water}	2	3	3	3	3	2	2	2	2
	$EPC_{sediment}$	179	162	496	315	1063	1049	N/A	1023	403
	Potential SRP release by sediment	15	15	31	26	57	78	233	190	25
2019	SRP_{water}	2	3	3	3.5	3	2	3	3	3
	$EPC_{sediment}$	835	721	1214	1133	845	1856	872	1829	129
	Potential SRP release by sediment	72	51	166	74	99	123	36	169	7
2020	SRP_{water}	2	2	2	2	2	2	2	2	2
	$EPC_{sediment}$	343	201	1792	605	572	891	631	479	N/A
	Potential SRP release by sediment	26	14	127	33	126	52	122	37	20

4.4.2. Temporal variation in particulate phosphorus sorption dynamics

Sediment buffer diagrams from batch experiments are presented in Figures 4.4.2a and 4.4.2b for burned and unburned river sediment, respectively. EPC_0 for burned and reference sediment across the three years of study were not significantly different. The average EPC_0 across all study sites was 670 μg P L^{-1}, 965 μg P L^{-1} and 677 μg P L^{-1} in 2018, 2019 and 2020, respectively. EPC_0 of sediment in burned rivers in 2018 ranged from to 7 μg P L^{-1} (upper Cameron River) to 2037 μg P L^{-1} (lower Blakiston River). In 2018, the EPC_0 of reference sediment ranged from 205 μg P L^{-1} to 1855 μg P L^{-1}, both in the Belly River. In 2019, the EPC_0 of sediment in burned rivers ranged from 185 μg P L^{-1} (Bauerman River) to 2047 μg P L^{-1} (Waterton River) and the EPC_0 of reference sediment ranged from 43 μg P L^{-1} (Belly River) to 1829 μg P L^{-1} (Spionkop River). In 2020, the EPC_0 of burned sediment ranged from 201 μg P L^{-1} (lower Cameron River) to 1792 μg P L^{-1} (upper Blakiston River) and the EPC_0 of reference ranged from 167 (Spionkop river) to 631 μg P L^{-1} (Yarrow River). The highest EPC_0 value in the study was recorded in 2019 in Waterton River. Results of batch experiments indicated that EPC_0 of ingressed sediment was significantly higher (929 μg P L^{-1}; U=23, p = 0.003) than suspended sediment (263 μg P L^{-1}). The mean maximum potential release of SRP into the water column from ingress sediment (96 μg P L^{-1}) was not significantly higher than the suspended sediment fraction (74 μg P L^{-1}).

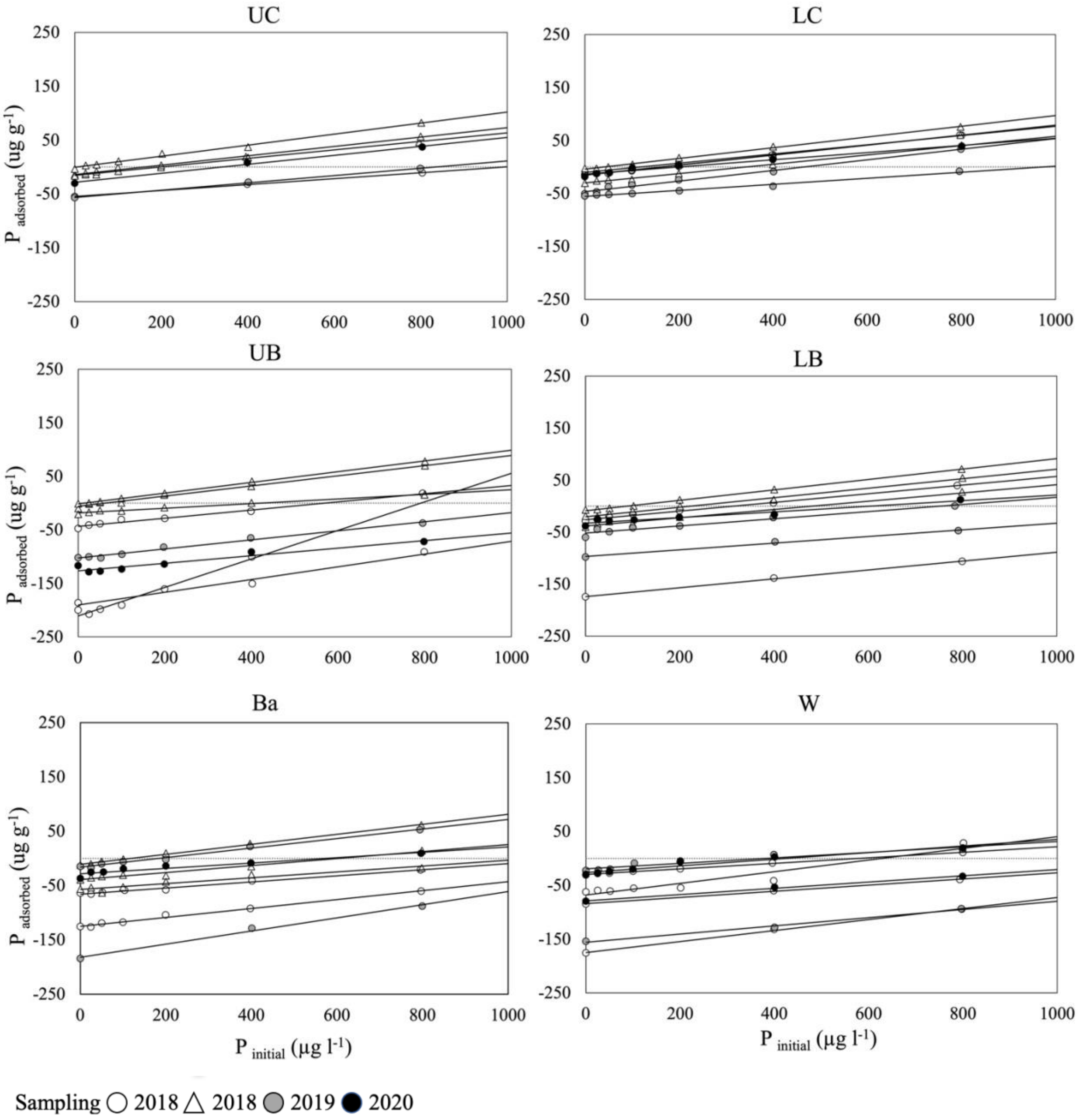

Figure 4.4.2a. – Results of P sorption experiments from burned study sites (2018 to 2020). Circles represent suspended sediment and triangles represent ingressed sediment. The x-intercept of each batch experiment represents the EPC_0.

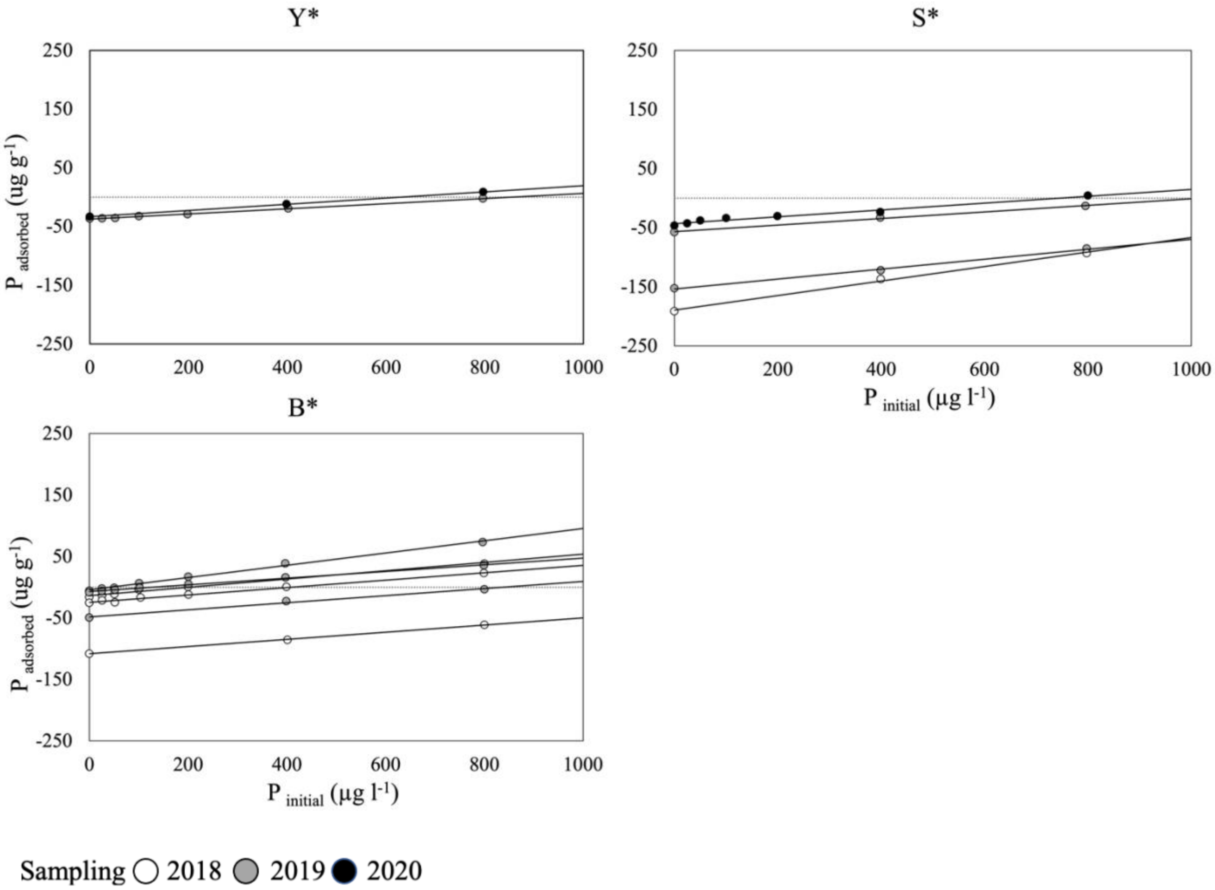

Figure 4.4.2b. – Results of P sorption experiments for suspended sediment from unburned reference sites (2018 to 2020). The x-intercept of each batch experiment represents the EPC$_0$.

4.5. Discussion

4.5.1. Equilibrium phosphorus concentrations

In freshwater, sediment EPC$_0$ can be used to quantify abiotic controls on the uptake or release of PP (Froelich, 1988). The lack of differentiation in sediment P sorption behaviour between burned and reference sites is likely related to the proximity of the sites, as reference sites were within < 30 km of the Kenow wildfire. Given the severity of the Kenow wildfire, wet and dry atmospheric deposition of pyrogenic materials in the unburned watershed likely contributed to increased mobility of PP at these sites and previous studies report that ash produced during high combustion completeness is typically P-rich (Bodí et al., 2014). Surface runoff from pastureland in the reference watersheds may also have contributed to elevated P mobility. The P sorption data clearly show that both fine suspended and ingressed sediment in rivers draining WLNP and surrounding areas represent key internal sources of SPR to the water column, particularly during low flow conditions. The downstream propagation of these fine-grained solids will also influence the nutrient status of lakes within WLNP. Within the current body of literature on phosphorus sorption dynamics in rivers, emphasis has been placed on anthropogenic sources of disturbance, namely agriculture and WWTPs (Table 4.5.1). In the present study, EPC_0 of sediment in both burned and reference rivers were comparable to those of highly degraded systems impacted by agriculture and WWTPs in North America. EPC_0 reported in the literature are highly variable, though $EPC_0 > 1$ mg L^{-1} are generally considered high and have been reported in rivers affected by agriculture (Reddy et al., 1999), WWTPs, (Ekka et al., 2006, Haggard et al., 2004) and wildfire (Son et al., 2015). In a study of P sorption from bed sediments of rivers affected by multiple land disturbance impacts (agriculture, WWTPs and wildfire), Watt et al., (2021) reported significantly lower EPC_0 than the present study and this may be attributed to sample collection occurring seven years post-fire. The wide variation in reported EPC_0 highlights the complicated and unpredictable nature of cumulative effects on sediment source and composition related to multiple landscape disturbances, as well as changing environmental conditions within a river over time.

Table 4.5.1. – Summary of previously reported EPC_0 (μg P L^{-1}) of river sediments in North America.

Location	**Site**	**Impact**	**Max EPC_0**	**Source**
New York, USA	Hoxie Gorge Creek	Poor drainage	2	Klotz, 1988
Florida, USA	Lake Okeechobee drainage basin	Dairy farms/pasture	4760	Reddy et al., 1995
Pennsylvania, USA	Manhantango Creek	Dominantly agriculture	39	McDowell and Sharpley, 2003
Arkansas, USA	Illinois River and Flint Creek Basin	WWTPs	7000	Haggard et al., 2004
Arkansas, USA	Illinois River	WWTPs	6030	Ekka et al., 2006
New York, USA	Bronx River	WWTPs, stormwater, urbanization	730	Wang and Pant, 2010
Kansas, USA	Upper West Emma Creek and Red Rock Creek	Intensive agriculture	160	Agudelo et al., 2011
Colorado, USA	Cache la Poudre River	Wildfire	1200	Son et al., 2015
Alberta, Canada	Crowsnest River	Wildfire	213	Emelko et al., 2016
Alberta, Canada	Crowsnest River	Wildfire, agriculture, WWTPs	579	Watt et al., 2021

In the present work, there was considerable variability in EPC_0 both within and between sites across all three years of study. This may demonstrate the potential unreliability of large-scale assessments of P mobility, as well as the relative ineffectiveness of point sampling EPC_0 to assess overall threats to ecosystem health following landscape disturbance. Gravel-bed rivers are dynamic systems and knowledge on how EPC_0 changes in response to sediment deposition or scouring of existing sediment is necessary to better contextualize the results of research in this area (McDowell, 2015). Variability in EPC_0 is a function of several physical, chemical and environmental processes that influence the mobility of PP in highly dynamic and environmentally sensitive river systems, such as those of WLNP. Sediment EPC_0 may be influenced by a several of physical and biogeochemical factors, some of which include mineralogy (House and Dennison, 2002; Withers and Jarvie, 2008), particle size (Stone and English, 1993), residence time of sediment, pH, temperature, sediment to solution ratios, solution chemistry and ionic strength (Lucci et al., 2010; Bhadha et al., 2012). The variable hydrodynamic nature of rivers within WLNP allow for wide variation in the amount and nature of fine sediment that may become ingressed in these systems, which could in part explain the intra- and inter-site variability in P mobility following landscape disturbance.

It is important to consider that the methodology for determining EPC_0 varies widely across the literature and therefore comparing the results of different studies should be done with caution. There is no standard in place for the collection of sediment samples for EPC_0 analysis, and many studies utilise different techniques with different associated errors (Simpson et al., 2021). These different techniques will have varying effects on the sediment in terms of disruption and resuspension of particles during collection, as well time elapsed between sampling periods and how accurately samples represent the actual distribution of river sediment. The storage of sediment prior to laboratory analysis will also influence P sorption. For instance, for practicality and convenience, samples are often stored frozen before being air or oven dried prior to analysis, and this can influence P-exchange dynamics of sediments (Withers and Jarvie, 2008). When comparing studies on P mobility in river sediment, it is important to consider how varying methodologies may influence sorption dynamics.

4.5.2. Particulate phosphorus sorption dynamics of suspended versus ingressed sediments

Although it is recognized that different sediment types have varying mechanisms that govern P adsorption (Cooper et al., 2015), knowledge of phosphorus sorption behaviour of suspended and ingressed river sediment is very limited (Owens and Walling, 2002). In this study, EPC_0 of suspended and ingressed sediment from burned rivers in 2018 were statistically significantly different, with ingressed sediment fractions displaying higher EPC_0 values. This is similar to the findings of Sharpley et al., (2013), which measured EPC_0 of suspended and ingressed sediment in agriculturally-impacted areas. The differences in sorption behaviour between suspended and ingressed sediment fractions in gravel-bed rivers can in part, be attributed to differing physical controls, particularly in terms of transport mechanisms. During transport in rivers, suspended solids move within the water column which may have layers with differing physical and chemical properties capable of altering P dynamics (Koski-Vähälä and Harikainen, 2001). Another important physical control on phosphate sorption is particle size, as smaller particles (clays) typically have associated Fe and Al-hydroxide coatings and larger specific surface areas to which P can sorb (Horowitz and Elrick, 1987; Withers and Jarvie, 2008). It should be noted however, that in the present study the grain size characteristics of suspended and ingressed sediment were not statistically significantly different (See Chapter 3) and therefore the significant difference in P mobility between suspended and ingressed sediment fractions is likely a function of other controls.

Chemical controls can also explain variation in sorption dynamics across sediment fractions in rivers. For instance, the movement of PP across the sediment-water interface and within the sediment profile will be influenced by the chemical characteristics of water (Reddy et al., 1999). It has been shown that interstitial waters typically have higher ionic strength than upper water layers and this can promote sorption of P from waters to solid surfaces due to changes in the net surface charge of variably charged particles and the electrical potential of oxide surfaces (Barrow et al., 1980). Conversely, in upper water layers where ionic strength is lower, the dispersion of aggregated mineral particles may be promoted, which in turn can promote the release of colloidal P (Koski-Vähälä and Harikainen, 2001). In the present work, Phillips samplers were used to collect suspended materials and any flocs present in the fine sediment fraction were likely not disaggregated, which may have had an influence on P forms measured during laboratory analysis. In future works examining P mobility behaviour of varying sediment types in gravel-bed rivers, chemistry data of the overlying water column would be beneficial to contextualize findings and provide explanations for differences between suspended and ingressed sediment fractions.

4.5.3. Controls on particulate phosphorus mobility in gravel-bed rivers

Along a river continuum, P dynamics may undergo change due to differing gradient or sediment supply (Bowes et al., 2003) (See Chapter 3). Rivers in this study vary greatly in terms of hillslope-river channel connectivity, slope and vegetation. Sediment was collected from two main river continuums, which drain two of the larger watersheds in WLNP that were affected by the Kenow wildfire; the Cameron river and the Blakiston River. Compared to the Cameron River, which is within a heavily incised “V”-shaped valley, the Blakiston River is within a glacier-carved U-shaped valley and has a large floodplain. This floodplain separates the river from surrounding steep slopes and acts as temporary storage area for eroded sediment originating in a drainage basin. This generally results in the Blakiston river having lower connectivity and slope than the Cameron River, which has more direct flow paths from hillslopes and thus is hydrologically more tightly connected. Due to this, the Cameron River is also more prone to undergoing mass wasting processes, which may contribute large amounts of sediment to receiving waters (Emelko and Sham, 2014). Contrary to the findings of similar studies (e.g., Emelko et al., 2016), the upper reaches of the Cameron and Blakiston rivers both displayed higher EPC_0 than their downstream counterparts, while also displaying greater variability in EPC_0. A possible explanation for this decrease in EPC_0 in downstream reaches could include sediment fining with distance from burn. EPC_0 values were also higher in the Blakiston River than the Cameron River, which could point to the extensive floodplain and relative lack of connectivity in this river acting as a trap for P-enriched ingressed fine sediment.

The dynamics of sediment within gravel-bed rivers are also important to consider when analyzing P sorption regimes. The morphology of river channels can influence the equilibrium between SRP in sediments and overlying water through flow velocity and in-stream contact time between water sediment (Withers and Jarvie, 2008). Stream features such as mid-channel bars, lateral-bars, stream banks and the stream bed itself may consist of different sediments, which could result in regular P fluxes between sediment pools (Agudelo et al., 2011). For example, during flood events, clay-sized particles, which represent significant sources of P transport, are prone to downstream transport, accumulation in pool beds, or deposition on stream banks (Hoffman et al., 2009). In the present work, both the upper Blakiston River and Waterton River contained sizeable mid-channel bars, and these two sites displayed the highest mean EPC_0 values in the study. Since in-stream sediment features can influence the dynamics of sediment associated P, in future works it is recommended to take into consideration the features within a river from which sediment samples are collected. In many areas of WLNP, riparian buffers and new-growth vegetation extend directly to the banks of rivers. The biogeochemical processes governing PP dynamics in riparian buffers are largely influenced by groundwater and surface water interactions in the hyporheic zone, as different hydrological flow paths will determine where and how P compounds transported by water will interact with Fe and Al-oxides or other minerals (Hoffman et al., 2009). During periods of low flow during summer months, groundwater flow is an important source of water for rivers in WLNP and it has been demonstrated that groundwater level plays in important role in P cycling and could explain up to 70% of SRP variability (Assegid et al., 2015).

The uptake and release of P in gravel-bed rivers is controlled by a combination of physicochemical and biogeochemical processes, some of which include sorption/desorption processes, co-precipitation with Al, and Fe hydroxides and Ca compounds, and assimilation by aquatic plants, biofilms and bacteria (Mainstone and Parr, 2002). Though not measured in this study, environmental factors such as temperature and redox conditions in rivers can exert strong influence on the mobility of P in gravel-bed rivers (Haggard et al., 1999; MacDowell et al., 2003; House, 2003). For instance, it has been demonstrated that EPC_0 increases due to low redox potential and high pH may result from changes in sorption components, particularly the release of Fe- and Al-bound P, as well as organic matter containing organic P (Koski-Vähälä and Harikainen, 2001). For this reason, it has been suggested that supplementary measurements of pH, alkalinity, redox potential and concentrations of dissolved Ca, Fe and Mn during batch EPC_0 measurements would better demonstrate and contextualize the buffer reactions that control P dynamics between sediment and solution, some of which include precipitation and dissolution reactions (House and Dennison, 2000).

4.6. Conclusions

This goal of this study was to determine the mobility of fine sediment and associated P in oligotrophic forested rivers affected by severe wildfire in WLNP, AB. The conclusions of this study are:

1. EPC_0 of burned and unburned reference sediment were not significantly different and this is likely due to the wet and dry deposition of pyrogenic materials in watersheds surrounding WLNP during and following the Kenow wildfire, as well as land use effects in reference sites.
2. There were no significant difference in EPC_0 with distance from burn or time since burn, and the highest EPC_0 was recorded in the Waterton River in 2019.
3. Differences in EPC_0 between suspended and ingressed sediment fractions are likely a function of differences in surface and groundwater controls, as well as geomorphic controls.
4. All sediment examined demonstrated the ability to act as a source of SRP to the overlying water column, particularly during low flow conditions, which may have implications for eutrophication and degradation of source water quality.
5. Ingressed sediments may act as legacy sources of bioavailable P in highly dynamic, oligotrophic gravel-bed rivers.

Chapter 5

Influence of wildfire on the form and mobility of sediment-associated phosphorus in forested river systems: Synthesis and conclusions

The current trend of enhanced climate warming is increasing both the frequency and severity of landscape disturbances, such as wildfire (Flannigan et al., 2005). Disturbance by wildfire can mobilize large quantities of sediment and associated nutrients such as phosphorus from hillslopes to receiving waters in forested source water environments, which can degrade the quality of valuable water supplies (Stone and English, 1993; Emelko et al., 2016). Recently, increased attention has been placed on enhancing the understanding the effects of increased sediment pressures following landscape disturbance on nutrient dynamics in rivers, as this can have negative implications for ecological communities, (eg. Silins et al., 2014) as well as the quality of downstream water supplies (Emelko and Sham, 2014). Nearly pristine freshwater systems throughout the Rocky Mountains, such as those of Waterton Lakes National Park are critically important in enhancing our understanding of global climate change and its influences on valuable source water supplies (Hauer et al., 1997). Since the cost and difficulty of adapting to water challenges are expected to increase with the magnitude and speed of global climate change, source water protection strategies are imperative to protecting these valuable supplies, particularly strategies that are not contingent upon precise predictions of said climate change (Kundzewicz et al., 2008). Therefore, studies examining the effects of wildfire on sediment dynamics over large basin scales and the impacts of this disturbance on valuable source water supplies will become increasingly important to water treatment providers and watershed managers.

Particulate phosphorus dynamics in rivers are controlled by several physical, chemical and biological factors. As the primary vector for P transport in aquatic systems, fine sediment has important implications for the form (NAIP, AP, OP) and mobility (EPC_0) of PP within these systems (House, 2003). Depending on in-stream P concentrations, fine sediment is capable of buffering and releasing SRP into the overlying water column and this is largely due to properties of fine sediment such as large surface area per mass of sediment and metal-oxide coatings to which P tends to sorb (Stone and Mudroch, 1989). Within the current body of literature on P mobility (Reddy et al., 1995; House and Dennison, 2002; McDowell and Sharpley, 2003; Jarvie et al., 2005; Ekka et al., 2006; Hoffman et al., 2009; Machesky et al., 2010, Agudelo et al., 2011; Wang and

Pant, 2010; Ekka et al., 2016) and fractionation (e.g. Beaty, 1994; Hauer and Spencer, 1998; Earl and Blinn, 2003; Spencer et al., 2003; Townsend and Douglas, 2004; Burke et al., 2005; Mast and Chow, 2008; Noske et al., 2010; Blake et al., 2010; Santos et al., 2015) in freshwater, most work has focussed on areas subjected to anthropogenic disturbance, such as agriculture and waste water treatment inputs. More recently within the literature, there has been increased focus on the effects of natural landscape disturbance, such as wildfire on P dynamics within rivers (Bladon et al., 2014; Emelko et al., 2016). These works have demonstrated that in fine sediment-dominated river systems draining glaciated mountain landscapes, elevated sediment-associated contaminant concentrations can persist for decades and have cascading effects on downstream water quality. The present study aimed to fill some existing knowledge gaps regarding P dynamics in rivers following natural landscape disturbance and the abiotic controls on fine sediment in gravel-bed rivers. This work examined the intra- and inter- site variability in sediment-associated P form and mobility across multiple typically oligotrophic gravel-bed rivers impacted by severe wildfire. Physical and geochemical properties of wildfire-impacted fine sediment were also examined.

Sediment-associated P from rivers in WLNP and surrounding areas displayed high variability within and between sites. This variability may be a function of sediment sampling sites differing in slope, vegetation and connectivity, as well as the inherently complex natural of gravel-bed rivers in terms of heterogeneity and morphology. It was found that TPP and NAIP concentrations were significantly higher in burned rivers and within burned rivers these concentrations were higher in suspended sediment fractions compared to ingressed sediment fractions. Mean TPP values across sites ranged from approximately 600 $\mu g/g_{sediment}$ to 950 $\mu g/g_{sediment}$ and these values are similar to those observed in highly degraded agricultural systems in North America and elsewhere globally, which demonstrates the ability of natural landscape disturbances such as wildfire to severely degrade pristine oligotrophic systems to the same degree as anthropogenic impacts (Emelko et al., 2016). It should be noted that further work in understanding how PP forms change with varying disturbances in conjunction with biogeochemical controls would better contextualize the results of both previous studies and the present work (Withers and Jarvie, 2008). Within fine river sediment, the bioavailable PP fraction (NAIP) was most dominant following wildfire in both burned and reference systems and this fraction has the potential to degrade water quality in reservoirs through enhanced cyanobacteria growth and potential eutrophication (Jarvie et al., 2005). These elevated NAIP concentrations did not change significantly throughout the three years of study, which demonstrates the ability of this nutrient to have lasting effects in highly dynamic river systems. Accordingly, enhanced understanding how PP forms can change with varying channel properties could benefit hysteresis and related nutrient transport studies in future works.

The geochemical constitution of riverine sediment and chemistry of the overlying water column can strongly influence SRP concentrations in aqueous environments (Froelich, 1988). In addition to PP fractionation, sediment geochemistry and particle size characteristics of fine sediment following wildfire in WLNP and surrounding areas were also examined. Peak particle size characteristics occurred across all sites two years post fire, and this corresponded to the timing of peak TPP concentrations. There were no significant grain size differences between suspended and ingressed sediment fractions within burned rivers, which may be a function of low flow conditions during time of sampling. There were significantly higher Mn concentrations in burned river sediment compared to reference sediment, which could be explained by ash produced during high combustion being rich in metal-oxides (Bodí et al., 2014). It is important to consider that the results of both the sediment geochemistry analysis and the PP speciation analysis described previously are gathered from point sampling, which could lead to inaccurate conclusions on the widespread influence of landscape disturbance. In future works, collecting information on surrounding aqueous chemistry is also recommended, as this would enhance the understanding of how sediment geochemistry relates to sediment-associated P forms in river environments.

P sorption dynamics are commonly determined through P isotherm experiments (e.g. McDowell and Sharpley, 2003; Wang and Pant, 2010), in which a known mass of sediment and a series of solutions of increasing SRP concentration are mixed (Froelich, 1988). The resulting data demonstrate the buffer capacity of sediment, as well as the equilibrium phosphorus concentration (EPC_0), which is the concentration at which sediment neither sorbs nor desorbs SRP from solution (Froelich, 1988). EPC_0 has been used to quantify sediment pressures on P dynamics in rivers, though this research has typically focussed on a single and often anthropogenic land-use impact (e.g. Agudelo et al., 2011, McDowell, 2015). In the current work, the sorption characteristics of fine riverine sediment following disturbance by wildfire in WLNP and nearby areas were examined. There was no significant difference in EPC_0 between burned and unburned river sediment. This contrasted the findings of other P sorption studies in areas affected by natural landscape disturbance by wildfire (e.g. Emelko et al., 2016) and was likely a function of the unburned reference sites being in close proximity to areas directly affected by the burn. Atmospheric deposition of P-rich pyrogenic materials likely contributed to the P mobility at reference sites being comparable to that of burned sites. Peak EPC_0 values across all sites were recorded two years post-wildfire and these concentrations were significantly higher than those recorded one and three years' post-wildfire. These peak concentrations also corresponded to peak grain size and TPP concentrations across all years of study. There were no significant differences in P mobility between suspended and ingressed sediment within burned river sediment, though the minor differences observed were likely a function of variation in surface and groundwater processes. Both ingressed and suspended sediment demonstrated the ability to act as legacy sources of P in highly dynamic, oligotrophic river systems, and displayed potential to be a source of SRP to the overlying water column, particularly during environmentally sensitive low flow conditions. The ability of sediment to modify streamwater SRP concentrations will depend on multiple factors, namely hydrologic interactions, as well as sediment surface chemistry, hyporheic exchange and biota (Simpson et al., 2021). Low flow conditions during summer are particularly vulnerable to enhanced primary productivity from increased nutrient availability (Jarvie et al., 2005) and therefore enhancing the understanding of in-stream P dynamics at this time is crucial.

This study examined the immediate effects of wildfire on sediment-associated P form and mobility in oligotrophic gravel-bed rivers draining a glaciated mountain landscape. This contrasts much of the existing research on sediment-associated P dynamics, which has largely focussed on smaller geographic areas and reported the effects of disturbance several years after the wildfire occurred. While this research provides insight on some existing knowledge gaps within the current body of literature on PP dynamics in rivers following landscape disturbance, it also highlights the need for further work in this area. While the present work demonstrated that wildfire can exert strong influence on sediment-associated P form and mobility in gravel-bed rivers, further work over a variety of landscapes, as well as differing degrees of landscape disturbance severity would better contextualize these findings. As demonstrated by the present work, even sites examined for reference conditions are still impacted to varying degrees by both natural and anthropogenic disturbances. Due to this, there is a strong need for increased research addressing the how various disturbances interact and co-influence PP forms and mobility in freshwater systems (Sharpley et al., 2013). Additionally, further work on the dynamics of fine sediment within gravel-bed rivers would be beneficial (Karna et al., 2014). For instance, while works including the present thesis have demonstrated that PP within riverbeds can contribute significant concentrations of P to the overlying water column, (eg. McDowell and Sharpley 2002) relatively little is known about the storage and fate of PP within riverine systems. Additionally, hillslope studies following wildfire would be beneficial to examine the connectivity and transport mechanisms of fine sediment between fire-affected landscapes and receiving streams. A significant remaining knowledge gap includes the post-fire impacts on water quality and water treatability, particularly in terms of enhanced sediment-associated P concentrations and proliferation of toxin-forming cyanobacteria within reservoirs. Further understanding of whether fine riverbed sediment in gravel-bed rivers could realize its potential to be sources of P to the overlying water column could inform management decisions in valuable source water areas (Withers and Jarvie, 2008).

This study is the first of its kind to be conducted in Waterton Lakes National Park, and distinguishing features of this research compared to previous studies include the size, duration, and immediacy of observation and data collection following disturbance by wildfire. Findings from this work may contribute new knowledge and enable technological innovation that is of strategic national and international importance, as it directly informs the difficult water supply challenge of evaluating trade-offs between investments in treatment technology reliance versus source water protection (Emelko and Sham, 2014). This new knowledge will be available for immediate use by utilities, reservoir mangers, land managers, regulators, and communities reliant on forested watersheds as drinking water sources. The research outcomes will enable and inform policy, technology and innovation by delivering valuable new knowledge regarding long-term impacts of wildfire on water quality and treatability. The evaluation of downstream transport and abiotic controls on wildfire-impacted fine sediment and associated bioavailable phosphorus released into drinking water supplies is critical to informing public health risks, reservoir management strategies, source water protection (SWP) strategies and potential needs for treatment process upgrades. Thus, this work may ultimately inform the development of climate change adaptation strategies and contribute to drinking water security in Canada and globally.

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Appendix A: Supplementary Information and Data

Photographs of Study Sites

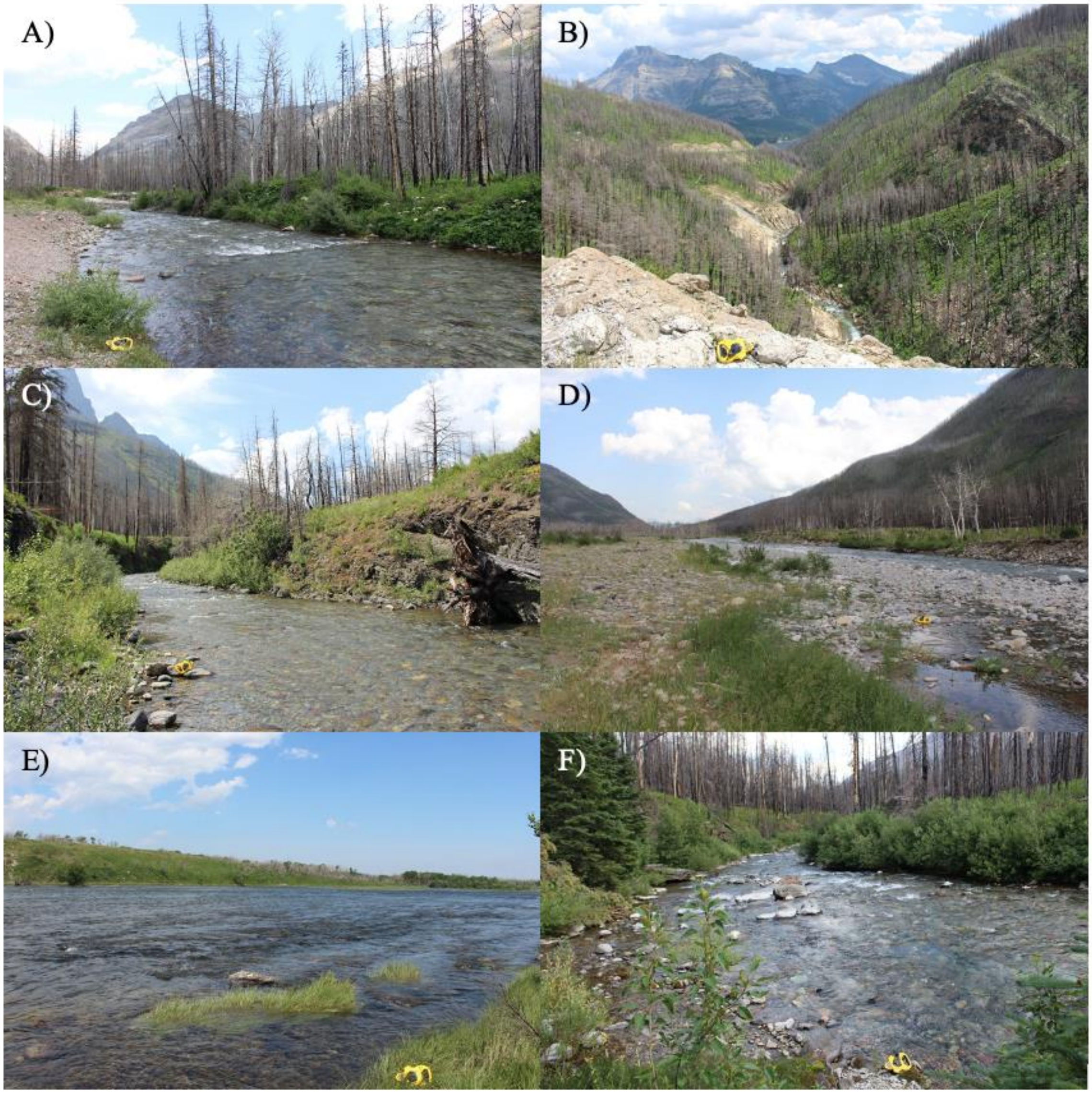

Figure A1 – Representative image of rivers within WLNP affected by the 2017 Kenow wildfire, including A) upper Cameron River B) lower Cameron River C) upper Blakiston River D) lower Blakiston River E) Waterton River and F) Bauerman River.

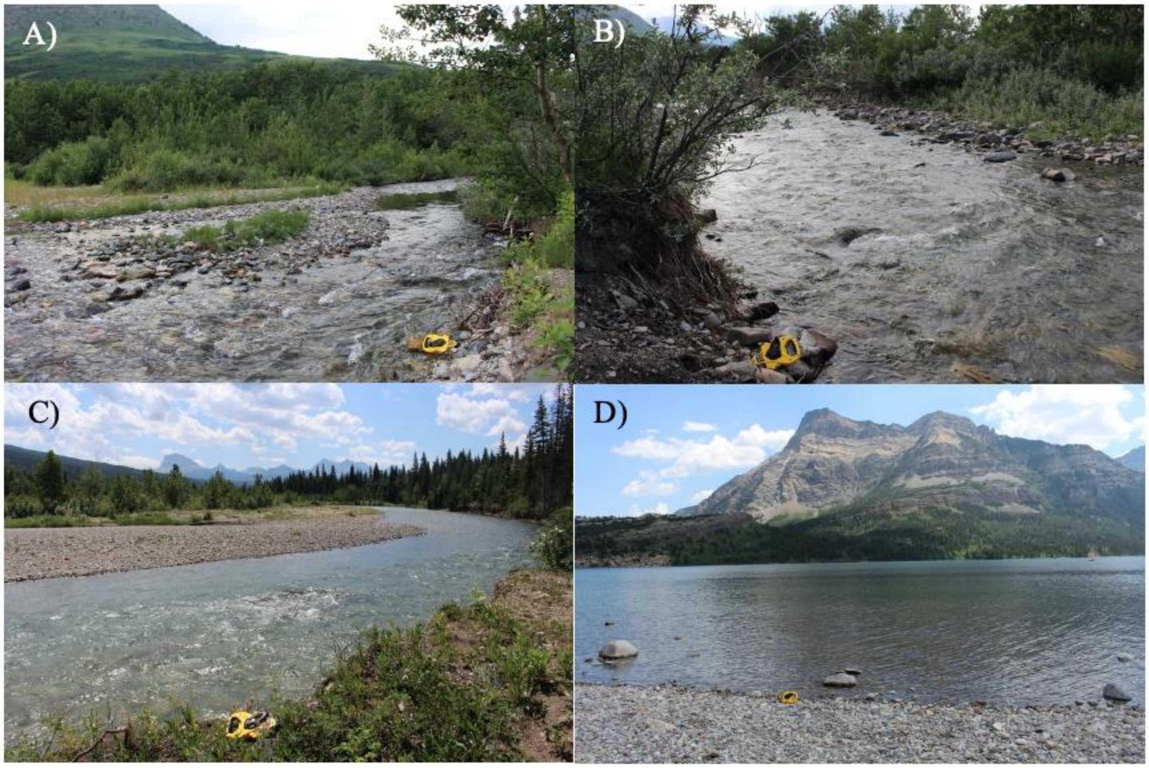

Figure A2 – Representative images of unburned reference rivers located within 30km of WLNP. A) Spionkop River, B) Yarrow River C) Belly River and D) upper Waterton Lake.

Supplementary Data

Table A1a – 2018 Mean Grain Size Distribution

River	Sediment Type	SSA (m^2/g)	d_{10} (mm)	d_{50} (mm)	d_{90} (mm)	n
UC	Suspended	0.393	0.010	0.044	0.130	1
	Ingressed	0.442	0.008	0.041	0.147	1
LC	Suspended	0.437	0.010	0.051	0.289	3
	Ingressed	0.367	0.010	0.053	0.245	2
UB	Suspended	0.217	0.021	0.104	0.358	2
	Ingressed	0.336	0.011	0.066	0.340	2
LB	Suspended	0.329	0.011	0.066	0.378	3
	Ingressed	0.368	0.010	0.051	0.209	2
Ba	Suspended	0.703	0.005	0.026	0.111	2
	Ingressed	0.446	0.008	0.044	0.311	2
W*	Suspended	0.657	0.005	0.035	0.144	1
S*	Suspended	0.488	0.009	0.044	0.132	1
B*	Suspended	0.735	0.005	0.031	0.134	2

Table A1b – 2019 Mean Grain Size Distribution

River	Sediment Type	SSA (m^2/g)	d_{10} (mm)	d_{50} (mm)	d_{90} (mm)	n
UC	Suspended	0.190	0.020	0.086	0.358	3
LC	Suspended	0.200	0.018	0.096	0.891	2
UB	Suspended	0.193	0.017	0.086	0.315	3
LB	Suspended	0.240	0.016	0.082	0.462	2
Ba	Suspended	0.215	0.021	0.103	0.387	2
W	Suspended	0.370	0.011	0.391	0.619	3
Y *	Suspended	0.113	0.032	0.426	0.783	3
S *	Suspended	0.224	0.019	0.093	0.359	2
B *	Suspended	0.292	0.012	0.403	0.665	3

Table A1c – 2020 Mean Grain Size Distribution

River	Sediment Type	SSA (m^2/g)	d_{10} (mm)	d_{50} (mm)	d_{90} (mm)	n
UC	Suspended	0.171	0.024	0.090	0.236	2
LC	Suspended	0.304	0.014	0.056	0.153	1
UB	Suspended	0.102	0.032	0.105	0.273	1
LB	Suspended	0.816	0.004	0.028	0.096	1
Ba	Suspended	0.159	0.030	0.120	0.322	2
W	Suspended	0.64	0.067	0.337	0.878	2
Y*	Suspended	0.094	0.034	0.122	0.358	2
S*	Suspended	0.437	0.011	0.046	0.122	2
B *	Suspended	0.476	0.008	0.042	0.115	1

Table A2a – Temporal distribution of mean (± standard deviation) of PP forms ($\mu g/g_{sediment}$) in suspended and bed sediment fractions from WLNP study rivers and nearby reference rivers from 2018-2020.

	NH_4Cl-RP	BD-RP	NaOH-RP	Total NAIP	AP	OP	TPP
2018 n=39	31.29 ±33.30	171.21 ±102.24	289.79 ±181.32	492.29 ±264.63	178.63 ±69.58	117.84 ±36.63	788.76 ±237.41
2019 n=24	15.36 ±14.82	126.87 ±65.92	258.13 ±141.93	400.35 ±203.42	293.17 ±108.31	67.77 ±15.90	761.28 ±137.65
2020 n=14	6.39 ±3.61	94.54 ±57.98	222.34 ±143.35	323.26 ±189.78	283.86 ±128.07	0.20 ±0.05	607.33 ±99.04

Table A2b – Distribution of particulate phosphorus forms (µg/$g_{sediment}$) in suspended and ingressed sediment fractions from WLNP study rivers and nearby reference rivers from 2018-2020 (n=77).

	NH_4Cl-RP	BD-RP	NaOH-RP	Total NAIP	AP	OP	TPP
Mean	233.46	80.84	127.42	37.82	267.66	432.90	750.61
Standard Deviation	±201.00	±75.80	±119.00	±20.30	±258.00	±413.00	±716.40
Median	109.15	51.98	101.12	44.38	163.43	240.95	199.23

Table A2c – NAIP enrichment factors in suspended and ingressed sediment fractions from WLNP study rivers and nearby reference rivers in a) 2018 b) 2019 (suspended sediment) and c) 2020 (suspended sediment).

a)

Site	Sediment	NAIP/TPP	n
UC	Suspended	0.76	3
	Bed	0.54	3
LC	Suspended	0.71	2
	Bed	0.72	2
UB	Suspended	0.77	3
	Bed	0.49	3
LB	Suspended	0.69	3
	Bed	0.70	1
Ba	Suspended	0.74	3
	Bed	0.50	2
W	Suspended	0.48	5
Y*	Suspended	0.60	3
S*	Suspended	0.55	3
B*	Suspended	0.31	3

b)

Site	NAIP/TPP	n
UC	0.59	3
LC	0.64	3
UB	0.74	3
LB	0.51	2
Ba	0.65	2
W	0.38	3
Y*	0.42	3
S*	0.41	2
B*	0.21	3

c)

Site	NAIP/TPP	n
UC	0.74	2
LC	0.49	1
UB	0.77	1
LB	0.25	1
Ba	0.62	2
W	0.31	2
Y*	0.67	2
S*	0.37	2
B*	0.30	1

Table A3 – Major elements (averages ± standard deviation by site) for suspended and bed sediment collected in Waterton Lakes National Park study rivers and nearby reference rivers from 2018-2020.

	Al	Fe	Mn	Mg	Ca	Na	K	P_2O_5	OC
Cameron River n=18	1.69 ±0.62	3.05 ±2.54	0.07 ±0.04	1.48 ±0.40	1.66 ±1.08	0.26 ±0.47	0.42 ±0.09	0.20 ±0.04 n=5	3.09 ±2.72 n=8
Blakiston River n=19	1.69 ±0.50	2.54 ±2.39	0.09 ±0.04	1.55 ±0.63	2.24 ±1.03	0.23 ±0.60	0.45 ±0.14	0.24 ±0.04 n=5	5.05 ±3.54 n=10
Bauerman River n=10	2.06 ±0.61	2.81 ±2.36	0.12 ±0.09	1.78 ±0.48	2.42 ±1.05	0.26 ±0.69	0.59 ±0.15	0.23 ±0.01 n=2	4.21 ±2.51 n=5
Waterton River n=10	2.34 ±0.41	2.08 ±0.28	0.17 ±0.09	2.31 ±0.23	3.02 ±0.57	0.04 ±0.02	0.56 ±0.13	0.19 ±0.02 n=3	2.86 ±0.83 n=5
Yarrow River* n=6	2.11 ±0.42	2.30 ±0.37	0.06 ±0.01	2.05 ±0.30	2.93 ±0.21	0.09 ±0.09	0.74 ±0.22	0.20 ±0.05 3	6.20 n=1
Spionkop River* n=6	1.97 ±0.27	2.09 ±0.28	0.05 ±0.01	1.37 ±0.22	2.13 ±0.37	0.04 ±0.02	0.53 ±0.12	0.21 ±0.03 n=2	5.80 ±4.10 n=2
Belly River* n=7	2.11 ±0.40	2.19 ±0.30	0.07 ±0.03	1.57 ±0.23	2.40 ±0.14	0.05 ±0.02	0.52 ±0.15	0.17 ±0.01 n=3	3.03 ±1.46 n=3

Table A4 – Sorption isotherm linear equations and ECP$_0$ concentrations (μgL^{-1}) for suspended and bed sediment from Waterton Lakes National Park study rivers and nearby reference rivers (2018-2020). Sampling in each year occurred in summer and fall campaigns due to weather and accessibility, with 2018 sampling occurring in early July (S1), late August (S2), early September (F1), early October (F2) and Early November (F3), 2019 sampling occurring in early June (S1), mid-August (S2) and mid-October (F1) and 2020 sampling occurring in early July (S1), early August (S2) and early October (F1) . Missing data is a result of a lack of adequate sediment mass for complete analysis, in which case partial analyses were completed.

Site	Year	Season	Sampling	Sediment Type	Slope	y-Intercept	EPC$_0$	R^2
UC	2018	S	1	suspended	0.06	-55	997	1.00
UC	2018	F	2	bed	0.08	-16	198	0.99
UC	2018	F	2	bed	0.09	-14	161	0.99
UC	2018	F	2	bed	0.10	-1	7	0.99
LC	2018	S	1	suspended	0.09	-15	162	1.00
LC	2018	S	2	suspended	0.09	-16	166	1.00
LC	2018	F	1	bed	0.10	-4	41	1.00
LC	2018	F	1	bed	0.09	-30	341	1.00
LC	2018	F	1	bed	0.09	-10	119	1.00
UB	2018	S	1	suspended	0.08	-44	569	0.98
UB	2018	S	2	suspended	0.12	-190	1601	0.98
UB	2018	F	1	bed	0.04	-18	422	0.98
UB	2018	F	1	bed	0.10	-2	17	1.00
UB	2018	F	1	bed	0.09	-6	64	0.99
UB	2018	F	2	suspended	0.27	-211	791	0.98
LB	2018	S	1	suspended	0.08	-26	315	0.99
LB	2018	S	2	suspended	0.09	-174	2037	1.00
LB	2018	F	1	bed	0.09	-20	222	0.99
LB	2018	F	1	bed	0.10	-9	87	1.00
LB	2018	F	1	bed	0.08	-38	480	0.98
Ba	2018	S	1	suspended	0.06	-66	1132	0.96
Ba	2018	S	2	suspended	0.08	-125	1522	0.99
Ba	2018	F	1	bed	0.05	-57	1063	0.91
Ba	2018	F	1	bed	0.06	-39	602	0.97
Ba	2018	F	1	bed	0.09	-11	118	1.00
W	2018	S	1	suspended	0.05	-30	577	1.00
W	2018	S	2	suspended	0.06	-84	1467	1.00
W	2018	S	2	suspended	0.10	-175	1711	1.00
W	2018	F	3	suspended		-78		
W	2018	F	3	suspended	0.11	-68	630	0.92

Y*	2018	S	1	suspended		-116		
Y*	2018	S	2	suspended		-233		
Y*	2018	F	3	suspended		-284		
S*	2018	S	1	suspended	0.27	-211	791	0.97
S*	2018	S	2	suspended	0.06	-57	1023	1.00
S*	2018	F	3	suspended	0.12	-190	1544	1.00
B*	2018	S	1	suspended	0.07	-14	205	0.99
B*	2018	S	2	suspended	0.06	-25	408	0.99
B*	2018	F	3	suspended	0.06	-108	1855	1.00
UC	2019	S	1	suspended	0.07	-57	835	1.00
UC	2019	F	1	suspended		-87		
LC	2019	S	1	suspended	0.10	-47	467	0.99
LC	2019	F	1	suspended	0.06	-56	974	0.99
UB	2019	S	1	suspended	0.08	-103	1214	0.99
UB	2019	S	2	suspended		-166		
LB	2019	S	1	suspended	0.06	-97	1512	0.99
LB	2019	F	1	suspended	0.07	-52	754	0.95
Ba	2019	S	2	suspended	0.09	-16	185	0.99
Ba	2019	F	1	suspended	0.12	-182	1504	0.99
W	2019	S	1	suspended	0.05	-19	381	0.91
W	2019	S	2	suspended	0.08	-156	2047	0.99
W	2019	F	1	suspended	0.07	-123	1856	0.99
Y*	2019	S	1	suspended	0.04	-36	872	0.97
S*	2019	S	1	suspended		-184		
S*	2019	F	1	suspended	0.08	-154	1829	1.00
B*	2019	S	1	suspended	0.10	-4	43	1.00
B*	2019	S	2	suspended	0.05	-7	129	1.00
B*	2019	F	1	suspended	0.06	-48	837	0.99
UC	2020	S	1	suspended	0.08	-29	343	0.99
UC	2020	F	1	suspended		-23		
LC	2020	S	1	suspended	0.07	-14	201	0.98
UB	2020	S	1	suspended	0.07	-127	1792	0.93
LB	2020	S	1	suspended	0.05	-33	605	0.94
Ba	2020	S	2	suspended	0.05	-28	572	0.91
Ba	2020	F	1	suspended		-224		
W	2020	S	2	suspended	0.06	-26	425	0.95
W	2020	F	1	suspended	0.06	-79	1356	1.00
Y*	2020	S	1	suspended	0.05	-33	631	1.00
Y*	2020	F	1	suspended		-210		

S*	2020	S	1	suspended	0.07	-11	167	0.99
S*	2020	F	1	suspended		-37		
B*	2020	F	1	suspended		-20		

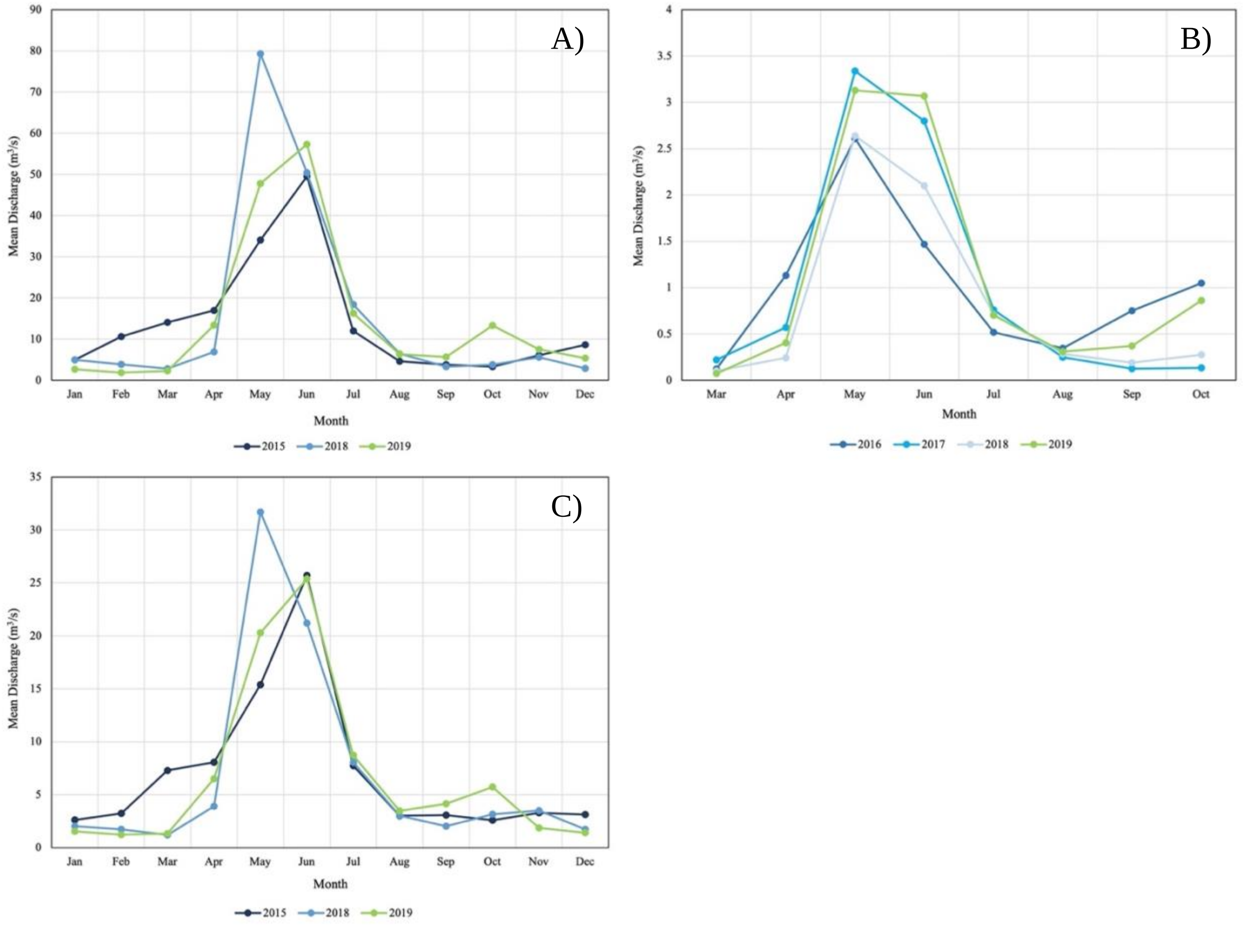

Figure A3 – Mean monthly discharge data from A) Waterton River Near Waterton Park, B) Yarrow Creek at Spread Eagle Road and C) Belly River Near Mountain View. Note the different y-axis values.

Appendix B: Quality Control/Quality Assurance

Phosphorus Speciation QA/QC

Table B1 – Particulate phosphorus speciation duplicate analyses from Act Labs.

Analyte Symbol Unit Symbol Detection Limit Analysis Method	AP ppm 0.02 HCL-RP	OP ppm 0.02 Refractory P	NAIP ppm 0.02 BD-RP	NAIP ppm 0.02 NH4CL-RP	NAIP ppm 0.02 NaOH-RP
UB#1 9_08_18 Orig	361	30.1	46.4	< 10	74.3
UB#1 9_08_18 Dup	361	34.9	41	< 10	74.6
UC#2 10_08_18 Orig	277	47.7	107	< 10	321
UC#2 10_08_18 Dup	272	46.2	109	< 10	322
UC#3 10_08_18 Orig	287	47.4	78.3	< 10	256
UC#3 10_08_18 Dup	281	46.2	79.4	< 10	254
Ba 8_03_19 Orig	223	56.8	158	10.2	344
Ba 8_03_19 Dup	222	61.8	155	< 10	328
UB 10_17_19 Orig	171	60.1	168	59.6	358
UB 10_17_19 Dup	176	59.8	164	55.7	359
W 8_14_19 Orig	362	75.2	186	10.2	153
W 8_14_19 Dup	370	75.8	181	< 10	156

Table B2 – Major element sediment geochemistry duplicate analyses from Act Labs.

Analyte Symbol	Al	Fe	Mg	Mn	Ca	Na	K	P2O5	C
Unit Symbol	%	%	%	ppm	%	%	%	%	%
Detection Limit	0.01	0.01	0.01	1	0.01	0.001	0.01	0.001	0.01
Analysis Method	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	AR-MS	CS
LC#2 10_08_18 Orig	1.96	1.77	1.62	595	1.42	0.04	0.37	0.067	7.02
LC#2 10_08_18 Dup	2.15	1.8	1.7	603	1.45	0.042	0.38	0.068	7
UB#3 8_09_18 Orig	2.41	2.26	2.81	433	3.19	0.024	0.74	0.053	
UB#3 8_09_18 Dup	2.34	2.3	2.77	439	3.22	0.023	0.75	0.053	
W 7_05_18 Orig									3.44
W 7_05_18 Dup									3.42
LB 8_27_2018 Orig									11
LB 8_27_2018 Dup									11.1
B 8_14_19 Orig								0.18	
B 8_14_19 Dup								0.18	
W 6_19_19 Orig	2.69	2.24	2.47	705	3.04	0.038	0.71		
W 6_19_19 Dup	2.85	2.33	2.57	732	3.14	0.039	0.73		

Phosphorus Sorption QA/QC

Table B3 – Quality control cups were placed in triplicate evenly throughout runs, with all standard deviations falling below 5μg P L^{-1}.

50μg P L^{-1} Calibrant	Mean	St Dev	200 μg P L^{-1} Calibrant	Mean	St Dev	400μg P L^{-1} Calibrant	Mean	St Dev
53.488 48.757 48.602	50.282	2.777	199.001 208.541 204.339	203.960	4.781			
53.029 51.102 55.904	53.345	2.417	190.449 198.524 194.908	194.627	4.045	381.407 390.358 388.13	386.632	4.660
49.035 52.658 46.57	49.421	3.062	205.127 200.7 195.215	200.347	4.965	390.088 398.807 398.37	395.755	4.913
47.023 47.097 51.074	48.398	2.318	196.796 197.203 201.105	198.368	2.379	395.007 395.869 396.572	395.816	0.784

Table B4 – Quality control cups with null samples were placed in triplicate evenly throughout runs to ensure cleanliness of glassware, with all samples indicating lack of phosphorus contaminations and all standard deviations falling below 5µgP/L.

0µg P L^{-1} Calibrant	Average	St Dev
-4.927 -5.555 -2.508	-4.330	1.609
-4.012 -3.955 -2.679	-3.549	0.754
-4.837 -5.486 -5.143	-5.155	0.325
-2.906 -7.363 -0.091	-3.453	3.667
-7.353 -10.053 -10.312	-9.239	1.639
-5.152 -4.541 -7.112	-5.602	1.343