# Impact of the Horse River wildfire on the form and mobility of particulate phosphorus in a drinking water reservoir: Efficacy of dredging to manage internal phosphorus loading

by

Brittany Francescangeli

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# Author’s Declaration

I hereby declare that I am the sole author of this 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.

# Abstract

Forests are critical source water regions that are under increasing threat of wildfire which can accelerate the transfer of sediment from hillslope to receiving streams and downstream environments such as reservoirs. These pyrogenic materials are often enriched in bioavailable forms of phosphorus (P) that can alter the nutrient status of reservoirs and challenge drinking water treatment and the provision of safe drinking water. The purpose of this study is to examine abiotic controls on the form and mobility of particulate phosphorus (PP) in fine benthic sediment of two drinking water reservoirs in Alberta, Canada with special emphasis on the effects of the 2016 Horse River Wildfire and post-fire dredging. Bottom sediment was collected from wildfire- and non-wildfire-impacted drinking water reservoirs post-wildfire in 2017 and after dredging in 2020. A sequential extraction scheme and bench-top sorption isotherm experiments were conducted to assess the influence of severe wildfire on the form (non-apatite inorganic P, apatite P, organic P) and mobility (equilibrium phosphorus concentration, $EPC_0$) of PP, respectively in these systems. Post-wildfire and post-dredge sediments in the wildfire-impacted reservoir were evaluated to assess the efficacy of dredging as a management technique to control internal P loading in the reservoir.

Total particulate P (TPP), bioavailable PP and $EPC_0$ in wildfire-impacted reservoirs were significantly higher than in non-wildfire-impacted reservoirs. Post-dredge sediments had lower concentrations of TPP but a higher proportion of that TPP was total bioavailable P (NAIP) relative to what was observed at initial post-wildfire conditions. The $EPC_0$ of post-dredge sediment was significantly higher compared to initial post-wildfire conditions, which suggests that sediment from the wildfire-impacted drinking water has the potential to act as a long-term source of soluble reactive phosphorus (SRP) to the water column. Due to persistent inputs of external P-enriched wildfire materials from the Athabasca River, one-time dredging is likely not a sufficiently effective strategy for mitigating the effects of internal P loading in the reservoir. Dredging, coupled with other treatment options such as the addition of coagulants and a redesign of the reservoir to reduce sunlight should be further investigated as a more sustainable solution to internal P loading and mitigation of algal blooms in drinking water reservoirs.



*Keywords:* fine sediment, particulate phosphorus speciation, equilibrium phosphorus concentration, dredging, water treatment

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# List of Abbreviations

AP- apatite phosphorus

BD-RP – bicarbonate-dithionite reactive phosphorus

$EPC_0$ – equilibrium phosphorus concentration

FMM – Fort McMurray Reservoir

GMR – Glenmore Reservoir

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

# Chapter 1

# Introduction

## 1.1 Background

Forest ecosystems play a critical role in providing clean source waters for many drinking water supplies worldwide (Brown et al., 2004; Neary et al., 2009; Jones et al., 2009, Vose et al., 2016). The annual value for the natural storage and filtration of water by forests is estimated at ~$4.1 trillion US (2013) globally (Costanza et al., 1998). However, the stability of forests to provide adequate and continuous amounts of clean drinking water is threatened by climate change (Emelko et al., 2011; Emelko & Sham, 2014). The frequency and severity of climate change-exacerbated hydro-climactic conditions and landscape disturbances are increasing (Robinne et al., 2016; Robinne et al., 2019; IPCC, 2022). In many parts of the world, extreme drought, and extended fire seasons (Liu et al., 2013) have increased the incidence and risk of more frequent and extreme wildfires (Overpeck & Udall, 2020). In North America and Australia, a new class of "mega-fires" exceeds all efforts of control and represents <1% of total annual fires yet is responsible for ~90-95% of total area burned (Gelber & Bach, 2007). Although wildfires are a critically important natural disturbance, with temperatures projected to increase beyond 1.5°C in the next two decades, the benefits of natural wildfire regimes are expected to be exceeded (IPCC, 2013; 2022).

Extreme wildfires significantly alter the hydrological cycle through the removal of vegetation cover and changes to soil properties which collectively impact the timing and magnitude of streamflow (Neary & Gottfried, 2003; Shakesby & Doerr, 2006; Verma & Jayakumar, 2012; Pechony & Schindell, 2010; IPCC, 2013; Williams et al., 2019). It is widely recognised that the amount fine sediment (<63 μm) and associated nutrients (i.e., P) entering streams via surface runoff is significantly higher in burned landscapes (Kunze & Stednick, 2006; Malmon et al., 2007; Silins et al., 2009, 2014; Moody et al., 2013; Son et al., 2015). These suspended particulate materials are transported downstream and become progressively finer (Paola et al., 1992; Fedele & Paola, 2007). Fine grained materials have low settling velocities and are propagated long distances downstream in rivers to receiving waters such as lakes and reservoirs where they settle and accumulate (Haralampides et al., 2003). In rivers, fine particulate matter (<63μm) can convey upwards of 90% of adsorbed contaminants, including phosphorus, despite making up only a small

fraction (<10%) of sediment mass transported (Wentworth, 1922; Crouch et al., 2006). Fine sediment is the primary vector for P transport (Binkley & Brown, 1993; Shantz et al., 2004) due to its biological, physical, and geochemical properties that preferentially bind and transport PP. These properties include - but are not limited to - large specific surface area, metal oxyhydroxide surfaces and environmental conditions such as redox (Stone & Mudroch, 1989; Stone & English, 1993; Withers and Jarvie, 2008; Emelko et al., 2016). While it has been widely reported that sediment originating from agricultural and urban landscapes can have elevated levels of P, only recently has more attention been directed towards understanding the effects of wildfires on the quality of particulate matter and implications of their downstream transport on water quality of receiving bodies such as lakes and reservoirs. More research in this area is crucial as the export of wildfire-impacted fine sediment to drinking water reservoirs can act as a legacy source of P which deteriorates water quality, promotes algal blooms, and significantly challenges drinking water treatment operations (Watt et al., 2021).

The accumulation of fine P-enriched benthic sediments in drinking water reservoirs has the potential to act as a legacy source of P by releasing P into the water column via desorption and dissolution through a process called internal loading (Withers & Jarvie, 2008; Nurnberg et al., 2013; Nurnberg & LaZerte, 2016). The sorption processes that cycle soluble reactive P (SRP) to/from benthic sediments into the overlying water column are largely influenced by physical and geochemical properties of sediments as well as environmental conditions in water bodies (Jarvie et al., 2006). Phosphorus (P) comes in many forms and has been identified as the limiting nutrient in freshwater ecosystems (Schindler, 1977; Schindler et al., 2008). It is well documented that streams draining wildfire impacted landscapes have elevated levels of total P (TP) and for many years following a moderate to severe wildfire, elevated levels of soluble reactive P (SRP) and particulate P(PP) can occur (Emelko et al., 2016). In burned landscapes PP can occupy >94% of TP (Lane et al., 2008; Blake et al, 2005) with a significantly higher fraction of bioavailable NAIP compared to non-wildfire-impacted landscapes (Stone et al., 2011; Emelko et al., 2016). Particulate-associated NAIP and dissolved SRP are the most bioavailable forms of P (Stone & Droppo, 1994; Emelko et al., 2016). These P forms are potentially available for the proliferation of algal blooms and toxic cyanobacteria, two of the biggest threats to the provision of safe drinking water in Canada and worldwide (Nurnberg, 1988; Crittenden et al., 2012). The resulting

deterioration and erratic fluctuations in source water quality can challenge water treatment operations and increase treatment costs (Emelko et al., 2011; Emelko & Sham, 2014).

In recent years, there has been an increasing interest in the impact of wildfire on the transformation of sediment chemistry and phosphorus characteristics (Bodi et al., 2014) and how these materials influence nutrient dynamics in both rivers (Emelko et al., 2016; Wilkes et al., 2018) and lakes (Sondergaard et al., 2013; Orihel et al., 2017; Mohamed et al., 2019). Research on potential management strategies to prevent the release of P from benthic sediments (i.e., additions of coagulants) have also been explored (Emelko et al., 2011; Huser et al., 2016; Knezic, 2021). Currently, the influence of wildfire impacted sediment-associate P on water quality and treatability in drinking water reservoirs as well as the efficacy of dredging as a reliable strategy to reduce internal P loading in the water column are poorly understood.

The primary goal of this study is to evaluate the composition and abiotic control of wildfire generated sediment-associated P on nutrient dynamics in drinking water reservoirs. Specifically, this study examines the effects of the 2016 Horse River Wildfire in Fort McMurray (FMM), Alberta, on the form and mobility of PP in drinking water reservoirs. To our knowledge, this study it is the first of its kind to examine the long-term efficacy of dredging as a management approach to mitigate the effects of internal P loading in a drinking water reservoir post-wildfire. This research provides a unique opportunity to explore the form and mobility of sediment-associated PP in a wild-fire impacted drinking water reservoir as well as quantifying the effects of dredging as a management technique.

## 1.2 Research Objectives

The overall goal of this research is to investigate the effects of the Horse River Wildfire on the form and mobility of P in benthic sediment and the evaluate the influence of post-fire dredging on internal P loading and water quality in the Region of Wood Buffalo Municipality (RWBM) drinking water reservoir in FMM. These data will be compared to P form and mobility data from the non-wildfire impacted Glenmore reservoir in Calgary, Alberta. The specific objectives of this investigation are to:

(1) Characterize the particulate phosphorus forms (NAIP, AP, OP) in benthic sediments of a wildfire-impacted and non-wildfire-impacted drinking water reservoir,

(2) Characterize the geochemical properties of reservoir benthic sediment in both reservoir types and examine their relationships with particulate phosphorus forms,

(3) Evaluate the mobility ($EPC_0$) of fine benthic sediment-associated phosphorus in wildfire-impacted and non-wildfire-impacted drinking water reservoir to evaluate the efficacy of post-fire dredging to reduce internal loading of P in reservoirs, and

(4) Discuss the implications of wildfire-impacted fine sediment on water quality and treatability and the efficacy of one-time dredging as a long-term water management solution to reduce internal P loading.

While increasing research has been directed toward evaluating effects of wildfire on P form and mobility in rivers, studies of the effects of wildfire-impacted materials on nutrient dynamics in reservoirs are scant. This study is unique because it (i) examines inter- and intra-site distribution in P form/mobility in a reservoir impacted by wildfire and contrasts it to that in a reference (unimpacted by wildfire) reservoir and (ii) discusses the efficacy of one-time dredging as a long-term water management solution to reduce internal P loading. These insights are foundational to developing effective and sustainable strategies for managing algae/cyanobacteria threats to the provision of safe drinking water.

# Chapter 2

# Literature Review

Chapter 2 is a review of the literature that focuses on 1) the impacts of wildfire on sediment delivery and quality; 2) the forms, transport and availability of P and the implications on water quality; 3) P cycling in reservoirs; and 4) the implications of internal P loading and the consequences and challenges to drinking water treatment. The research gaps in the literature and subsequently the importance of this research for drinking water quality are stated throughout.

## 2.1 The Importance of Forested Landscapes for Water Supply

Worldwide, the highest source water quality originates from forested landscapes (Brown et al., 2004; Neary et al., 2009; Vose et al., 2016; Murphy, 2020). Forests cover approximately one-third (4 billion ha) of the global land mass (Constanza et al., 1997) and provide a wide range of economic and ecosystem services (Constanza et al., 1997; Ovando & Brouwer, 2019). Forested landscapes play a critical role in the movement of water through the ecosystem from hillslopes to receiving waters (Shakesby & Doerr, 2006), offering protection to headwaters and reservoirs through natural storage and filtration as well as maintaining the global water balance by cycling water between the land, ocean, and atmosphere (Andreassian, 2004). Streamflow quality and quantity is regulated through a range of hydrological and biogeochemical processes such as evapotranspiration (ET) and infiltration, water storage, nutrient cycling, soil erosion and sediment transport (Andreassian 2004; Farley et al., 2005; Ellison et al., 2017; Filoso et al., 2017; Li et al., 2021).

In healthy ecosystems, the forest floor is typically rich in organic matter creating an environment with a diverse network of organisms. Natural processes such as root growth and decay, seasonal changes, weather events, subsurface erosion and animal burrows all increase soil porosity, the amount and size of macropores, and water conductivity of the soil (Neary et al., 2009). Forests are often located in regions with high levels of precipitation (Costanza et al., 1997). The vegetation acts as a canopy, intercepting rainfall and facilitating evapotranspiration that cycles water from the earth's surface back to the atmosphere (Moody et al., 2001; Neary & Gottfried, 2003; Woods & Balfour, 2010). Leaf litter disperses raindrop energy and soil organic matter

improves stability of soil aggregates, together promoting high infiltration rates and protecting against soil erosion (Loaiciga et al., 2001; Neary et al., 2009). The majority of rainfall runoff occurs during large precipitation events and in landscapes with high topographical relief, precipitation may exceed infiltration rates forcing water downslope as Hortonion overland flow (Shakesby & Doerr, 2006; Neary et al., 2009). In low lying forest landscapes (i.e., wetlands, floodplains, etc.), large precipitation events can increase the water table to the soil surface preventing infiltration resulting in variable source area runoff (Richardson et al., 2012). Forests infiltrate precipitation into the soil where it is used for plant transpiration or will enter streams or groundwater from subsurface pathways (DeBano, 2000; Neary et al., 2009) producing large quantities of high-quality water (Costanza et al., 1997).

The annual value for natural water storage and filtration by forests is estimated at ~ $4.1-trillion US (2013) globally. Forests are critical in the supply of high-quality water for domestic, agricultural, industrial, and ecological needs (Costanza et al., 1997). The annual value for natural water storage and filtration by forests is estimated at ~ $4.1-trillion US (2013) globally. In fact, nearly two-thirds of municipalities in the United States and roughly one-third of the world's largest cities rely predominantly on forests for the provision of drinking water (CHIFM, 2008). Between 2000 and 2012, roughly 1.5-1.7 million $km^2$ (~3.2% globally) of forest cover was lost to agricultural land conversion, logging, and wildfires (Ellison et al., 2017). Increased anthropogenic pressure on watersheds is raising concern about the effects of landscape change on water cycles and the degradation of downstream water supplies (Jarvie et al., 2013; Emelko & Sham, 2014; Goyette et al., 2018; Watt et al., 2021). All drinking water requires at least some treatment (Emelko et al., 2019)—deteriorating source water quality not only threatens human health, but it also increases both capital and operations and maintenance costs associated with drinking water treatment (Ernst et al., 2004; Emelko & Sham, 2014; Price et al., 2017; Pan et al., 2022). Treatment should not be the only safeguard for clean drinking water. Protecting source water forested regions reduces erosion and sediment, improves source water quality, and reduced the costs of drinking water treatment (Ernst et al., 2004; Emelko & Sham, 2014).

## 2.2 Impacts of Climate Change on Surface Water Quality

Water is arguably the most essential natural resource on earth, yet freshwater systems are critically threatened by human activities (Vorosmarty, 2005; WWAP, 2009) and further exacerbated by climate change (Paerl et al., 2012; Emelko & Sham, 2014; IPCC, 2022). The Intergovernmental Panel on Climate Change (IPCC) reports that averaged over the next two decades, global temperatures will likely exceed 1.5°C from present conditions. Higher temperatures are a strong driver of greater aridity and more severe climate extremes and drought thereby increasing hydrologic stress on agriculture, river, and forest systems. (Dale et al., 2001; Pechony & Shindell, 2010; Overpeck & Udall, 2020). It has been widely acknowledged that some of the major rivers in the American west (i.e., Colorado, Rio Grande, Columbia) have experienced a decline in flow which has largely been attributed to the burning of fossil fuels (Das et al., 2011; Vano et al., 2014; Woodhouse et al., 2016; Overpeck & Udall, 2017; Lehner et al., 2017; Milly & Dunne, 2020). Recent reports indicate more northerly temperature-driven river flow declines in the Rocky Mountains and Missouri river basins (Martin et al., 2020). Warmer conditions also contribute to drier soils (Williams et al., 2020), widespread tree death (Breshears et al., 2005), insect infestation (Dale et al., 2001; Kurz et al., 2008) and more frequent severe wildfires across western North America (Flannigan et al., 2006; Westerling et al., 2006; Abatzoglou & Williams, 2016). Forested landscapes are critical source water regions that supply abundant renewable water resources for humans and freshwater ecosystems. However, climate change-exacerbated landscape disturbance is impacting the quality of water originating from these landscapes that challenges the treatment and provision of sustainable drinking water supply in North America (Emelko & Sham, 2014).

### 2.2.1 Wildfire Effects on Soils, Sediment Delivery, and Water Quality

Wildfires are an important natural disturbance for healthy terrestrial and aquatic ecosystems because of their influence on the function and structure of ecological communities and biogeochemical cycling (Boerner, 1982). Historically, climate change has strongly influenced fire events, with periods of drought experiencing more frequent and severe fires (Dale et al., 2001; Pierce et al., 2004; Overpeck & Udall, 2020). The IPCC reports that climate warming will exacerbate the risk of more frequent and larger fires (IPCC, 2013) and extended fire seasons (Liu et al. 2013), particularly in Canada, the western U.S., South America, central Asia, southern

Europe, southern Africa, and Australia (Pechony & Shindell, 2010; Wotton et al., 2010). New evidence reports that 2020 was the worst year for wildfires on record, globally (IPCC, 2022). Despite advancements in fire suppression technology and management, the combination of climate change and incidents of increased droughts, fuel load accumulation, and greater human presence in forests are increasing the incidence of large extreme wildfires (Westerling et al., 2006; Wotton et al., 2010; Abatzoglou et al., 2016). Globally, there has been an alarming increase in "mega-fires", a rare new class of wildfire that exceed all efforts at control (TBI, 2005). In North America and Australia, mega-fires represent <1% of total annual wildfires yet are responsible for ~90-95% of area burned (Gelber & Bach, 2007). These fires are catastrophic, significantly threatening human safety and result in enormous ecological and economic losses (Teague et al., 2009; GFMC). The projected increase of catastrophic fires raises particular concern for the security of high-quality drinking water originating from forested landscapes (Emelko et al., 2011; Emelko & Sham, 2014).

Wildfire threats to water supplies are recognized globally (Robinne et al., 2016; 2019; Mishra et al., 2021). They can significantly alter the hydrological cycle through the removal of vegetation cover and changes to soil properties impacting the timing and magnitude of streamflow (Veenhuis, 2002; Neary & Gottfried, 2003; Shakesby & Doerr, 2006; Jones et al., 2009; Verma & Jayakumar, 2012). The spatial extent of these landscape changes is largely dependent on the temperature and duration of fire (Shakesby & Doerr, 2006). The combustion of forest vegetation and surface organic matter temporarily eliminates or reduces interception, thereby reducing evapotranspiration and increasing the amount of precipitation reaching the soil surface (Loaiciga et al., 2001; Neary & Gottfried, 2003). In combination with the latter, the consumption of soil organic matter reduces infiltration (Neary & Gottfried, 2003) leading to increased soil moisture, runoff, and streamflow (Neary et al., 2003). Wildfires can also cause either short-term, long-term, or permanent changes to soil characteristics (Veenhuis, 2002). In some environments (most prominent in coarse, dry soils), wildfires can result in the development of a hydrophobic layer at or near the soil surface (Shakesby & Doerr, 2001; Huffman et al., 2001; Wilkinson et al., 2020). Water repellent layers obstruct soil wetting and infiltration leading to more rapid overland runoff (Huffman et al., 2001; Neary & Gottfried, 2003). Furthermore, wildfires reduce infiltration by the sealing of pores by fine soil and ash particles (Campbell et al., 1977; Neary et al., 1999) development of a fungal crust (Lavee et al., 1995) and compaction of soil surface by raindrop impacts (Chanasyk et al., 2003). High severity fires also have varying impacts on soil aggregate

stability - from disaggregation to strong aggregation - depending on soil characteristics (Huffman et al., 2001).

The complete or partial conversion of organic matter (i.e., biomass, detritus, soil organic matter) into ash and combustion products have different physical and chemical properties (Verma & Jayakumar, 2012). Ash consists of organic, inorganic (i.e., mineral ash), mineral soil particles and exogenous fractions (Boerner, 1982; Bodi et al., 2014). Depending on the severity of the burn, the nutrient elements in organic biomass will either be lost to the atmosphere, deposited as ash, or remain tied up in incompletely burned organic matter (Boerner, 1982). Carbon (C) is the main organic constituent in ash (Almendros et al., 2003). Wildfires with incomplete combustion (~ T< 450 °C) produce ash with a darker colour and high organic C content. During fires with high combustion completeness (~ T>450 °C), most carbon is volatized, and ash is lighter in colour with an elevated pH in solution (Pereria et al., 2012; Bodi et al., 2014). Incomplete combustion transforms organic matter into C-enriched pyrogenic compounds that are highly aromatic and hydrophobic in nature (Bodi et al., 2014). Depending on plant species present, inorganic constituents are mainly Ca, Mg, K, Si, and less so P, Na, S as well as metals Al, Fe, Mn and Zn (Wang et al., 2015). Following wildfire, the input of these elements can increase (P, Ca, Mg, K, Mn) or decreased (C, N) based on volatility which is contingent on fire temperature (White et al., 1973; Boerner, 1982) as exemplified by Bodi et al., (2014) in Figure 1. Therefore, burn severity controls the relative proportion of elements contained in ash which, when eroded and redistributed, can alter downstream biogeochemical dynamics and deteriorate water quality (Boerner, 1982; Bodi et al., 2014).

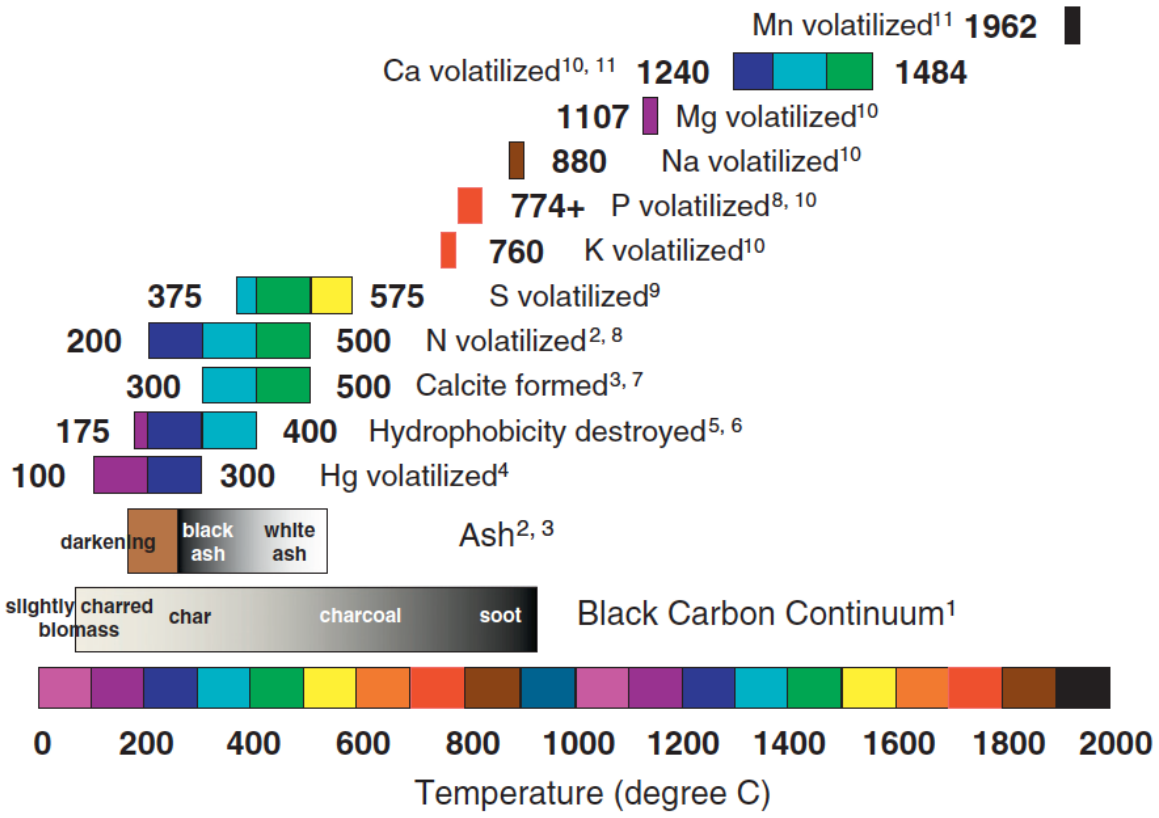


**Figure 1:** Major Temperature Thresholds that Affect Ash and Soil Chemistry (Bodi et al., 2014)

After wildfire, vegetation is reduced or absent and more precipitation reaches the land surface (Williams et al., 2019). It is widely documented that wildfires lead to elevated discharges and higher peak flows in streams draining burned catchments (Loaiciga et al., 2001; Moody & Martin, 2001; Legleiter et al., 2002). In burned landscapes, moderate to heavy precipitation can elevate peak flows 5-870x compared to non-wildfire-impacted reference sites (Moody & Martin, 2001; Neary & Gottfried, 2003). The magnitude and recovery of the increase in post-fire peak flow is different in various landscape and depends greatly on multiple variables (i.e., topography, soil and vegetation type, catchment size) which makes the accuracy of these studies limiting. A unique study by Moody & Martin (2001) compares stream flow data from the same catchment pre- and post-wildfire revealing a 2- to 5x increase in peak flow over a 6–7-year period. Overall, wildfires can enhance precipitation runoff generating disproportionately large peak flows, shortened lag time and increased flooding in a variety of landscapes (DeBano, 1981; Morgan & Erickson, 1995; Price, 1997; Zwolinkski, 2000; Moody & Martin 2001; Thompson & Waddington, 2013).

Wildfires increase sediment erosion rates (Kunze & Stednick, 2006; Silins et al., 2009; Moody et al., 2013) and significantly increase the proportion of fine-grained sediments in the landscape, increasing with fire severity (Malmon et al., 2007; Son et al., 2015) as these sediments are particularly vulnerable to erosion and strongly influenced by hydroclimatic controls (Silins et al., 2009; Moody et al., 2013). Fine sediments require lower runoff and stream flow velocities to erode and transport the material from hillslope to stream network (Legleiter et al., 2002; Haralampides et al., 2003; Emelko et al., 2011; Stone et al., 2011). Accordingly, smaller precipitation events and low-moderate flows can increase sediment erosion rates (Junze & Stednick, 2006; Shakesby & Doerr, 2006; Silins et al., 2009; Smith et al., 2011; Moody et al., 2013), suspended sediment concentrations and sediment yields, often by several orders of magnitude (Malmon et al., 2007; Ryan et al., 2011). Although markedly less than headwater regions, streams draining burned catchments in low relief, peat dominated landscapes, can have suspended sediment yields 1.2-10x higher than those draining non-wildfire-impacted landscapes (Emmerton et al., 2020). Soil erosion (i.e., detachment, entrainment, transport, distribution, and deposition) throughout aquatic systems is the primary cause of water pollution around the world, largely because of its strong association with phosphorus (P) (Stone & Droppo, 1994; Stone et al., 2011; Sharpley et al., 2013; Emelko & Sham, 2014; Emelko et al., 2016).

Solids-associated metals (Abraham et al., 2017), nutrients (Emelko et al., 2011; Silins et al., 2014; Gustine et al., 2021), and other contaminants (Crouch et al 2006; Mansilha et al., 2017) can be elevated post-fire. Bioavailable phosphorus release from sediments to the water column also has been observed over many years post-fire (Stone et al., 2014; Emelko et al., 2016). These effects are magnified in combination with those from anthropogenic landscape disturbances (Watt et al., 2021). It is because of these collective impacts that wildfire can challenge treatment plants beyond their design capacity, resulting in increased infrastructure and operating costs or service disruptions (Emelko et al., 2011; Price et al., 2017). Notably, while increases in suspended/solids/turbidity can be treated with conventional technologies, elevated/altered NOM can challenge treatment, especially when rapidly fluctuating (Kundert et al. ,2014; Skwaruk et al., 2022). Accordingly, techno-ecological nature-based solutions such as forest management-based source water protection approaches and biological treatment processes are increasingly advocated to mitigate these threats (Emelko & Sham,2014; Blackburn et al., 2021; 2022).

### 2.2.2 Sediment P and its relation to Climate Change and Water Quality

Phosphorus (P) is present in variety of chemical forms in aquatic systems including both dissolved and particulate forms (APHA, 2012; Maher & Woo, 1998) that are operationally defined according to techniques in standard methods (APHA, 2012; US EPA, 2012). In surface waters, the dissolved P portion is dominated mainly by the bioavailable dissolved P form orthophosphate (Raven et al., 1986; APHA, 2012; US EPA, 2012). In natural aquatic systems, phosphate can occur in organic and inorganic forms, both of which can be present in solid and aqueous phases. The organic phosphate fraction is related to living and dead/dying cellular matter (i.e., detritus, feces, decaying algae) as a portion of proteins, lipids, metabolic waste, to name a few. (Raven et al., 1986). Orthophosphate ($PO_4^{3-}$) is the most basic form of the phosphate molecule but depending on the pH can also be found as $H_2PO_4^-$ or $HPO_4^{2-}$ (Raven et al., 1986). The term orthophosphate is commonly referred to as dissolved or soluble reactive P (SRP). Polyphosphates are complex groups of multiple inorganic phosphate forms (APHA, 2012; US EPA, 2012) while other inorganic phosphate forms are associated with metal oxy-hydroxides on or within sediment particles such as clay (Carlson & Simpson, 1996; Engstrom, 2005; Ashley et al., 2011).

Total P (TP) is the sum of dissolved P (DP) and particulate P (PP) (APHA, 2012). DP is determined by measuring water filtered through a 0.45 µm membrane whereas PP refers to P bound to the surface (sorbed) or contained within particle surfaces and is referred to as insoluble, suspended, or particulate P (House, 2003; APHA, 2012). Particulate P also contains P in organic coatings, P precipitated on particle surfaces, as well as P in minerals in the sediment (i.e., Apatite P). The dissolved fraction includes orthophosphate and P sorbed to colloidal materials <0.45 µm. Particulate P fractions are identified through an operationally defined sequential extraction scheme using the modified Psenner method (Pettersson et al., 1988; Stone & English, 1995; Katsaunos et al., 2007; Meng et al., 2014). These techniques sequentially extract the following P forms. (1) Apatite P, extracted by HCl (0.5M) leach, is a calcium-phosphate mineral that is related to natural weathering and is considered geochemically stable (Stone & Droppo, 1994). (2) Organic P (OP) is extracted with NaOH (1.0M, 85°C) leach and is considered potentially available if it undergoes mineralization or is released through hydrolysis (Golterman, 2004). Non-apatite inorganic P (NAIP) is considered the most bioavailable P fraction (Emelko et al., 2016) and is the sum of three operationally defined fractions: (3) loosely sorbed (1.0 M, $NH_4Cl$-RP extractable P),

(4) reductant soluble (0.11 M $NaHCO_3.Na_2S_2O_4$ -RP) and (5) metal oxide bound (1.0 M NaOH-RP) (Bodstrom et al., 1982; Pettersson & Istvanovics, 1988, see Table 1). NaOH extractable P is generally associated with metal hydroxide surfaces (i.e., Fe) (Emelko et al., 2016) and some studies suggest it is the most 'agal available' form (De Pinto et al., 1981; Lottig & Stanley, 2007). Soluble reactive P (SRP) and NAIP represent the most biologically available fractions of DP and PP, respectively (Stone & Droppo, 1994; Emelko et al., 2016).

**Table 1:** The environmental significance of particulate phosphorus determined using sequential extraction (adapted from Spivakov et al., 1999 and Kleeberg & Kohl, 1999)

| **Form** | **Extractant** | **Significance** |
|---|---|---|
| Total Particulate P | | Sum of particulate P forms |
| Non-Apatite Inorganic P | | Most bioavailable particulate form |
| $NH_4Cl$-Reactive P | 1.0 M, $NH_4Cl$ | Most easily desorbable form |
| BD-Reactive P | 0.11 M $NaHCO_3.Na_2S_2O_4$ | Reductant-soluble, bound to Fe-hydroxides, Mn compounds |
| NaOH-Reactive P | 1.0 M NaOH | Reactive, bound to metal-oxides (mainly Al and Ca), and Ca and Mg; inorganic P compounds that are alkaline soluble |
| Apatite P | HCl (0.5M) | P bound to carbonates (mineral bound), traces of hydrolized organic P geochemically stable, not bioavailable |
| Organic P | NaOH (1.0M, 85°C) | Unreactive, predominantly not bioavailable |

It is well documented that wildfires increase TP concentrations downstream of wildfire-impacted landscapes (Emelko et al., 2016). This – in part – has to do with the lack of the gaseous biogeochemical component in P vital for volatization (Bodi et al., 2014). For many years following a fire, it is common to see elevated levels of SRP and PP in draining tributaries that can be exacerbated by intense rainfall (Burke et al., 2005; Blake et al., 2010, Son et al., 2015; Emelko et al., 2016). In moderately and severely burned landscapes, PP is commonly the most dominant fraction (Burke et al., 2005; Emelko et al., 2016) and can occupy >94% of TP (Lane et al., 2005; Blake et al., 2010). The bioavailable NAIP fraction is often very high compared to pre-fire levels (Stone et al., 2011; Emelko et al., 2016) and in some instances can be 2-fold higher than SRP (Blake et al., 2010).

## 2.3 The Effect of Sediment Composition and Environmental Factors on the Form and Mobility of Particulate P

Sediment is the primary vector for P transport (Binkley & Brown, 1993; Shantz et al., 2004) and P mobility (Froelich, 1988; Dunne et al., 2005) in aquatic systems. Sorption processes (P mobility) are complex and highly dependent on sediment characteristics (i.e., particle size and geochemistry) and environmental conditions (i.e., redox, temperature, competitor ions, pH) that strongly influence the bioavailability of P (Lijklema, 1980; Davies-Colley & Smith, 2001).

### 2.3.1 Particle Size

The surface area of sediment and the concentration of metal oxide coatings (Horowitz & Elrick, 1987) increases with decreasing grain size (Droppo & Ongley, 1992; Wood & Armitage, 1997; MWH, 2012; Yang et al., 2013). Concentrations of sediment-associated nutrients (i.e., P) and contaminants are inversely proportional to grain-size (Forstner, 1987; Stone and Mudroch, 1989; Stone & English, 1993). Fine sediments are found to have higher concentrations of NAIP and OP fractions while the AP fraction is often decreased (Stone & English, 1993). This presents a potentially large source of bioavailable P.

### 2.3.2 Sediment Geochemistry, Environmental Conditions, pH, Redox

Metal oxy-hydroxides (Al, Fe and Mn) and organic matter coatings (Horowitz & Elrick, 1987) are important for P sorption on fine sediment and have been correlated with total PP concentrations (Nurnberg, 1988; Evans et al., 2004). The surface area and positive charge of Fe and Al hydroxides act as electron acceptors for negatively charged phosphate ions. Sediment P adsorbed to Fe hydroxides, and to a lesser extent, Mn hydroxides, can be released into the overlying water column through reduction under anaerobic conditions (Mortimer, 1971; Bostrom, 1988; Golterman, 1995; Orihel et al., 2005; Nurnberg et al., 2018). Sediment with high Al content is effective in suppressing P release (Kopacek et al., 2005; Liu et al., 2009; Cai et al., 2020) as Al-bound P is stable under aerobic and anaerobic conditions if pH is circumneutral (pH ~7) (Huser et al., 2016). Precipitation/dissolution reactions are often due to quick changes in pH (Aminot & Andieux, 1996) and often occur during periods of high primary production (Niemisto et al., 2011).

Redox conditions also change the binding of Fe and Mn to mineral surfaces (Mortimer, 1941; Evans et al., 2004) and create the potential for organic P to be released with hydrolysis under anerobic conditions. Fewer available metal hydroxides will likely result in less P sorption to sediments (Golterman, 2004). Phosphate is a highly reactive element, responding differently under a myriad of biogeochemical and environmental conditions. Understanding these conditions is essential to describe P mobility more accurately in natural systems.

In aquatic systems, sediment can influence P mobility through sorption processes (Stone & Murdoch, 1989; Dunne et al., 2005). The uptake/release of P to/from sediments occurs in a two-step process. Rapid surface adsorption occurs first, followed by a slow 'solid-state diffusion'; the inverse occurring for desorption (Froelich, 1988). Various P isotherm experiments and sorption models (e.g., Langmuir, Fruendlich, Tempkin) determine the potential of sediment to buffer P from solution. The capacity of sediment to adsorb/desorb P can be described by the equilibrium concentration of particulate and dissolved P. When ambient SRP concentrations ($S_o$) are low, P is desorbed from sediment into the water column. If external processes cause a rise in dissolved P concentrations, sediment will adsorb SRP until equilibrium has been re-established, or when maximum sorption capacity has been reached ($S_{max}$). When the equilibrium between SRP and sorbed P has been reached neither adsorption nor desorption occurs, defined as the 'equilibrium phosphate concentration' ($EPC_0$). In aquatic systems, the $EPC_0$ is a measure of the potential of sediments to adsorb or release SRP depending on ambient SRP concentrations (House & Denison, 1998; 2000). The $EPC_0$ is often determined using batch experiments by mixing a series of known SRP concentrations with a known mass of sediment for a time sufficient to establish equilibrium between sediment and solution (Golterman, 2004). The data are plotted by known SRP concentration (P initial) on the x-axis versus P adsorbed/desorption on the y-axis. The $EPC_0$ is calculated using the following equation (1):

$$P_{ads} = [(P_{initial} - P_{final}) * 0.025L] * wt_{sed} \quad (1)$$

The slope of the line at the $EPC_0$ describes the potential for P release or uptake on particulate matter (Figure 2). Sediments with a greater ability to buffer P are represented by a steeper slope. $EPC_0$ values and P isotherms are important in estimating the sorption potential to/from various sediment types in the water column (House et al., 1995). However, the sediment

biogeochemistry and environmental factors discussed in section 1.1.3 strongly influence sorption processes in natural systems. Therefore, sorption studies (P isotherms) should serve only as a relative proxy and used in conjunction with research on sediment biogeochemistry and environmental condition to better understanding P sorption dynamics and the potential impacts for water quality.

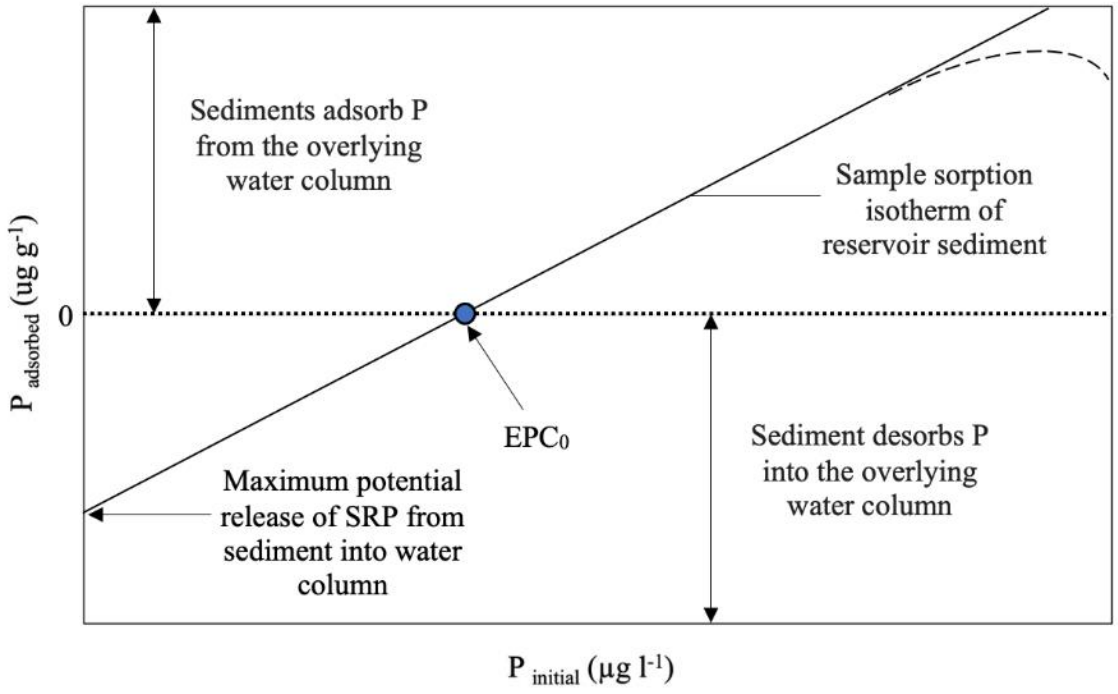


**Figure 2:** Example of sorption profile of reservoir system, where x=0 (dotted line) represents equilibrium conditions between reservoir bottom sediments and the overlying water column. (Froelich, 1988)

## 2.4 Implications of Phosphorus Cycling in Reservoirs on Water Treatability

Globally, reservoirs are used to manage source water for a myriad of uses including crop irrigation, energy production, flow equalization, flood protection and domestic water supply. Domestic water supply often requires reservoirs for the storage of raw (i.e., untreated) water prior to treatment to ensure a consistent supply of drinking water. Reservoirs store water along the river continuum and typically are designed as either online or offline systems depending on the landscape, river characteristics and retention time (Figure 3). In online designs, rivers are impounded, and water storage occurs in the channel and/or floodplain. Offline designs divert water

from the river channel to an engineered facility or depression in the landscape where water is stored (Ackers et al., 2010). Historically, reservoirs have prioritized managing water quantity over water quality (U.S. Environmental Protection Agency, 2001). With the increasing threat of climate change and landscape disturbance (i.e., wildfires) on surface water quality, management objectives are rapidly shifting.

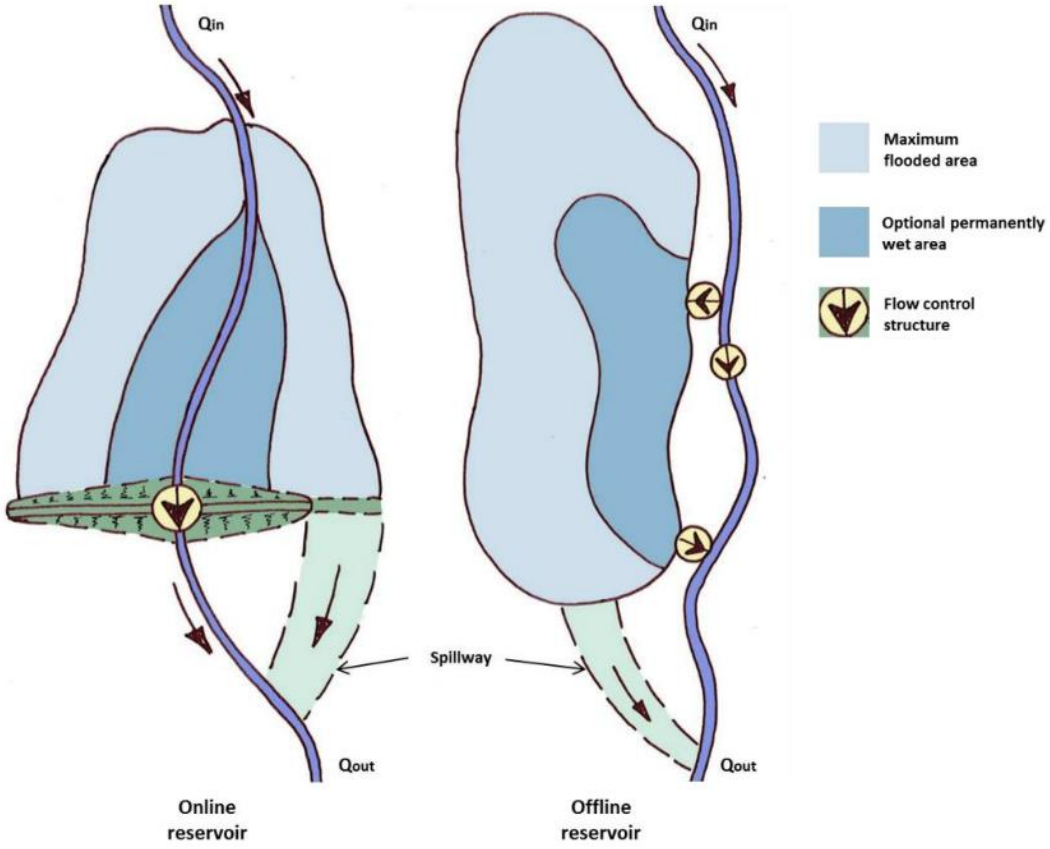


**Figure 3:** Flow characteristics of online and offline reservoirs. (Patterson et al., 2016)

The phosphorus concentration in aquatic systems is intrinsically linked to water treatability (Emelko et al., 2011). The Canadian Council of Ministers of the Environment identify critical "trigger" ranges of P concentrations for varying water quality classes. Oligotrophic systems are considered low productivity waters with TP concentrations ranging between 4 and 10 µg/L and concentrations can range all the way to hyper-eutrophic systems where P is >100 µg/L (CCME 2004, See Table 2). Systems with elevated levels of P may experience eutrophication which is defined as an increase in primary production or algal biomass resulting in toxic algal blooms (e.g., cyanobacteria), oxygen depletion, fish kills and drinking water taste and odor problems from disinfection by-products (Jeppesen et al., 2005; Drewry et al., 2006; Schindler, 2006). Therefore,

eutrophication is generally attributed to excess P inputs (i.e., external P loading) into water bodies (Smith & Schindler, 2009; Schindler, 2012) from human activities (i.e., phosphate mineral extraction, food consumption and sewage production, fertilizer application and livestock production) (Bennett et al., 2001; Filippelli, 2002, 2008; Emelko et al., 2011; Yuan et al., 2018) as well as the consequences of human induced climate change (i.e., wildfires). Wildfires increase the downstream propagation of sediment and associated contaminants (i.e., phosphorus) that can cause significant changes to biogeochemical processes, ecological health and degrade water quality (Wood & Armitage, 1977). It is widely recognized that even after external inputs of P have been reduced, eutrophication often persists and a recovery in water quality can be significantly delayed from anywhere to 5-30 years (Cullen & Forsberg, 1988; Marsden, 1989; Jeppesen et al., 2005; Sondergaard, 2013; Jarvie, 2013; Nurnberg & LaZerte, 2016; Yu, 2020). The incomplete or delayed recovery of water bodies after reductions in external loading is largely attributed to the cycling of internal P (i.e., internal P loading).

**Table 2:** Guidelines for P concentrations in freshwater rivers and lakes in Canada. (CCME, 2014)

| 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 |

Internal loading is a term to describe the partitioning of P between the particulate and dissolved phase in aquatic systems that is governed by a complex set of biogeochemical and environmental processes (Nurnberg, 1988; Orihel et al., 2017). Under certain conditions the accumulated sediment-associated P (legacy P) stored in reservoir bottom sediments can be re-released as bioavailable SRP (Sondergaard, 2003; Meals et al., 2010; Jarvie et al., 2012; Sharpley et al., 2013; Orihel et al., 2017). The release of SRP from fine sediment is identified as the main driver for algal growth in most freshwater systems (Nurnberg, 1988; Welch & Cooke, 2005). The rate at which internal loading occurs is strongly influenced by sediment characteristics and environmental conditions. As mentioned in Section 1.1.4, certain conditions (e.g., pH, redox) can provide a buffer

for sediment to retain P that initially delays the movement of bioavailable SRP to ambient waters (Froelich, 1988; Powers et al., 2016; Nurnberg et al., 2018). However, if maximum sorption capacity of sediment has been reached and external P loading continues, P release can be accelerated as sediment P sinks turn into P sources (Jarvie et al., 2012, 2013; Powers et al., 2016; Goyette et al., 2018). The chronic release of P from sediment to the water column can lead to extreme delays in reaching water quality management goals (Sondergaard, 2003; Meals et al., 2010; Jarvie et al., 2012; Sharpley et al., 2013; Orihel et al., 2017).

The accumulation of legacy P in reservoir sediment significantly threatens water quality due to its role in the proliferation of algae and toxic cyanobacteria (Winter et al., 2011; Hallegraeff, 1993). In small seasonally stratified lakes and reservoirs, physical controls such as the resuspension of benthic sediment can play a significant role on internal P loading (Niemisto et al., 2011; Yu, 2020). Furthermore, the shallow depths and warm temperatures create ideal conditions for these organisms to grow (Paerl & Huisman, 2008; Paerl & Paul, 2012). As drinking water reservoirs are not typically designed to optimize water quality, they are particularly susceptible to bloom occurrences (Crittenden et al., 2012). The presence of algae in reservoirs presents major challenges for conventional water treatment technologies (i.e., coagulation, flocculation, clarification, granular media filtration, and disinfection). Algal blooms can not only reduce the quantity and quality of output, but the addition of water treatment by-products can lead to taste and odor problems (Emelko et al., 2011). Therefore, the increase of legacy P under a changing climate with increased wildfire occurrences promotes the proliferation of algae that can pose significant threats to the provision of adequate and safe drinking water in the future (Carpenter et al., 1998; Westrick et al., 2010; Emelko et al., 2011; Emelko et al., 2016).

For decades, many management approaches have been applied to reduce internal P loading in lakes and reservoirs, These include bio-manipulation (Liu et al., 2008), *in situ* capping (Yin et al., 2016), hypolimnetic aeration (Dittrich et al., 2011), aluminum hydroxide ($Al(OH)_3$) additions (Welch & Cooke, 1999; DeVicente et al., 2008) and sediment dredging (Kleeberg and Kohl, 1999; Oldenborg and Steinman, 2016), to name a few. Dredging can reduce the probability of internal P release (Jing et al., 2015; source) and cyanobacteria bloom occurrence (Lurling and Faassen, 2012; Bormans et al., 2016; Liu et al., 2016). Dredging is effective in removing the uppermost organic- and nutrient-enriched sediments (Wen et al., 2020). In built, offline resevoirs essentially all deposited sediment can be removed. Long-term control of internal P loading to the water column

requires sufficient concurrent reduction of external P loads, however (Jeppesen et al., 1990; Kleeberg & Kohl, 1999; Jing et al., 2015; Wen et al., 2020; Lui et al., 2020). If external loads are sufficiently reduced, nutrient- and organic-enriched sediments will accumulate again (Yin et al., 2020).

# Chapter 3

# Materials and Methods

## 3.1 Experimental Design

The goal of this research was to characterize the geochemical composition, particulate P forms and P mobility of fine-grained benthic sediment in two Alberta drinking water source reservoirs. Understanding the effects of wildfires on the form and mobility of P and the potential long-term impacts on water quality is critical to identifying and implementing effective management strategies. Although many studies have examined the effects of wildfires on sediment-P dynamics in streams and lakes, very little, if any research has been conducted on these processes in drinking water reservoirs.

To evaluate the effects of the Horse River wildfire on the quality of reservoir sediment and the potential for benthic sediment to act as a sink/source of soluble reactive phosphate (SRP) to/from the water column, deposited sediment was first collected from the source water reservoir in Fort McMurray, Alberta, Canada on November 26, 2016. Between the months of August and November 2018, the FMM reservoir was dredged, and accumulated sediment was removed. Two years thereafter, sediment was collected from the reservoir again on August 25, 2020. Sediment samples also were collected in the Glenmore Reservoir, Calgary, Alberta, Canada on July 27, 2017, and September 3, 2020, to provide a non-wildfire-impacted point of comparison. Given the substantial differences in the physiographic settings between the two sites, the study design provides general perspective regarding sediment-associated nutrient chemistry, P form and mobility spatially (intra-site comparison) and temporally (inter-site comparison) in drinking water source reservoirs whose water originates in the easter slopes of the Rocky Mountains in Alberta, Canada.

To address the objectives described in Section 1.2, the research was conducted in two phases. Phase 1 was designed to address objective #1 and #2, consisting of fine sediment characterization including geochemical composition and particulate P speciation. Phase 2 consisted of conducting a series of sorption ($EPC_0$) isotherm experiments to address objective #3.

**Phase 1 – Physical and Geochemical Composition of Sediment:** To address objective #1 and #2, the first experimental phase of this research was designed to characterize the geochemical composition and particulate P forms of fine benthic sediment collected from the Fort McMurray reservoir in Alberta and the Glenmore Reservoir in Calgary, Alberta in 2016/2017 and 2020. The data are presented to contrast spatial (inter-site) and temporal (intra-site) differences as a function by reservoir and year. Inter-site distribution was examined between wildfire-impacted benthic sediment in Fort McMurray and non-wildfire-impacted sediment in Glenmore Reservoir in 2017 and 2020. Intra-site sediment characterization was primarily executed to examine temporal differences within each reservoir.

**Phase 2 – Sorption Studies:** The second experimental phase was designed to evaluate inter- and intra-site distribution in the sediment P mobility as a function by reservoir and year. To address objective #3, batch sorption ($EPC_0$) experiments were conducted to evaluate the potential for reservoir bottom sediment to act as a source/sink of P to the water column.

## 3.2 Study Area

### 3.2.1 Fort McMurray

Fort McMurray is located at the confluence of the Athabasca and Clearwater rivers in the northeastern portion of the Athabasca River basin (Figure 4) which drains an area of ~159,000 $km^2$ (ARBRI, 2017; see Figure 5). The Athabasca River originates at the Columbia Glacier in Jasper National Park then flows approximately 1400 km eastward until draining into Lake Athabasca (ARBRI, 2017; Tondu, 2017). Mean annual flow is >500 $m^3 s^{-1}$. In the lower reaches of the Athabasca River near FMM, the concentration of suspended sediment and associated water quality parameters (e.g., nutrients, metals, organic carbon) originating from upstream tributaries and channel resuspension can often exceed national water quality guidelines for a significant portion of the year (Glozier et al., 2018).

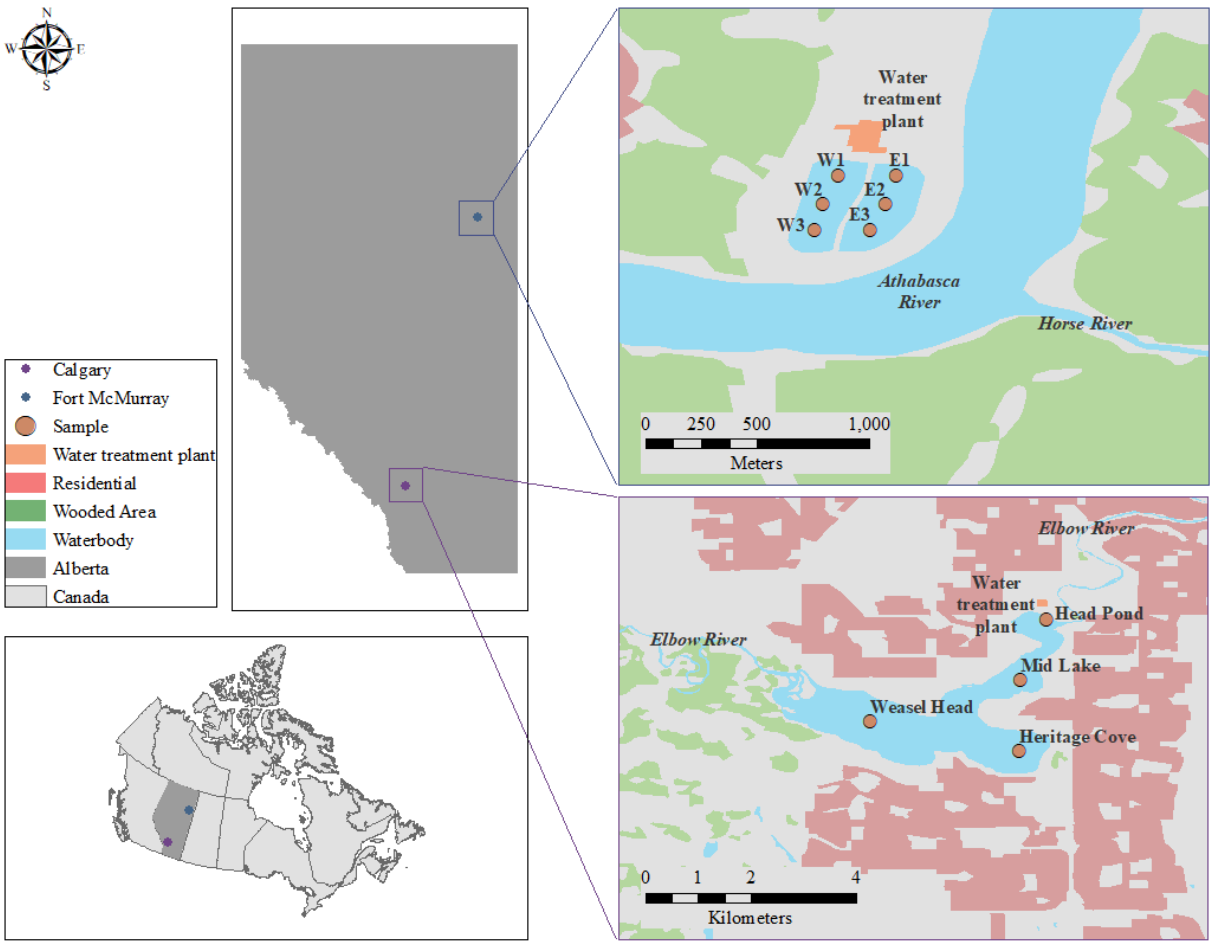


**Figure 4**: Map of Alberta showing the locations of Fort McMurray and Calgary. Lower left inset map of Canada, lower left inset shows map of Alberta, upper right inset shows sediment sampling sites in Fort McMurray reservoir, and lower right inset shows sediment sampling sites at the Glenmore reservoir.


**Figure 5:** Map of Alberta showing boundary of the Regional Municipality of Wood Buffalo and the Athabasca River watershed boundary (Athabasca River Hydrological Profile, n.d.)

Fort McMurray's source water supply reservoir is located at the Regional Municipality of Wood Buffalo (RMWB) water treatment plant (Figure 6). The RMWB is situated in the Boreal Plains ecozone comprised of the mid boreal mixed-wood ecoregion that is characterized by a flat and rolling landscape, mixed coniferous forests, and wetlands (i.e., peatlands) (Strong & Leggat, 1992; Emmerton et al., 2020; Chanasyk et al., 2003; Devito et al., 2017). This ecoregion covers more than half (>50, 500 km$^2$) of the surrounding landscape (AEP, 2018; Volik et al., 2020). Thick glacial till soils dominate the landscape, that include Luvisolic and Brunisolic order soils in higher elevations and Gleysolic and Organic soils in lower slopes and depressions (Chanasyk et al., 2003;

Volik et al., 2020). Fort McMurray has a relatively dry and cold continental climate with a mean annual precipitation of 419 mm (1981-2010) (Emmerton et al., 2020). Anthropogenic landscape disturbance in this region (i.e., major oil sand strip-mining, coal extraction, timber harvesting and urban development) are of increasing concerns for water quality for watershed managers, drinking water providers as well as remote and indigenous communities (ARBRI, 2017; Emmerton et al., 2020; Volik et al., 2020).

The FMM source water reservoir at the RMWB water treatment plant includes two ponds (east and west) located on the western side of the Athabasca River (Figure 6). The RMWB treatment plant utilizes an offline reservoir system (Figure 3). Water is diverted from the Athabasca River into the east pond by an intake structure located near sample site E3 (Figure 4). Before entering the pond, a treatment process pre-screens coarse sediment (>2mm) fractions at the reservoir inflow by way of a centrifuge. Coarse sediments are filtered and returned to the river, while finer-grained particulate matter (< 200 µm) entrained in river water is deposited into the east pond. The east pond serves as the primary settling pond before water and any remaining fine suspended solids enter the west pond through underground equalization tubes. Apart from colloids, most of the suspended solids in the west pond settle before water is pumped into the treatment plant. The east and west ponds are relatively similar in size. Prior to dredging in 2018, the storage capacity of the east pond was 243,122 $m^3$ of which 663 $m^3$ was sediment while the storage capacity of the west pond was 269,303 $m^3$ with 1,229 $m^3$ of sediment. Total storage capacity of both ponds is ~513, 000 $m^3$ (Kuzemchuk, 2018).

**Figure 6:** Regional Municipality of Wood Buffalo water treatment plant and Athabasca River (photo credit RMWB)

*2016 Horse River Wildfire*

On May 1st, 2016, a lightning strike started a small fire in a forested area ~7 km west of Fort McMurray (Emmerton et al., 2019). A combination of extremely dry conditions across Alberta in 2015, low snowpack over winter, seasonably high spring temperatures, low humidity and strong variable wind gusts quickly fuelled extreme wildfire conditions that spread rapidly northeast (Figure 7). The fire escaped initial control on May 2nd threatening First Nations communities, oil sand camps and facilities, critical infrastructure, and the Fort McMurray township causing a mass evacuation of ~90,000 people by May 3rd.

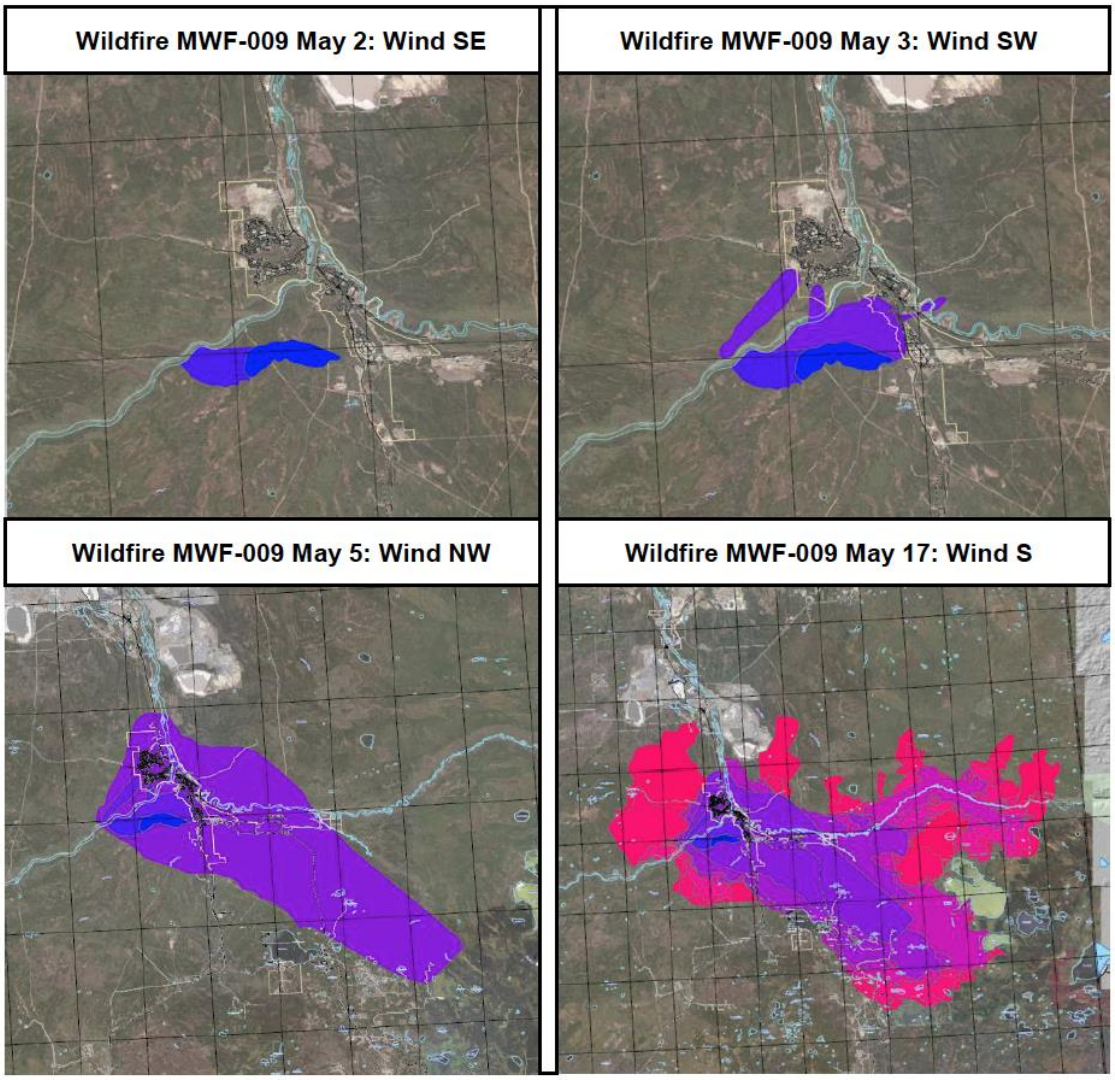


**Figure 7**: Spatial extent of the Horse River Wildfire on May 2, 3, 5 and 17 (RHRW, 2017)

The Horse River wildfire was declared under control on July 4th and resulted in a loss of 3000 structures and an estimated 589,552 ha of forest and peatland (RHRW, 2017). Of the total area burned, roughly 50% burned at high severity (Emmerton et al., 2020). The Horse River wildfire is considered the worst and most costly wildfire in Canadian history with estimated direct costs of $8.9 billion (Alam et al., 2018) and $3.7 billion in insurable losses (RHRW, 2017). The fine wildfire-impacted sediment was dredged between the period of August to November 2018 (Figure 8) .

**Figure 8:** Bottom sediment removed from the west source water reservoir in Fort McMurray (August 2020). (Photo credit Dr. M. Stone)

### 3.2.2 Glenmore Reservoir

The Glenmore Reservoir (GMR), Calgary, Alberta, (Figure 4 & 9) is an online reservoir created by impoundment of the Elbow River. Total capacity of this reservoir is 28.4 x $10^6$ $m^3$ (Hollingshead et al., 1973; Water for Life, 2007). The GMR receives inflow from the Elbow River which originates in snow melt dominated forested headwater regions on the eastern slopes of the Rocky Mountain. The Elbow River flows across the west end of the City of Calgary before entering the GMR.

**Figure 9:** Glenmore Reservoir in Calgary, Alberta. Photo taken in 2016 (www.stockaerialphotos.com)

The Glenmore Reservoir has four sections: Weasel Head (WH), Heritage Cove (HC), Mid Lake (ML) and Head Pond (HP) (Figure 4). Weasel Head is in the west end of the reservoir closest to the Elbow River inflow. Heritage Cove is in the southern portion of the reservoir and Mid Lake is positioned in the center near the golf course. Head Pond is in the northeastern portion of the reservoir closest to the Glenmore dam and drinking water intake. The critical forested headwater source regions on the eastern slopes of the Rocky Mountains have historically produced high quality water to supply the City of Calgary. Although this headwater region has not been affected by wildfire for 90 years the average time of fire return in this area is ~112 years. Agricultural and urban landscape changes in the lower reaches of the Elbow River have reduced water quality through higher concentrations of nutrients and suspended sediment (Water for Life, 2007). The once oligotrophic Glenmore reservoir (Water for Life, 2007) is now classified as mesotrophic-oligotrophic with total P concentrations typically ranging from 2 to 4 μg/L (Alberta Lakes).

### 3.2.3 Field Equipment and Sampling Design

Fine sediment was collected from the non-wildfire-impacted drinking water reservoir GMR (WH, HC, ML, HP) and FMM's (E1-E3, W1-W3) wildfire-impacted drinking water reservoir following the Horse River wildfire in 2017 and again following dredging in 2020. Samples were collected using a Ponar "grab" sampler at three equidistant locations in both FMM's east and west ponds, and at the 4 locations in GMR to ensure representative materials were collected (Figure 4). Only the uppermost surface sediments (0 to 5 cm) were collected as this fine material is the most important in the potential release of SRP to the water column and algal growth. An ORB probe was used to measure the redox condition in the top 10 cm of bottom sediment on August 25$^{th}$, 2021, and September 3$^{rd}$, 2020 in FMM and Glenmore Reservoir, respectively.

## 3.3 Sediment Characterisation (Geochemical Composition and P forms)

Particle size data and geochemical composition of reservoir bottom sediment was analyzed at a commercial laboratory (Act Labs, Burlington, ON, Canada) according to standard methods. Geochemical composition (Si, Al, Fe, Mg, Ca, Na, K, Mn) was determined by Aqua Regia "Partial" digestion and analysed using ICP-MS for all Fort McMurray and Glenmore Reservoir samples. Results for most major elements (Si, Al, Fe, Mg, Ca, Na, K and Ti) were presented as percent dry weight except for Mn which was presented as ppm (Murdoch, 1985). A Malvern Mastersizer 2000 was used to measure the median diameter ($D_{50}$) of benthic sediment in FMM 2017. Analytical accuracy was confirmed using Canadian Reference Standards AGV-1, MRG-1, NCM-N, GSP-1, and SY-3 and comparing results with the stated reference values for major elements.

Particulate P fractionation was characterized using the modified Psenner sequential extraction scheme reported by Pettersson et al., (1988). This method removes particulate P fractions from sediment in order of decreasing bioavailability using solutions of increasing chemical strength (Stone & English, 1993). Non-apatite inorganic P (NAIP) is the most bioavailable particulate P form and is a proxy for the potential of phosphate ($PO_4^{3-}$) to desorb readily from the surface of sediment into the ambient water column (DePinto et al., 1981; Jarvie et al., 2002; House, 2003). Non-apatite inorganic P is the sum of three reactive phosphorus

fractions beginning with the most easily desorbable; loosely sorbed P (1.0 M $NH_4Cl$–RP extractable P) followed by reductant soluble P (0.11 M $NaHCO_3.Na_2S_2O_4$- RP) and metal oxide bound P (1.0 M NaOH – RP) (Williams et al, 1976; Boström & Pettersson, 1982). Apatite P (AP) is the 0.5 M HCl-RP fraction that is mineral bound (Pettersson et al., 1988), predominantly to Ca and Mg carbonates (Watt et al., 2021) The organic fraction (OP) is extracted using hot 1 M NaOH-RP (85 °C) and is considered biologically unavailable but has the potential to become available after hydrolysis or mineralization (Golterman, 2004). Total particulate phosphorus (TPP) indicates the total P burden and is the sum of NAIP, AP and OP fraction. The enrichment factor is calculated by dividing NAIP by TPP.

## 3.4 Phosphorus Sorption Experiments: Determination of $EPC_0$

A series of batch experiments were used to determine the equilibrium phosphate concentration ($EPC_0$) of each sediment sample. The $EPC_0$ is a measure of the potential of sediments to adsorb/desorb SRP to/from the water column depending on the ambient SRP concentrations (House & Denison, 1998; 2000). The $EPC_0$ was calculated using the method reported by Froelich (1988). Various concentrations of phosphate (0, 25, 50, 100, 200, 400 and 800 μg P $L^{-1}$ P) were added to 0.25 g of dry sediment in 50-ml centrifuge tubes in triplicate. Centrifuge tubes were placed on a shaker table and mixed at 100 rpm at room temperature for 18 hours. An aliquot of 15-ml was filtered (0.45 μm) into scintillation vials then analyzed using a Technicon Autoanalyzer using the ammonium molybate/stannous chloride method, which has a detection limit of 1 μg P/L (Froelich, 1988; Stone and Murdoch, 1989; Stone and English, 1993)

## 3.5 Statistical Analysis

*Evaluating spatial (inter-site) differences*

All statistical analyses were performed with SPSS (SPSS 21, IBM Corp., 2012). Mann-Whitney rank sum tests were used to evaluate the inter-site differences in sediment geochemical properties particulate P forms, and $EPC_0$ between GMR and FMM in 2017 and 2020. To test for differences in the medians of two groups, the assumption of same shape distribution must be met. If distributions had different shapes, the Mann-Whitney U test was employed to determine

differences in distributions between two groups. For inter-site differences (FMM vs. GMR) in 2017, all particulate P forms and $EPC_0$ met the assumption of same shape distribution and therefore were evaluated based on differences in medians. Of the major elements, four (Al, Na, K and Mn) met same shape distributions medians. Major elements Ca, Fe and Mg failed to meet the assumption and were evaluated for mean differences in distributions. For inter-site differences in 2020, five (BD-RP, AP, Refractory P, Total PP and NAIP:TPP) particulate P forms met the same shape distribution assumption whereas two (NaOH and Total NAIP) did not. Most major elements (K, Al, Fe, Mg, Ca, Mn) met the same shape distribution assumption while Na was tested for differences in distribution.

*Evaluating temporal (intra-site) differences*

Wilcoxon signed-rank tests were used to determine the intra-site median differences in sediment geochemical properties, particulate P forms, and $EPC_0$ in FMM and GMR in 2017 and 2020. The Wilcoxon signed-rank test requires the distribution of the differences between the two related groups to be symmetrical in shape. When this assumption was not met, a Sign test (reference) was used to determine the median difference between years. For FMM, Wilcoxon signed-rank tests were used for five major elements (Al, Ca, Na, Mn and Fe), four particulate P forms (BD-RP, NaOH, Total NAIP and AP) and $EPC_0$. Signed rank was used to test intra-site median differences for major elements (Mg and K) and particulate P forms (Refractory P and Total PP). For Glenmore reservoir, Wilcoxon signed-rank tests were run for five of the major elements (Al, Ca, Na, K and Fe), five (BD-RP, NaOH, Refractory P, Total NAIP and NAIP:TPP) of the particulate P forms and $EPC_0$. Sign tests were used for two major elements (Mg and Mn) and two particulate P forms (Total PP and AP).

Non-parametric Spearman's rank correlation coefficients were calculated between particulate phosphorus forms and major elements to compare results with those of previously reported studies. Spearman's rank correlation coefficients were used to explore relationships between major elements to aid in the interpretation of regressions with reduced parameters.

# Chapter 4

# Results

## 4.1 Results

### 4.1.1 Phase 1: Physical and Geochemical Composition of Reservoir Bottom Sediment in Fort McMurray and Glenmore Reservoir

Geochemical composition of bottom sediment in FMM and GMR is presented in Table 3 and Figure 10 to contrast spatial (inter-site) and temporal (intra-site) differences as a function by reservoir and year. Median concentrations of Al, Fe, N, K, Mn, Ca and Mg were significantly different in post-wildfire FMM sediment ($p=0.016$) compared to GMR sediment. Specifically, concentrations of Fe, Al, Na, K, Mn were higher in FMM, whereas Ca and Mg concentrations were lower. After dredging, levels of Al, Fe and Mn in FMM sediment were significantly lower than the initial post-wildfire FMM sediment ($p=0.043$). In 2020 post-dredge sediments, concentrations of Al, Fe and Mn were significantly higher in FMM sediment compared to GMR ($p=0.01$), whereas levels of Ca and Mg were significantly lower ($p=0.01$). Major elements Na and K were not significantly different between the two reservoirs in 2020. The median diameter ($D_{50}$) of the FMM reservoir bottom sediment in 2017 was ~35 µm consisting of mainly of silt and clay sized fractions.

**Table 3:** Geochemical Composition of FMM and GMR bottom sediment

| | GMR 2017 (n=4) | | GMR 2020 (n=4) | | FMM 2017 (n=5) | | FMM 2020 (n=6) | |
|---|---|---|---|---|---|---|---|---|
| | Median | SD | Median | SD | Median | SD | Median | SD |
| Fe % | 2.15 | 0.15 | 2.07 | 0.39 | 4.24 | 0.12 | 3.02 | 0.16 |
| Al % | 3.58 | 0.53 | 1.90 | 0.41 | 8.46 | 0.47 | 2.98 | 0.40 |
| Mn ppm | 396.83 | 24.26 | 391.00 | 83.49 | 601.00 | 36.15 | 521.00 | 21.45 |
| Ca % | 12.25 | 0.93 | 8.53 | 0.79 | 3.48 | 0.14 | 2.37 | 0.25 |
| Mg % | 1.99 | 0.13 | 1.83 | 0.38 | 1.46 | 0.07 | 1.04 | 0.03 |
| Na % | 0.05 | 0.01 | 0.02 | 0.00 | 0.46 | 0.16 | 0.03 | 0.00 |
| K % | 0.88 | 0.12 | 0.43 | 0.09 | 2.38 | 0.85 | 0.44 | 0.05 |

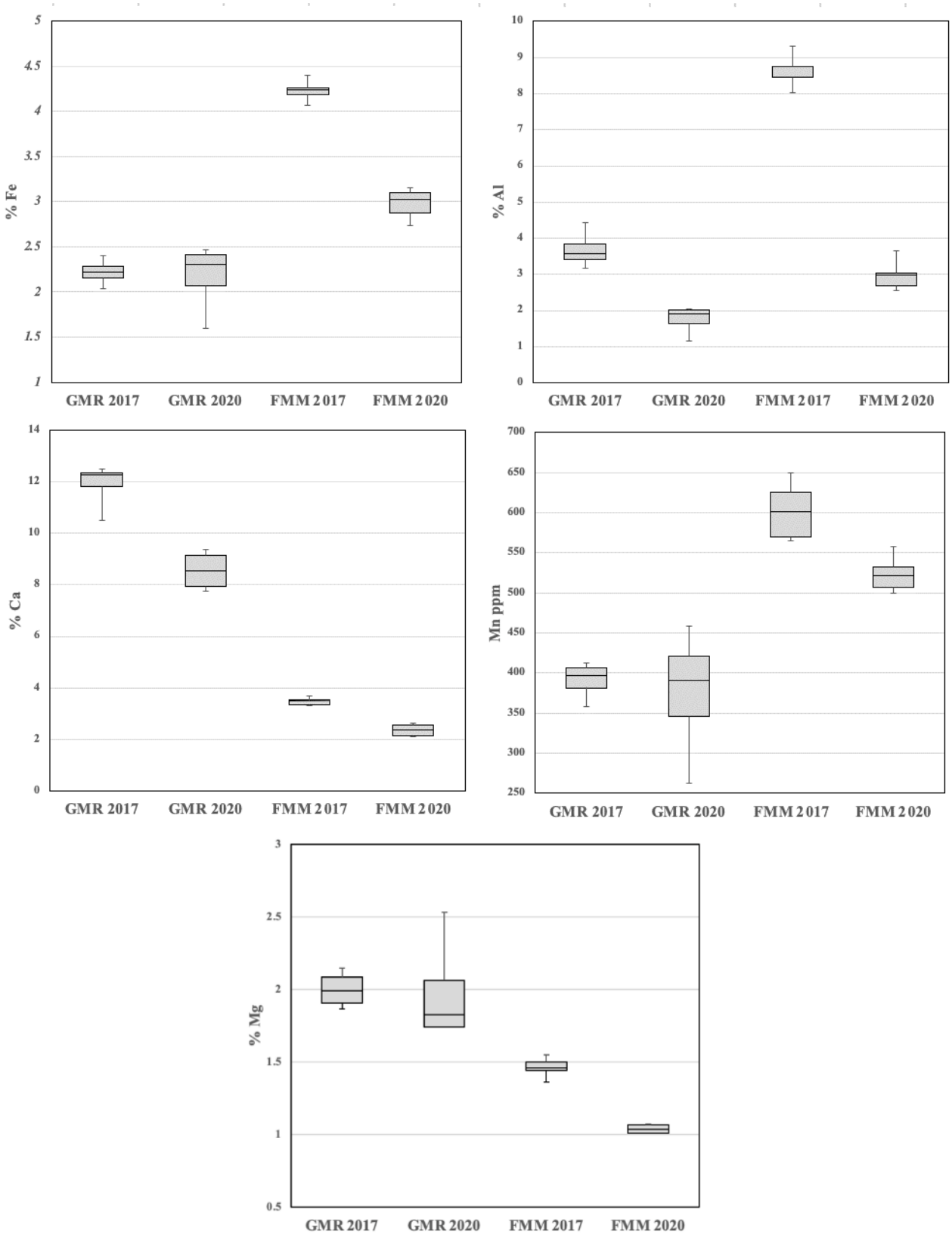


**Figure 10:** Distribution of major elements in Glenmore reservoir (2017, 2020) and Fort McMurray reservoir (2017, 2020)

Intra-site comparison shows a significant decrease in Al (p=0.043), Fe (p=0.043), Mn (p=0.043), and Na (p=0.042) post-dredge compared to post-wildfire in FMM sediments. Notably, concentrations of Al decreased substantially from post-wildfire (8.04-9.31%) to post-dredging (2.55-3.64%). However, despite decreased levels of Al, Fe and Mn in post-dredge FMM sediment, inter-site comparison revealed concentrations of these elements remained significantly higher than GMR sediment. Compared to post-wildfire, there was a slight, but not significant decrease in K, Ca, and Mg post-dredge in FMM sediments. Notably, in 2017 and 2020, average Mn, Al, and Fe concentrations were highest in the FMM east pond, whereas average concentrations of Mg, Na and K were slightly higher in the FMM west pond. The chemical constituents of GMR benthic sediment were not fundamentally different between 2017 and 2020. Redox and temperature data collected in FMM and GMR in 2020 are presented in Table 4.

**Table 4:** Redox and temperature below the sediment water interface in Fort McMurray and Glenmore Reservoir 2020

| | Site | Eh (mv) | T°C |
|---|---|---|---|
| FMM | W1 | -123 | 17.8 |
| | W2 | -113 | 17.9 |
| | W3 | -155 | 17.8 |
| | E1 | -132 | 17.6 |
| | E2 | -128 | 17.7 |
| | E3 | -124 | 17.6 |
| GMR | 1 | -195 | 18.6 |
| | 2 | -137 | 15.4 |
| | 3 | -145 | 15.6 |
| | 4 | -133 | 15.4 |

4.1.2 Phase 1: Total Particulate P Speciation

Variation in the particulate P forms (TPP, NAIP, NaOH-RP, BD-RP, AP, OP) are presented in Table 5 and Figures 11 and 12 to illustrate spatial (inter-site) and temporal (intra-site) differences as a function by site and year. Concentrations of TPP, NAIP, NaOH-RP and BD-RP were significantly higher in post-wildfire FMM sediment (p=0.016) compared to GMR sediment, whereas levels of AP were significantly lower (p=0.016). Compared to post-wildfire sediments in FMM, post-dredge levels of TPP, BD-RP and OP and were significantly lower for AP (p=0.043).

Interestingly, levels of NAIP and NaOH-RP in post-dredged FMM sediments were higher and subsequently the bioavailable P-enrichment was higher (Figure 13). Post-dredged FMM sediments had significantly higher concentrations of TPP, NAIP, NaOH-RP and BD-RP compared to GMR sediment ($p=0.01$), whereas AP was significantly lower ($p=0.01$).

**Table 5:** Distribution of Particulate P Fractions in two drinking water reservoirs

| | | | NAIP | | Apatite P | | Refractory P | | Total Particulate P | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | NAIP ($\mu g\ P^{-1}$) | | AP ($\mu g\ P^{-1}$) | | OP ($\mu g\ P^{-1}$) | | TPP ($\mu g\ P^{-1}$) | |
| | Site | n | Median | SD | Median | SD | Median | SD | Median | SD |
| FMM 2017 | East | 2 | 332.5 | | 383.5 | | 116.5 | | 837.5 | |
| | West | 3 | 261.3 | 44.9 | 408.0 | 16.7 | 94.4 | 1.8 | 776.7 | 30.4 |
| FMM 2020 | East | 3 | 322.4 | 30.7 | 347.0 | 16.5 | 94.6 | 13.0 | 766.0 | 27.6 |
| | West | 3 | 330.5 | 58.4 | 279.0 | 54.0 | 95.2 | 13.2 | 769.8 | 26.0 |
| GMR 2017 | | 4 | 73.0 | 38.0 | 448.0 | 29.6 | 95.4 | 17.7 | 616.3 | 83.5 |
| GMR 2020 | | 4 | 102.9 | 31.9 | 401.0 | 13.6 | 77.7 | 14.2 | 597.9 | 49.2 |

Concentrations of TPP were more variable in FMM sediments after the wildfire (765.8-897 $\mu g/g_{sed}$) and less so post-dredging (725.6-783 $\mu g/g_{sed}$). Bioavailable NAIP, NaOH-RP and BD-RP concentrations were elevated in sediments in the FMM east pond. OP concentrations were also highest in the FMM east pond sediments, whereas sediments in the FMM west pond had higher levels of AP. Post wildfire sediments had the highest TPP levels at the FMM site E2 and E3. No significant intra-site spatial patterns were evident within FMM. Intra-site comparison of GMR bottom sediments reveal no notable differences in particulate P concentrations but some spatial

patterns were observed. In 2017 and 2020, the highest concentrations of TPP and AP were measured at the Head Pond (HP) site.

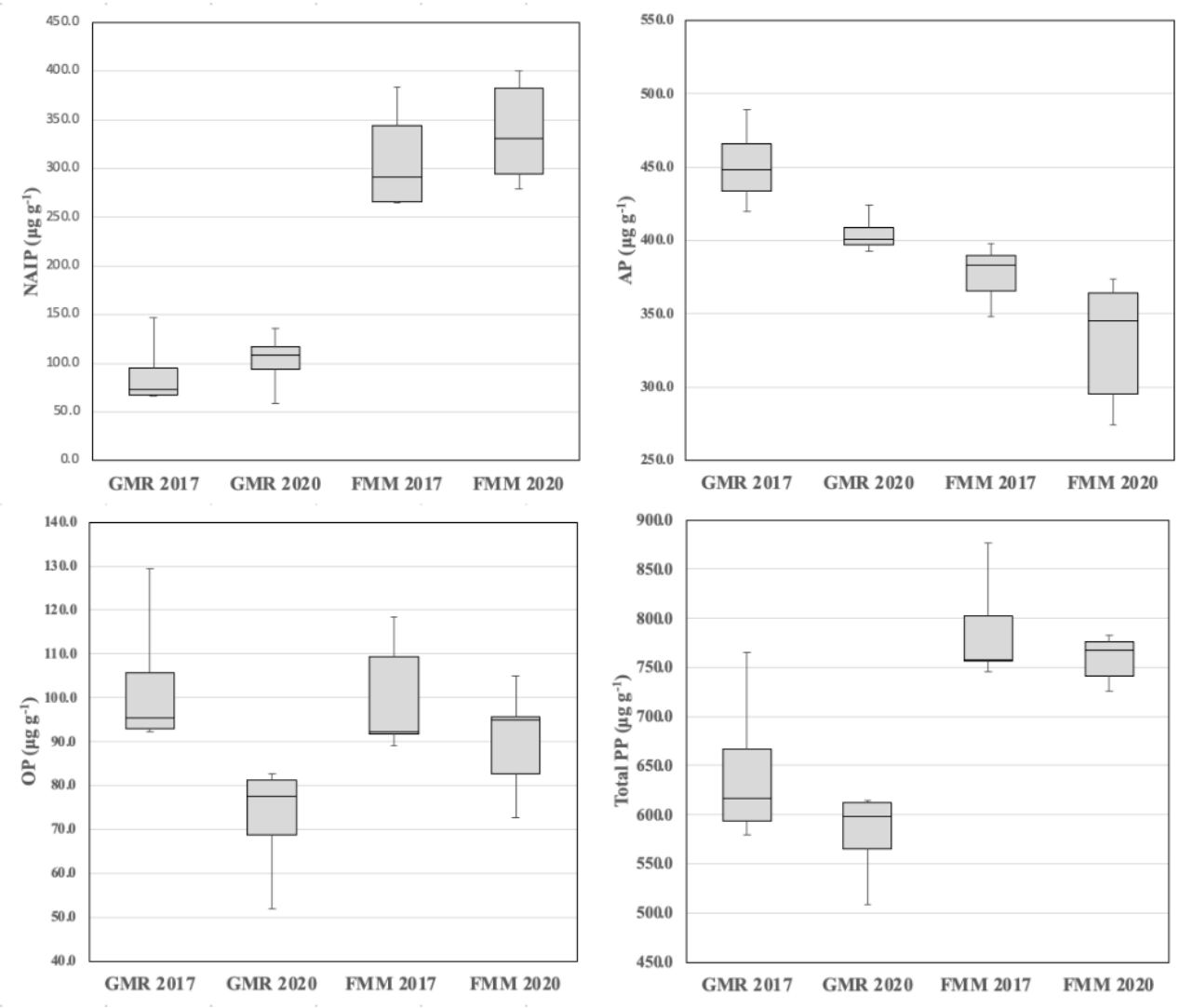


**Figure 11:** Distribution of Particulate P Fractions in Sediment from Glenmore (2017, 2020) and Fort McMurray (2017, 2020) Reservoirs

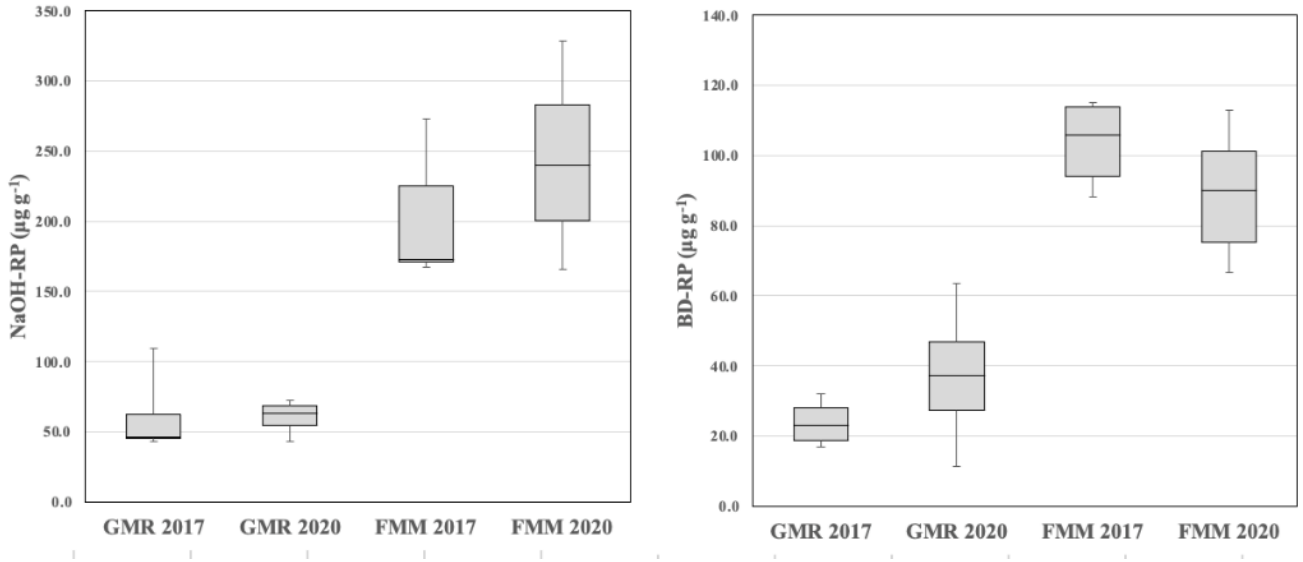


**Figure 12:** Distribution of NAIP Fractions in Sediment from Glenmore (2017, 2020) and Fort McMurray Reservoirs (2017, 2020)

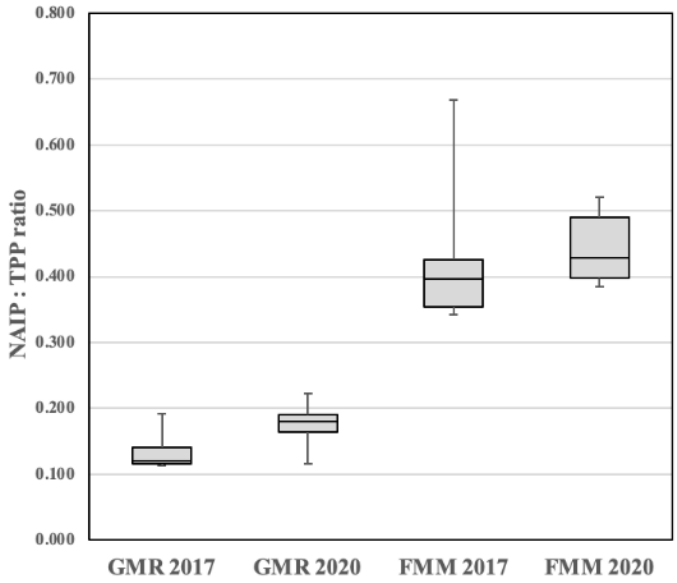


**Figure 13:** NAIP:TPP as a Bioavailable P Enrichment Indicatory in Glenmore (2017, 2020) and Fort McMurray (2017, 2020) Reservoirs

4.1.3 Phase 2: Phosphorus Sorption Characteristics: Determination of $EPC_0$

Variation in the equilibrium phosphorus condition for FMM and GMR sediment are presented in Table 6 and Figure 14. These figures provide information related to the sorption kinetics (P release potential) of sediment and SRP in the water column. The data are presented to

contrast spatial (inter-site) and temporal (intra-site) differences as a function by site and year. The highest average $EPC_0$ values were associated with post-wildfire FMM sediments. In 2017, the average $EPC_0$ was 64.76 and ranged from 56.01-56.21 μg P $L^{-1}$ in the east reservoir and 60.7-77.05 μg P $L^{-1}$ in the west reservoir. After dredging in 2020, the average $EPC_0$ was 31.7 μg P $L^{-1}$ ranging from 27.49-36.25 μg P $L^{-1}$ in the east reservoir and 12.72-50.63 μg P $L^{-1}$ in the west reservoir. The lowest average $EPC_0$ values were associated with GMR sediment in 2017 (13.7 μg P $L^{-1}$) and 2020 (14.1 μg P $L^{-1}$).

The $EPC_0$ was significantly higher in pyrogenic impacted FMM sediment compared to non-wildfire-impacted GMR sediments in 2017 ($p=0.016$) and 2020 ($p=0.019$). Intra-site comparison of FMM was conducted to evaluate the potential of reservoir benthic sediment to release SRP to the ambient water column and to determine the potential role of bottom sediment as an internal loading source of P to the water column post-wildfire and post-dredging. On average, $EPC_0$ values were significantly lower in post-dredged sediments ($p=0.043$). The average $EPC_0$ value of wildfire impacted sediment was 70.5 μg P $L^{-1}$ in the FMM west pond and 56.1 μg P $L^{-1}$ in the FMM east pond. The $EPC_0$ values of post-dredged FMM sediments were nearly identical in the east (31.46 μg P $L^{-1}$) and west (31.89 P $L^{-1}$) ponds. No clear patterns in $EPC_0$ values were observed for individual sampling sites (W1-W3, E1-E3) in FMM sediment. Intra-site comparison of GMR showed no significant differences in $EPC_0$ values.

**Table 6:** Mean $EPC_0$ (μg P L-1) of bottom sediment for wildfire-impacted, dredged, and non-wildfire-impacted reservoirs (n=3)

| **FMM** | **2017** | **2020** | **GMR** | **2017** | **2020** |
|---|---|---|---|---|---|
| **W1** | 73.84 | 12.72 | **HP** | 23.63 | 24.95 |
| **W2** | 60.7 | 50.63 | **ML** | 10.59 | 9.04 |
| **W3** | 77.05 | 32.62 | **HC** | 11.7 | 10.95 |
| **E1** | 56.01 | 27.49 | **WH** | 8.88 | 11.66 |
| **E2** | 56.2 | 36.25 | | | |
| **E3** | | 30.63 | | | |

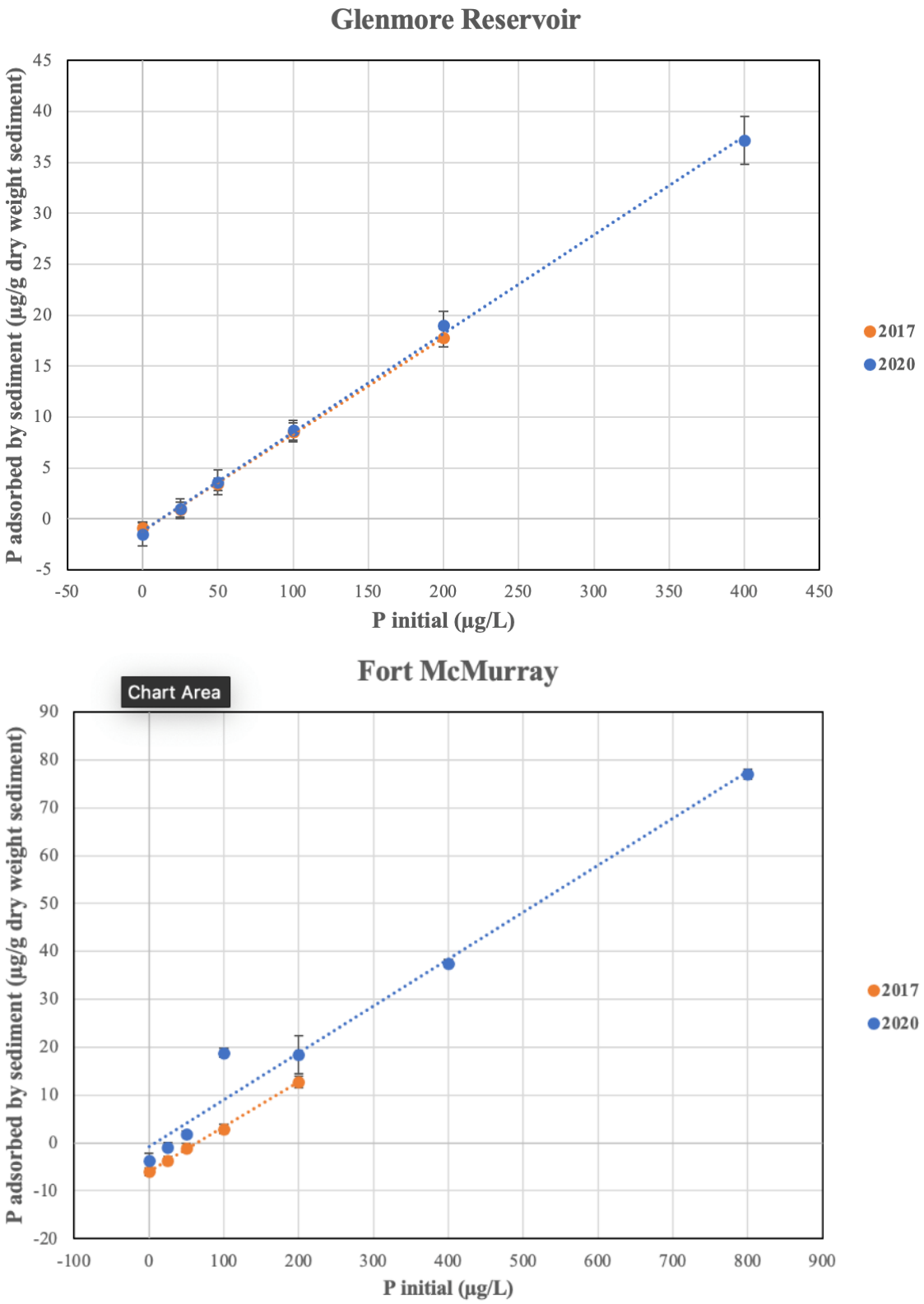


**Figure 14:** Results of P sorption experiments for GMR & FMM bottom sediments (2017 and 2020)

# Chapter 5

# Discussion and Conclusions

## 5.1 Wildfire Alters Particulate Phosphorus Forms in Drinking Water Source Reservoirs

The form and concentration of PP in benthic sediments of lakes and reservoirs (herein referred to as reservoirs) can vary greatly in water bodies around the world (Pettersson & Istvanovics, 1988). Both natural (i.e., wildfire) and anthropogenic (i.e., urban, agricultural, industrial) landscape disturbance can significantly impact the quality and composition of the material in these systems. The concentration of TPP concentrations in reservoirs can range from <600 μg P $g^{-1}$ (Pettersson & Istvanovics, 1988) to > 6400 μg P $g^{-1}$ (Pettersson, 1986). A comparison of previously published data on particulate P forms (NAIP, AP, OP) with data from the present study presented in Figure 15 underscores the effect of land use change on the nature and distribution of PP forms in bed sediments (Stone & Murdoch, 1989; Stone & English, 1993; Fogal et al., 1995; Emelko et al., 2016). Compared to these data, TPP and NAIP concentrations in FMM wildfire-impacted sediments were in the lower end of the reported range. Relative proportions of NAIP (38% and 44%), AP (49% and 44%) and OP (13% and 12%) in FMM sediments in 2017 and 2020, respectively, were most comparable to Flaming George, Concensus Lake and Lake Wivenhoe (Figure 15). The data shows that PP forms and concentrations in wildfire-impacted sediments of the FMM reservoir were comparable to some urban and agriculturally impacted reservoirs.

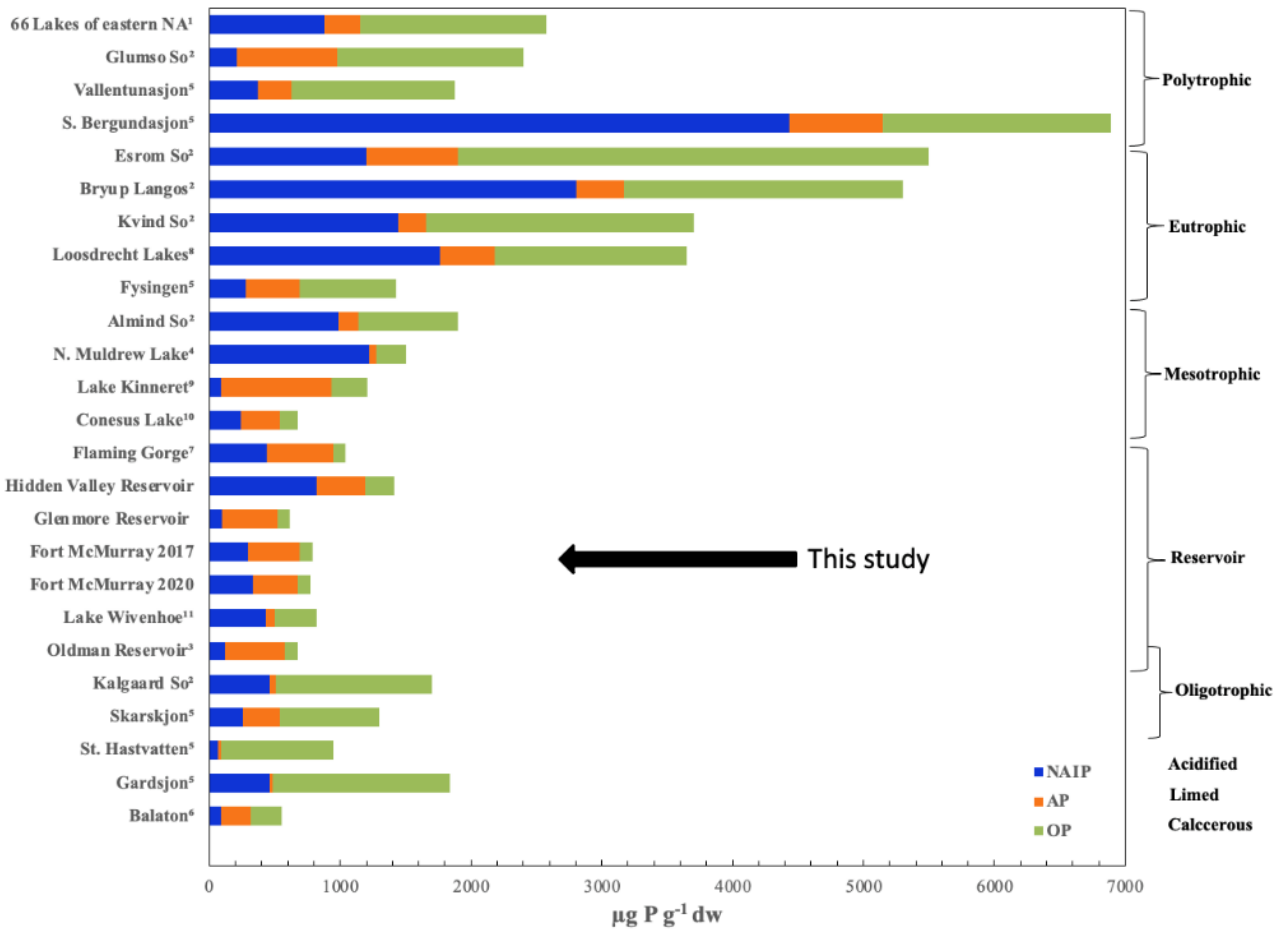


**Figure 15:** Comparison of sediment associated particle P (PP) forms of agricultural and urbanized lakes and reservoirs around the world. 1) Ostrofsky, 1987; 2) Pettersson et al, 1988; 3) Emelko et al, 2015; 4) White & Stone, 1996; 5) Pettersson, 1986; 6) Pettersson & Istvanovics, 1988; 7) Messner et al, 1984; 8) Boers et al, 1984; 9) Eckert et al, 2003; 10) Noll et al, 2009; 11) Kerr et al, 2011. (Adapted from Knezic MSc Thesis, 2021)

The impacts of urbanization and agriculture on water quality and eutrophication are well documented in rivers and lakes. Rivers draining landscapes disturbed by agriculture (Stone & English; Stone & Droppo; Fogal et al., 1995) or urbanization (Owens & Walling, 2002; Ballantine et al., 2008) typically have concentrations of NAIP and TPP that are higher than undisturbed catchments. Similar results have been observed in lakes impacted by agriculture (Pettersson, 1986; Noll et al., 2009) and urbanization (Messner et al., 1984; Pettersson, 1986; Petterson et al., 1988). However, there is a paucity of data on PP forms in wildfire-impacted drinking water reservoir sediment. Recent studies of PP in riverine suspended and bed sediment (Son et al., 2015; Emelko

et al., 2016; Watt et al 2021) found that concentrations of TPP and bioavailable NAIP were higher in river sediments draining burned catchments ~3-7 years after wildfire in high relief forested landscapes compared to non-wildfire-impacted landscapes (Figure 16). Elevated levels of post-wildfire fine sediment and associated phosphorus yields are well documented in headwater landscapes such as the Rocky Mountains (Emelko et al., 2016). However, much less is known about how wildfire impacts sediment chemistry and P yields in low-relief, wetland dominated forested sub-catchments such as the Athabasca River.

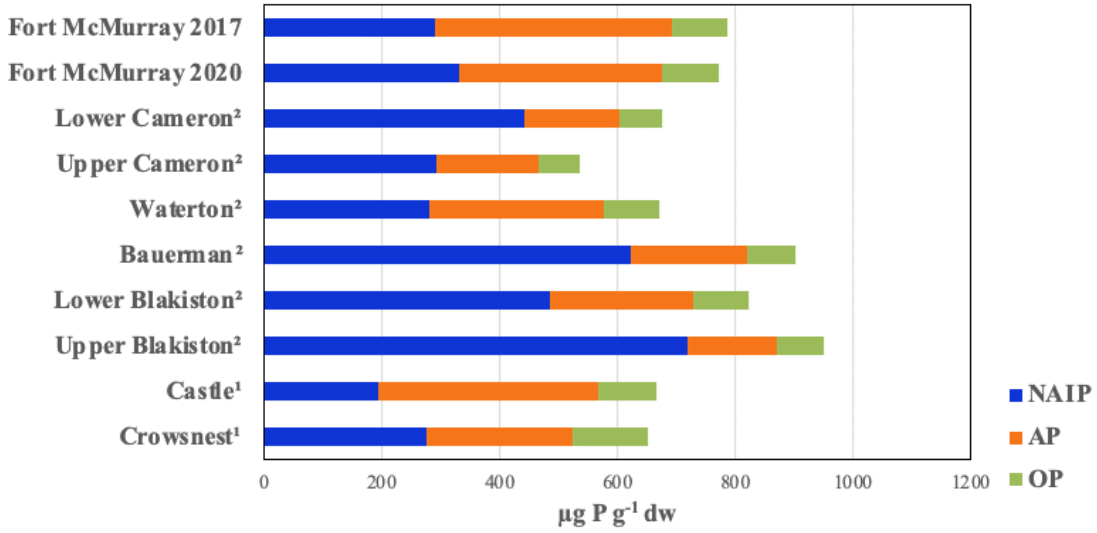


**Figure 16:** Sediment associated particulate P (PP) forms in wildfire impacted rivers in Alberta. 1) Emelko et al., 2016; 2) Tullio MSc Thesis University of Waterloo, 2021

### 5.1.1 Physical and geochemical factors controlling P forms

Many abiotic factors such as redox conditions, temperature, particle size, sediment geochemistry and fluid shear stress can influence the distribution and spatial variability of particulate P forms in aquatic environments. Wildfires are amongst the most severe landscape disturbance types that can impact the physical and geochemical characteristics of sediment and alter the form and release potential of P bound to sediment (Emelko et al., 2016; Watt et al., 2021). The Horse River wildfire burned at high severity resulting in complete combustion of the peat layer in some areas (Wilkinson et al., 2018). Severe wildfires can substantially affect ash and sediment chemistry (Bodi et al., 2014) and is demonstrated in the geochemical analyses of FMM sediment in Table 3 and Figure 10. Wildfire-impacted sediment had elevated levels of Mn, Fe and

Al that are known adsorptive surfaces for binding bioavailable P (Figure 10 & 11). These results are consistent with the significantly higher concentrations of reductant soluble P (i.e., redox sensitive P generally associated with Fe hydroxides and Mn compounds) and metal oxide bound P (Bodi et al., 2014). Concentrations of TPP and NAIP in benthic sediment of the FMM reservoir were significantly higher compared to GMR sediments in 2017 and 2020 (Table 5 & Figure 11). These results are comparable to data from other studies that report elevated metal levels (Gallaher et al., 2002; Ranalli & Stevens, 2004; White et al., 2006; Biswas et al., 2007; Silins et al., 2009b; Writer & Murphy, 2012; Otero et al., 2015; Tecle & Neary, 2015) and bioavailable PP forms in both soil and river sediment after wildfire (Blake et al., 2010; Emelko et al., 2016; Watt et al., 2021). There is a paucity of research on the impacts of wildfire on sediment biogeochemistry in peat dominated landscapes outside of dissolved organic carbon (Brown et al., 2015). Consistent with results in FMM, one study found that after a high intensity peat fire – like that of the Horse River Wildfire – there was an increase in P in the upper layers of soil and there was a significant change in P forms from organic P to inorganic and more bioavailable forms of P (Smith et al., 2001).

The metal-oxide bound P (NaOH-RP) fraction which is associated with Al-hydroxides and to a lesser extent Fe-hydroxides, was the most abundant NAIP fraction in FMM sediment accounting for 25% and 32% of TP in 2017 and 2020, respectively. Although Fe and Al post-dredge concentrations declined, these elements were significantly higher compared to GMR in both years. These results are consistent with previously published studies and indicate that not only are fire impacted sediments higher in Al and Fe, but these elements are key drivers of P dynamics in reservoirs (San Clements et al., 2009). Notably, total manganese (Mn) concentrations prior to the wildfire were low (~40 μg/L) in river reaches immediately downstream of RMWB Water Treatment Plant (Tondu, 2017). Post-wildfire Mn concentrations in FMM reservoir sediments were significantly higher compared to GMR ($p=0.016$) and were elevated by a factor of 5.1 compared to Athabasca River sediment. In 2017 and 2020, total NAIP concentrations were higher in the first settling pond (east pond) of FMM. Specifically, compared to the west pond, the east pond had higher concentrations of Mn and associated bioavailable BD-RP, likely a result of sediment fining (Stone, 1987; Paola et al., 1992; Haralampides et al., 2003; Fedele & Paola, 2007; Watt, 2018). Increased post-wildfire levels of Mn in sediment are commonly reported in the literature and have a strong association with bioavailable P forms (Bodi et al., 2014). The

distribution and relatively high concentration of sediment-associated metals (Al, Fe, and Mn), when compared to non-wildfire-impacted GMR sediments indicate that post-wildfire reservoir sediments have highly sorptive surfaces that preferentially bind bioavailable P (Stone & English, 1993; Emelko et al., 2016). Furthermore, elevated levels of redox sensitive NAIP and the observed anoxia below the sediment-water interface suggest that FMM sediments represent a potentially significant bioavailable P source that could contribute to the internal loading of P to the water column.

## 5.2 Wildfires Enhance P Mobility and Increase the Risk of Internal Loading in Drinking Water Reservoirs

The equilibrium phosphate concentration ($EPC_0$) is typically used as a surrogate measure of the P release potential of sediment in aquatic systems (House & Denison, 1998; 2000). A series of bench-scale batch experiments were conducted to analyze the $EPC_0$ and evaluate the potential impacts of wildfire impacted sediment on internal loading of P in two drinking water reservoirs (Table 6 and Figure 14). While there is a paucity of sediment $EPC_0$ data for reservoirs impacted by wildfire, the pattern of higher post-wildfire sediment $EPC_0$ in the FMM reservoir are consistent with those studies conducted in rivers draining burned landscapes (Emelko et al., 2016; Son et al., 2015; Watt, 2018). Within the literature, freshwater phosphorus sorption dynamics are mainly focused on anthropogenic disturbances such as agriculture and urban impacted systems (i.e., sewage). The data in Table 7 are presented to compare $EPC_0$ values of the FMM reservoir with studies of rivers and lakes impacted by a variety of anthropogenic disturbances. Sediment $EPC_0$ varies greatly in aquatic systems ranging from <1 (Jarvie et al., 2005) to 1300 $\mu g\ P\ L^{-1}$ (Agudelo et al., 2011) depending on type and severity of landscape disturbance. Table 7 also exemplifies that there is often wide variability in sediment $EPC_0$ along the river continuum in systems impacted by different disturbances such as agricultural (Jarvie et al., 2005) and wildfire (Son et al., 2015; Watt, 2018). The mean $EPC_0$ of the present study are comparable to the lower values of previously reported aquatic systems impacted by wildfire (Son et al., 2015; Watt, 2018), agricultural (Jarvie et al., 2005) and urban (Jarvie et al., 2006; Knezic, 2020) disturbances. The mean $EPC_0$ in FMM post-wildfire (62.74) and post-dredge (31.7) sediment were higher than the slightly contaminated industrial wastewater and domestic sewage in China (Jin et al., 2005) and far lower than systems severely impacted by dairy farms and pastureland (Reddy et al., 1996). The GMR is mainly

impacted by urban disturbances and was of the lowest reported $EPC_0$ values in Table 7. The data in the present study indicate that the accumulation of fine P-enriched sediment in the FMM reservoir represent a key internal source of SRP to the water column.

**Table 7:** Comparison of sediment EPC0 concentrations (µg P L-1) for river, lake, and reservoir sediments across a variety of landscapes and landscape disturbances (Adapted from Watt, 2018)

| **Citation** | **Location** | **Impacts** | **Site** | **Mean $EPC_0$ (µg P $L^{-1}$)** |
|---|---|---|---|---|
| **Present Study** | Alberta, Canada | Wildfire | FMM Drinking Water Reservoir | 64.76 (2017)<br>31.7 (2020) |
| **Present Study** | Alberta, Canada | Urban | GMR Drinking Water Reservoir | 13.7 (2017)<br>14.2 (2020) |
| **Jin et al., 2005** | Jiangsu, China | Industrial wastewater, domestic sewage (heavily contaminated) DW | Wuli Lake | 157 |
| **Jin et al., 2005** | Jiangsu, China | Industrial wastewater, domestic sewage (slightly contaminated) | East Taihu Lake | 20 |
| **Wang et al., 2006** | Hubei, China | Industrial wastewater, domestic sewage | Yehu Lake | 87.9-214.8 |
| **Knezic, 2020** | Ontario, Canada | Urban, agriculture | Hidden Valley Drinking Water Reservoir | 47-407 |
| **Watt, 2018** | Alberta, Canada | Wildfire, sewage | Crowsnest River | 41-579 |
| **Son et al., 2015** | Colorado, USA | Wildfire | Cache la Poudre River | 30-1200 |
| **Jarvie et al., 2005** | SW UK | Agriculture, pasture, grazing | Avon River | 2-178 |
| **Jarvie et al., 2005** | SW UK | Agriculture, pasture, grazing | Wye River | <1-195 |
| **Reddy et al., 1996** | Florida, USA | Dairy farms/pasture | Otter Creek | 120-230 |
| **Agudelo et al., (2011)** | Kansas, USA | Intensive Agriculture | Upper West Emma Creek/Red Rock Creek | 800-1300 |

Sediment $EPC_0$ varies greatly throughout the literature based on type and severity of landscape disturbance, environmental conditions and geochemical characteristics that influence sediment P mobility. Additionally, mineralogy (House and Dennison, 2002; Withers and Jarvie, 2008), particle size (Stone and English, 1993), residence time, water to sediment ratio, temperature (Nurnberg, 2012), solution chemistry and ionic strength (Lucci et al., 2010; Buhadha et al., 2012) also influence P release. The complex nature of phosphorus sorption dynamics in aquatic sediment exposed to cumulative landscape disturbances are further exacerbated by climate change. Moreover, methods for determination of $EPC_0$ vary greatly throughout the literature and sorption data should be compared with caution.

Post-wildfire and post-dredge P sorption data show that the P release potential of FMM reservoir sediment increased from the east to the west pond. The higher release potential in the west pond is likely related to the phenomenon of sediment fining (Stone, 1987; Paola et al., 1992; Haralampides et al., 2003; Fedele & Paola, 2007; Watt, 2018). Suspended particulate matter will settle differentially based on size and density (Haralampides et al., 2003). Larger and more dense particles settle first in the east pond and finer particulate matter with elevated bioavailable P are preferentially transported to the west pond. The sediment fining phenomenon has previously been observed in a study of P in the Hidden Valley drinking water reservoir where Knezic (2020) found that $EPC_0$ increased substantially from the first settling pond (47 $\mu g\ P\ L^{-1}$) to the fourth and final settling pond (407 $\mu g\ P\ L^{-1}$). Interestingly, inverse to results from other research, fine particulate matter in the west pond had lower concentrations of bioavailable NAIP and higher concentrations of AP compared to the east pond post-wildfire (Stone & Murdoch, 1989; Stone & English, 1993). Post-dredge, the west pond had slightly higher bioavailable NAIP and lower AP. This in part could be a consequence of the higher levels of Al, Mn, and Fe in sediment in the east pond that are known sorptive surfaces for bioavailable P. Nevertheless, the preferential deposition and subsequent accumulation of fine sediment is a key driver of the observed higher $EPC_0$ in FMM's west pond.

Fine-grained sediments have the potential to release phosphorus to the water column when SRP concentrations are < $EPC_0$. Although no SRP data were available for the FMM reservoir post-wildfire, there are several lines evidence to suggest that SRP levels within the east and west ponds are below the reported $EPC_0$. Prior to the wildfire in 2015, SRP (orthophosphate) concentrations in the Athabasca River measured directly downstream of the RMWB water treatment intake were ~18 $\mu g\ P\ L^{-1}$ (Tondu, 2017). A comparable study by Knezic (2020) found the mean dissolved

phosphorus concentrations in the Hidden Valley drinking water reservoir to be 15.3 μg P $L^{-1}$ and reported much higher TPP enrichment and $EPC_0$ (149.25 μg P $L^{-1}$) when compared to FMM reservoir. Therefore, it is likely that the dissolved phosphorus concentrations in FMM reservoir are below those found by Knezic (2020) and are in the trophic range of oligotrophic (4-10 μg P $L^{-1}$) and mesotrophic (10-20 μg P $L^{-1}$) (Table 2). Considering average $EPC_0$ values in FMM were 64.76 and 31.7 μg P $L^{-1}$ in 2017 and 2020, respectively, and SRP concentrations are estimated within the range of 4 to 20 μg P $L^{-1}$ this indicates a significant potential for P release and a source of internal P loading. This is further exemplified as temperature can be an important driver of $EPC_0$. Nurnberg et al., (2012) found that in a shallow mesotrophic lake in Finland, internal loading was positively correlated with high summer (i.e., August) temperatures which averaged 18.5°C across the 26 years study. Average temperatures in FMM on August 25$^{th}$ were 17.7°C (Table 4) which provides evidence that the environmental conditions in FMM enhance the potential of sediments to release a significant amount of SRP into the overlying water column. Considering the geochemical analyses described previously, both the east and west ponds demonstrate sediments (i) enriched with bioavailable phosphorus (i.e., NAIP) and (ii) have a higher phosphorus release potential compared to non-fire impacted sediments.

Collectively, this demonstrates that post-wildfire and post-dredged FMM sediments have the potential to release substantial amounts of bioavailable phosphorus into the overlying water column. Post-dredged sediment in the west pond had higher concentrations of NAIP and a higher release potential than the east reservoir making it of particular concern for management authorities. Internal P loading in drinking water reservoirs presents major challenges for conventional drinking water treatment operations. Under these conditions, sorption kinetics can enhance access of bioavailable P to primary producers (Wen et al., 2020). The release of bioavailable P to shallow water bodies with warm temperatures are ideal conditions for the proliferation of algae. Algal blooms reduce both the quality and quantity of water, and the addition of water-treatment by-products can lead to taste and odor problems (Emelko et al., 2011). In freshwater ecosystems, algal blooms are often dominated by toxic cyanobacteria (Yan et al., 2017; Zhu et al., 2019) which can significantly alter biogeochemical factors (e.g., create anoxic environments and water opacity) of ambient water (Chen et al., 2016), poison aquatic organisms and threaten the quality and safety of drinking water (Emelko et al., 2016; Wan et al., 2020). As mentioned, several techniques are available to control internal P loading. It is essential that drinking water reservoirs control the

release of SRP to reduce costs and maintenance on treatment infrastructure and to ensure a reliable and safe supply of clean drinking water to communities.

## 5.3 Implications of One-time Dredging on Mitigating P Release in Reservoirs

Sediment was removed from Fort McMurray's drinking water reservoir by dredging ~2-years after the Horse River Wildfire. The results of biogeochemical analyses (Figure 10), PP forms (Table 5, Figures 11 & 12) and $EPC_0$ (Table 6 and Figure 14) were summarized and reported above. The associated implications of one-time dredging for mitigating risks from algal blooms are discussed below.

### 5.3.1 Effects of Dredging on Particulate Phosphorus Form and Mobility

The composition of PP forms in FMM sediment were markedly different in 2017 (one year after wildfire) and in 2020 (teo years after dredging). In 2017, the dominant P fractions in order of decreasing concentrations were AP (49%), total NAIP (38%) which is the sum of NaOH-RP (25%) and BD-RP (13%) and lastly OP (13%). The sediment P fractions were relatively different in 2020 with NAIP (44%) and AP (44%) as the dominant fractions, followed by NaOH (32%), BD-RP (12%) and OP (12%). From 2017 to 2020, there was a decrease in TPP and bioavailable BD-RP concentrations and an increase in bioavailable NAIP and NaOH-RP concentrations. The $EPC_0$ in FMM sediment was also significantly lower. While these observations cannot be causally linked to reservoir dredging, they nonetheless underscore the importance of considering the implications of one-time dredging for mitigating P release to the water column in drinking water reservoirs, especially in absence of reductions in external P loading.

Table 8 summarizes findings of multiple studies evaluating different parameters (i.e., biogeochemical composition, PP forms, $EPC_0$, cyanobacterial biomass) in lakes/reservoirs before- and after-dredging. These data highlight the complex nature of internal P loading and emphasize the importance of temporal scale, external P load control (LC) vs. no external P load control (NLC) and *in-situ* techniques for dredging.

**Table 8:** Studies on efficacy of dredging to control internal P loading with and without external load P control. *LC = External Load Control *NLC = No External Load Control

| Method | Length of Study | Key Findings | Reference |
|---|---|---|---|
| **LC** | 58 days | Dredging lowered SRP and TP.<br>Combination of Phoslock and dredging would control cyanobacteria biomass.<br>Dredging alone not effective. | Lurling & Fassen (2012) |
| **LC** | 360 days | Major elements (Al, Fe, Ca, Mg) generally greater in non-dredged sediments.<br>$NH_4Cl$-RP, NaOH-RP, BD-RP (total NAIP) significantly reduced directly post-dredge.<br>BD-RP increased over time; $NH_4Cl$-RP decreased over time.<br>25% reduction of NAIP in immediately post-dredged sediment. *<br>$EPC_0$ and adsorption capacity increased post-dredge. | Yu et al., (2017) |
| **LC vs NLC** | 1 year | TP in sediments increased gradually post-dredge.<br>With external P loading, higher proportion of BD-RP than NaOH post-dredge.<br>If external loads are controlled, dredging can reduce internal loading and P mobility, increase P adsorption and retention capacity of sediment, and improve oxidation environment at SWI.<br>External loading post-dredge reduces effectiveness of dredging risking resupply and release of P. | Wen et al., (2020) |
| **LC after 3 years** | ~15 year | Post-dredge, the reduction of internal P loading is sustained for ~18 months if external loading not reduced. | Lui et al., (2016) |
| **LC** | 360 days | Dredging did not change percentage of mobile P ($NH_4Cl$-RP, BD-RP, and OP) to TP compared to control.<br>Lanthanum-modified bentonite (LMB) inactivation may provide better internal P control than dredging. | Yin et al., (2020) |
| **NLC** | 1 year | BD-RP fraction increased post-dredge.<br>Dredging without reduction of external loading would give only temporary improvement followed by return to initial rates of internal P loading. | Kleeberg & Kohl (1999) |
| **NLC** | 3 years | Immediately post-dredge no changes in BD-RP and Res-P, increase in NaOH, decrease in AP.<br>3 years post-dredge TP increased (compared to first year) primarily from increase of bioavailable BD-RP & NaOH-RP and Fe accumulated in new surface sediments compared to non-dredged control.<br>Dredging should only be used once external loading is blocked. | Jing et al., (2015) |

The reduction of TP (Bjork et al., 2010; Lurling & Faaseen 2012; Yu et al., 2017; Pokorny & Hauser; Kleeberg & Kohl, 1999) and BD-RP (Yu et al., 2017) in post-dredged sediments were consistent with the literature in studies of <1-year duration under varying efforts at controlling external P loads. Contrary to the present study, it was commonly reported that redox sensitive P (i.e., reductant soluble, BD-RP) dominated the total NAIP fraction ~1-year post-dredge (Kleeberg & Kohl, 1999; Yu et al., 2017; Wen et al., 2020). Yu et al., (2017) noted that Fe-bound BD-RP significantly reduced immediately post-dredge but increased over 1-year. This is supported across the literature and highlights that for both LC and NLC efforts, BD-RP concentrations increased over time (Kleeberg & Kohl, 1999; Jing et al., 2015; Wen et al., 2020). One-year post-dredge, Yin et al., (2017) reported an overall reduction (~25%) of NAIP in sediments that was dominated by BD-RP and concentrations of Al, Fe, Ca, and Mg increased.

Across the literature, it is widely reported that a crucial prerequisite for achieving long-term success at controlling internal P loading post-dredge is a sufficient, if not complete reduction of external P loads (Kleeberg & Kohl, 1999; Jing et al., 2015; Wen et al., 2020; Lui et al., 2020). In general, reductions in TP concentrations post-dredge are often parallel with external loads that were eliminated or controlled by strict environmental policy (Van der Does et al., 1992; Bjork et al., 2010; Yu et al., 2017). A long-term (~15 year) study reported that under persistent external P loading, the reduction of internal loading is sustained for ~18 months before returning to near original condition (Lui et al., 2016). Studies <1 year with no external load control (NLC) also reported temporary improvements of internal P loading followed by the return to initial rates (Kleeberg & Kohl, 1999; Pokorny & Hauser, 2002; Jing et al., 2015; Wen et al., 2020) due to an accumulation of new, often nutrient- and organic-enriched sediment (Yu et al., 2020).

In built environments it can be difficult to sufficiently reduce external loading. In undisturbed (i.e., non-wildfire-impacted) peatland ecosystems, the surface layers contain non- or partially decomposed high hydraulic conductivity *Sphagnum* moss that can regulate water table fluctuations and runoff production (Waddington et al., 2015). When this layer is oxidized, particularly after high severity fires such as the Horse River Wildfire: (i) the depth and variability of the water table increases (Brown et al., 2015) as older peat with a higher bulk density and capacity for water retention is exposed at the surface (Thompson & Waddington, 2013; Brown et al., 2015) and (ii) large expanses of fine particulate matter is exposed to erosion, particularly during precipitation events (Shakesby & Doerr, 2006; Rothwell et al., 2007; Brown et al., 2015).

Moreover, severely burned peatlands can develop hydrophobic compounds in surface peat (Hayward & Clymo, 1983). Collectively, these physical changes to peat are key drivers for local hydrology and sediment transport. Wildfires increase the potential for particulate matter, nutrients, and contaminants to be mobilized downstream (Neary et al., 2005; Rothwell et al., 2007) and produce a flashier water-table that is more responsive to small rain events thus producing hydrographs with shorter lag time and higher peak compared to non-wildfire-impacted systems (Price, 1997; Thompson & Waddington, 2013).

The magnitude and duration of water quality impacts depends on the intensity of storm events and the erosive potential of the landscape (Emelko & Sham. 2014). Headwater regions are typically extensively burned and steep and flashy landscapes produce substantial increases in suspended sediment yields compared to non-wildfire-impacted watersheds (Smith et al., 2011). Following the Horse River wildfire, suspended sediment yields, nutrients (N and P) and metals were 1.2-10x higher in rivers draining burned low-relief peat dominated catchments after storm events (Emmerton et al., 2020). Rates of erosion during precipitation events are markedly lower compared than in headwater regions (Smith et al., 2011; Emmerton et al., 2020) as sediment is flushed from peat landscapes in smaller pulses due to a higher runoff storage capacity (Devito et al., 2012; Emmerton et al., 2020). However, this study by Emmerton et al., (2020) highlights that burned peatlands are more responsive to rain events and can contribute high concentrations of wildfire impacted sediment that is heavily saturated with bioavailable P to river systems such as the Athabasca (Emmerton et al., 2020). Low-relief peat dominated landscapes do not recover from wildfire as quickly as headwater regions as fine material of pyrogenic origin can persist in the environment contributing to long-term source of external P loading downstream.

The suspended particulate matter originating from burned peatlands in the Athabasca River is diverted into the reservoir and is filtered by way of centrifuge preferentially depositing fine material – the primary vector for contaminants – with a large surface area for binding P into the east pond. Consistent with the literature, the lack of sufficient external P load control through continual deposition of wildfire impacted material into the FMM reservoir has reduced the effectiveness of dredging (Kleeberg & Kohl, 1999; Jing et al., 2015; Wen et al., 2020) and subsequently failed at effectively controlling algal biomass (Lurling & Faasan, 2012). This could also suggest that although $EPC_0$ concentrations were reduced between 21-24 months post-dredging when compared to post-wildfire $EPC_0$, the small consistent inputs of external P-enriched material

could increase $EPC_0$ back to near original states over time. It is important to note that even in systems practicing LC, it was reported that over time dredging alone was not effective. Accordingly, the impact of wildfire on peatland hydrology and related surface erosion dynamics in low-relief peat dominated landscapes may represent a critical legacy source of P enriched particulates that can impact the quality of water in off-line reservoirs used for drinking water supply.

Dredging is costly and has other draw backs that include a range of detrimental impacts on the ecosystem (Lürling & Faassen, 2012). As an individual management technique, it may not be effective in controlling internal P loading, and thereby should be carefully considered in the context of several factors (i.e., timing, frequency, cost, ecosystem, external P loading). Combined treatments such as Phoslock (Lurling & Faassen, 2012), lanthanum-modified bentonite inactivation (Yin et al., 2020) and chemical coagulant addition for P inactivation (i.e., $FeCl_3$, alum, coagulants) have produced more favourable long-term results. Lurling & Faassen (2012) found that over the 58-day experiment, combined treatments of Phoslock and dredging were most successful in reducing cyanobacteria mass. Over the short-term study, dredging alone reduced cyanobacteria whereas combined treatments reduced concentrations below levels of detection. A longer-term study (360 days) comparing dredging to *in situ* LMB inactivation found that similarly, combined treatments were far more effective and prolonged at reducing P flux (Yin et al., 2020). Combined treatment requires further investigation to establish the optimal frequency in relation to combined treatments depending on timing of dredging and application of treatment (e.g., seasonal), accumulated sludge volumes and degree of external P loading.

## 5.4 Implication of Wildfire for Sediment Management of Water Supply Reservoirs: Synthesis and Conclusions

Among many environmental, societal, and economic functions, forest ecosystems play a critical role in the supply of clean source waters to many downstream populations worldwide (Brown et al., 2004; Neary et al., 2009; Jones et al., 2009; Vose et al., 2016). In Canada, the eastern Rocky Mountain headwater regions supply water to hundreds of communities throughout Alberta and the Prairie provinces (Emelko & Sham, 2014). It is recognized that wildfires are an important natural disturbance that are essential to ecosystem structure and health (Boerner, 1982). Alarming evidence throughout the scientific community demonstrates that in Canada and around the world,

climate change has increased the frequency of large, uncontrollable fires (mega-fires) (Gelber & Bach, 2007; Pechony & Shindell, 2010; Wotton et al., 210; Flannigan et al., 2016). Anthropogenic degradation of forested wetlands, particularly peatlands such as those found in northern Alberta, has led to greater occurrences of severe wildfires (Wilkinson et al., 2018). Globally, 2020 was the worst year for wildfires on record (IPCC, 2022) and these dangerous fire regimes will continue to be exacerbated by climate change (IPCC, 2013; Flannigan et al., 2016). Frequent and extreme wildfires present a myriad of ecological, public and health related concerns; among these, the provisioning of safe and clean drinking water is of particular concern (Emelko & Sham, 2014).

Wildfires drastically alter the composition of sediment resulting in an increase in fine particulate matter with different chemical composition (Verma & Jayakumar, 2012; Bodi et al., 2014). In burned landscapes, precipitation events can significantly increase fluxes of fine sediment that is heavily saturated with metals (i.e., Fe, Al and Mn) and associated nutrients (i.e., bioavailable phosphorus) into water courses (Wentworth, 1992; Binkley & Brown, 1993; Moody et al., 2013; Son et al., 2015; Emelko et al., 2016). This material can be transported for long distances downstream and can accumulate in lakes and reservoirs (Haralampides et al., 2003; Kunze & Stednick, 2006; Silins et al., 2009; Son et al., 2015) where internal P loading can lead to long-term water quality issues. The current body of literature on P speciation (Pettersson et al., 1988; White & Stone, 1996; Townsend & Douglas, 2004; Burke et al., 2005; Blake et al., 2010; Kerr et al., 2011) and P mobility (Jin et al., 2005; Wang et al., 2006; Reddy et al., 1996; House and Dennison, 2002; Jarvie et al., 2005; Agudelo et al., 2011) is mainly focussed on areas of anthropogenic disturbance (i.e., agriculture and wastewater) in freshwater systems. Recently, more attention has been placed on improving understanding on the effects of increased sediment pressures following a wildfire disturbance on P dynamics in rivers (Emelko et al., 2016; Watt et al., 2021). These studies exemplify that in rivers draining burned catchments, elevated sediment-associated contaminant concentrations can persist for decades and have legacy impacts on downstream water quality. Less is known about how wildfires impact P dynamics in lakes and reservoirs and this may be the first study of its kind to focus specifically on P dynamics in a wildfire-impacted off-line drinking water reservoir. The present study aimed to fill existing knowledge gaps on P dynamics in fresh shallow water bodies following a wildfire as well as present new data on (i) the impacts of wildfire on the abiotic controls of fine sediment in an off-line drinking water reservoir and (ii) the efficacy of dredging in a wildfire impacted off-line drinking water reservoir. This work

examined intra- and inter-site variability as a function of site (GMR & FMM) and year (2017 & 2020) in sediment-associated P form and mobility in reservoir benthic sediment. As climate change and the subsequent frequency and severity of wildfires increase, supplying adequate and safe drinking water will become progressively more challenging and expensive for drinking water system operators (Emelko et al., 2011; Emelko & Sham, 2014). Therefore, developing a deeper understanding of the effects of wildfire on nutrient dynamics in drinking water reservoirs will be become increasingly crucial for an abundant supply of clean safe drinking water in the future.

Particulate phosphorus dynamics in lake and reservoirs are controlled by several physical, chemical, and biological factors. In aquatic systems, fine sediment is the primary vector of P transport and strongly influences the form (NAIP, AP, OP) and mobility ($EPC_0$) of PP (House, 2003). Fine sediment of pyrogenic origin has a large surface area for binding P and typically contains high concentrations of metal coatings to which P tends to sorb (Stone & Murdoch, 1989). Consistent with the literature, FMM sediment had significantly higher concentrations of Fe and Al when compared to GMR. Wildfire-impacted sediments also had significantly higher levels of Mn which can be explained by the extremely high (~1962°C) temperatures required for this specific metal to become volatile (Bodi et al., 2014). Wildfire-impacted sediments had significantly higher concentrations of TPP and NAIP. Mean TPP concentrations in FMM ranged from 765.8-897 $\mu g/g_{sed}$ in 2017 and 725.6-783 $\mu g/g_{sed}$ in 2020 with total composition being 38% and 44% bioavailable NAIP in 2017 and 2020, respectively. These TPP levels and high proportions of the bioavailable fraction indicate that FMM's wildfire-impacted sediment is consistent with sediments from heavily impacted urban and agricultural aquatic systems. This highlights that natural disturbances such as wildfires have the potential to severely impact water quality in a similar way to anthropogenic disturbances that have been widely recognized as a major threat to freshwater quality (Emelko et al., 2016; Jarvie et al., 2005). In future research, it is recommended that the collection of baseline data would be extremely useful in understanding the impacted of wildfire on sediment geochemistry and P forms. Drinking water reservoirs with receiving waters in landscapes that are particularly at risk for wildfire would be excellent candidates for sediment chemistry and P form data collection.

Phosphorus isotherm experiments are used to determine P sorption dynamics in aquatic systems. The data determine the capacity of sediment to adsorb/desorb P to/from the water column as well as the $EPC_0$ which described the point at which sediment neither sorbs nor desorbs SRP

from solution (Froelich, 1988). Consistent with similar research conducted in rivers (Emelko et al., 2016), data from the present study shows that the $EPC_0$ was significantly higher in wildfire-impacted material compared to non-wildfire-impacted material. A recommendation for future research on P mobility in drinking water reservoirs is the collection of both baseline data as well as SRP data in the water column. Based on multiple lines of evidence, it is suggested that SRP < $EPC_0$ in FMM, and therefore sediment is a source of SRP to the water column. However, more concrete SRP data would be highly beneficial to understanding the internal P loading processes in the reservoir.

In freshwater ecosystems, the internal loading of bioavailable NAIP to the water column is a driver of algal growth (Nurnberg, 1988; Stone & Droppo, 1994; Emelko et al., 2016). Algae blooms, in particular cyanobacteria, are one of the biggest threats to the provision of safe drinking water worldwide as they drastically alter water quality and affect drinking water treatment processes (Crittenden et al., 2012). Higher levels of nutrients and cyanobacterial biomass increase turbidity and may reduce the efficiency of coagulation and flocculation processes, clog filters and shorten run times (MWH, 2012). Cyanobacteria have the potential to release cyanotoxins during treatment and are typically the primary cause of taste and odor problems that are difficult to resolve by conventional water treatment processes (Emelko et al., 2016; Westrick, 2010). Fluctuations in water quality (i.e., turbidity, dissolved organic carbon, nutrients such as P, heavy metals) can present major challenges for drinking water treatment as source water quality frequently exceeds treatment and/or operation capacities and existing treatment may be rendered inadequate (Smith et al., 2011; Emelko & Sham, 2014).

Following the 2016 Horse River Wildfire, wildfire-impacted material was removed by dredging. Intra-site comparison in FMM revealed that although concentrations decreased from 2017 to 2020, FMM sediments were richer in Fe, Al and Mn compared to GMR sediments. In 2020 sediments, TPP and BD-RP concentrations decreased but total NAIP and NaOH-RP concentrations increased. Contrary to the results of this study, much of the literature reported that BD-RP was the dominant NAIP fraction post-dredge and that over time concentration of this fraction increased (Kleeber & Kohl, 1999; Jing et al., 2015; Yu et al., 2017; Wen et al., 2020). It is recommended that P speciation experiments be conducted more frequently to better understand the dynamics of P forms over time. If FMM's BD-RP concentrations increase over time and anoxic conditions such as those reported in 2020 in FMM persist, this fraction can be an increasingly

substantial source of bioavailable P to the water course. It is widely supported that a crucial prerequisite for achieving long-term success at controlling internal P loading post-dredge is controlling external P loads (Jeppesen et al., 1990; Kleeberg & Kohl, 1999; Jing et al., 2015; Wen et al., 2020; Lui et al., 2020). Without external P load control, internal P loading returned to near original conditions after ~12-18 months (Kleeberg & Kohl, 1999; Pokorny & Hauser, 2002; Jing et al., 2015; Lui et al., 2016; Wen et al., 2020). This can largely explain why algal blooms have persisted in FMM despite dredging.

Burned peatlands are more responsive to rain events and can contribute high concentrations of wildfire-impacted sediment that is heavily saturated with bioavailable P to river systems such as the Athabasca (Emmerton et al., 2020). Unlike some mountainous headwater regions, low-relief peat dominated landscapes recover very slowly after wildfire disturbance and fine material of pyrogenic origin can be eroded into water courses where it contributes to long-term external P loading downstream. Despite a continuous supply of external P into the FMM reservoir, mean $EPC_0$ concentrations reduced from 64.76 μg P $L^{-1}$ post-wildfire to 31.7 μg P $L^{-1}$ post-dredge. Based on the evidence gathered, it is likely that the SRP is well below the 2020 $EPC_0$ suggesting that sediment remain a large source of bioavailable P to the water column. Although there needs to be more research to understand the influence of external P loading on $EPC_0$, this line of evidence suggests that over time small consistent external inputs of PP into the reservoir could lead to an increase in $EPC_0$. Although sediment $EPC_0$ data after reservoir dredging are scant, it has been reported that sediments from lakes with strict controls on external P loads have exhibited increased $EPC_0$ after dredging (Yu et al., 2017). Interestingly, despite a reduction in $EPC_0$ the same study reported a post-dredge decrease in P flux from sediment when combined inactivation of P to Fe (hydroxy)oxides. Collectively this highlights two important considerations for dredging found in the present study; (i) a crucial prerequisite of dredging is the sufficient if not complete reduction of external P loads which can be extremely difficult in natural systems and (ii) the long-term success of dredging to control internal P loading is far more effective alongside combined treatment (Yu et al., 2017; Yin et al., 2020).

As our climate continues to warm, the risk of natural disturbances such as extreme wildfires are of increasing concern for water quality and supply. An integrative management strategy encompassing both watershed management and water supply infrastructure is necessary to mitigate the impacts of wildfire of the provision of safe drinking water. Watershed management preserves

natural water storage and improves drought resistance, as well as preventing the risk of severe wildfires in source watersheds (Emelko & Sham, 2014; Robinne et al., 2021). Combined investments in wildfire prevention, fuel management (i.e., thinning, prescribed burns) and watershed restoration are more successful and lucrative than firefighting and investing in frequent and often less effective post-fire landscape management strategies (North et al., 2015; Robinne et al., 2021). However, severe wildfires events are becoming a climate reality in Canada and around the world and drinking water treatment facilities must evolve and adapt alongside the changing climate. Improving water supply infrastructures is key in reducing vulnerability to wildfire.

Wildfires can significantly alter the water quality in drinking water reservoirs. The sediment chemistry, PP forms and $EPC_0$ in these systems are dynamic and unpredictable depending on the nature of the sediment. Further research is required to understand P dynamics over time and to make the most sustainable management decisions for controlling internal P loading and cyanobacterial blooms. As natural systems are a complex mix of physical, environmental, and biogeochemical factors that influence sediment phosphorus form and mobility, the best management techniques for controlling internal P loading should be considered on an individual basis to address the specific needs that are appropriate to regional situations.

### 5.4.1 Conclusions

The goal of this study was to evaluate the abiotic controls on fine sediment-associated PP form and mobility in a wildfire-impacted and non-wildfire-impacted drinking water reservoir in Alberta, Canada as well as examine the efficacy of dredging to mitigate internal P loading. The conclusions of this study include:

(1) Wildfire-impacted reservoir sediment contained elevated metal (i.e., Al, Fe and Mn) levels - compared to non-fire impacted sediment – that have absorptive surface that bind with phosphorus.

(2) Compared to non-wildfire-impacted sediments, wildfire-impacted sediments had elevated levels of bioavailable phosphorus fractions (Total NAIP, BD-RP, NaOH-RP) that are recognized in promoting algae growth in aquatic systems

(3) Measurement of low redox potential post-dredge, coupled with high concentrations of redox sensitive (i.e., BD-RP) particulate phosphorus in reservoir bottom sediment post-

wildfire and post-dredge indicated high potential for iron reduction and release of bioavailable phosphorus,

(4) Higher equilibrium phosphate concentrations ($EPC_0$) in wildfire-impacted sediments compared to non-wildfire impacted sediments alongside evidence to suggest SRP < $EPC_0$ indicating a significant source of sediment-associated bioavailable P to the water column,

(5) Elevated $EPC_0$ in the west FMM pond – likely a result of sediment fining – highlights a management priority of downstream reservoirs,

(6) In 2020, FMM sediments had lower TPP and bioavailable BD-RP concentrations and increased total NAIP and NaOH-RP concentrations compared to 2017 sediments, and

(7) The TPP:NAIP ratio increased in FMM sediments in 2020 as NAIP comprised 35% and 44% of TPP in 2017 and 2020, respectively.

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