Biological and physicochemical mechanisms affecting phosphorus and arsenic efflux from prairie reservoir sediment, Buffalo Pound Lake, SK, Canada.

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ABSTRACT

Eutrophication and algal blooms pose environmental and economical issues in freshwater lakes globally. Algal bloom development is primarily attributed to phosphorus (P), which can be released from lake bottom sediments under certain environmental conditions. Simultaneous to P release, arsenic (As), which is a geochemical P analogue, can be mobilized from sediments and exert toxicity in aquatic organisms. Recent studies within the Canadian prairies have focused on concerns regarding water scarcity and the increased development of algal blooms. However, lake sediments within the Canadian prairies, which are susceptible to P and As mobilization, have received little attention. Using a regionally important freshwater lake (Buffalo Pound Lake, SK, Canada), the goal of this study was to identify environmental mechanisms and geochemistry that influenced P and As mobilization from Canadian prairie lake sediment.

Laboratory sediment core incubation experiments demonstrated that warm temperatures (19°C) had the greatest influence on P mobilization from sediment, followed by high pH (pH=9.2), and then low dissolved oxygen (DO) concentrations (<1 mg O_2 L^{-1}). High pH had the greatest influence on As mobilization from sediment, followed by warm temperatures, and then low DO concentration. The content of total P, relatively labile P fractions, and total As in sediment were not significantly different among sites. However, concentrations of aluminum (Al) and iron (Fe), common P and As sorbents in sediment, were significant different among sites. In sediment core incubations, the site that displayed less P and As mobilization under anoxic conditions also contained greater concentrations of Al in sediment. Redox-insensitive Al likely mitigated P and As mobilization under anoxic conditions, as evident by decreased P and As mobilization.

Phosphorus and As were also mobilized from sediment *in situ* during ephemeral periods of bottom water stratification and suboxia. Although these conditions are known to facilitate P release in Fe-poor, polymictic lakes, this paradigm appears to also apply to As mobilization. Similar to the laboratory results, less P and As were mobilized *in situ* from sediment containing greater Al content.

Overall, results demonstrated that, in addition to the above environmental variables, sediment geochemistry has a major influence on P and As mobilization from sediment in this Canadian prairie lake. Overall, it is important to determine concentrations of geochemical sorbents (i.e., Fe and Al) when studying P and As mobilization in shallow freshwater lakes globally.

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LIST OF ABBREVIATIONS

$\mu g\ kg^{-1}$	Microgram per kilogram
$\mu g\ L^{-1}$	Microgram per liter
Al	Aluminum
ANOVA	Analysis of variance
AP	Apatite phosphorus
Ar	Argon
As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
ATP	Adenosine triphosphate
BPWTP	Buffalo Pound Water Treatment Plant
C	Carbon
Ca	Calcium
CFAP	Authigenic carbonate fluorapatite
DGT	Diffusive gradients in thin films
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DMA^{III}	Dimethylarsenous acid
DMA^{V}	Dimethylarsinic acid
d.w.	Dry weight
EDTA	Ethylenediaminetetraacetic acid
FAP	Detrital apatite of igneous or metamorphic origin
Fe	Iron
FeOOH	Iron oxides/hydroxides
H	Hydrogen
HAB	Harmful algal bloom
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ISQG	Interim sediment quality guideline
MDL	Method detection limit

mg kg^{-1}	Milligram per kilogram
MMA^{III}	Monomethylarsenous acid
MMA^{V}	Monomethylarsonic acid
Mn	Manganese
N	Nitrogen
O	Oxygen
O_2	Molecular oxygen
OP	Organic phosphorus
P	Phosphorus
PEL	Probable effect level
mg L^{-1}	Milligram per liter
RR	Release rate
TDP	Total dissolved phosphorus
TP	Total phosphorus
TRP	Total reactive phosphorus
S	Sulfur
S^{2-}	Sulfide
SO_4^{2-}	Sulfate
SRP	Soluble reactive phosphorus
SWI	Sediment water interface

PREFACE

This thesis has been organized as a manuscript thesis. Therefore, there will be some reiteration of information among chapters. Chapter 1 is a literature review and general introduction to the research and Chapter 4 will provide an overall discussion and conclusion of this thesis. Chapters 2 and 3 are in the process of being submitted to peer-reviewed scientific journals for publication.

The author contributions to the chapters of this thesis were as follows:

Lawrence D'Silva (University of Saskatchewan) collected, processed, and analyzed all samples, performed all statistical analyses, drafted both manuscripts (Chapters 2 and 3) and wrote the thesis.

Karsten Liber (University of Saskatchewan) was co-principal investigator of the research project and thoroughly involved throughout the research of this thesis.

Lorne Doig (University of Saskatchewan) was co-principal investigator of the research project and thoroughly involved throughout the research of this thesis.

Helen Baulch (University of Saskatchewan) was co-principal investigator of the research project and thoroughly involved throughout the research of this thesis.

Katherine Raes (University of Saskatchewan) provided input and assistance to experimental design and sampling for Chapter 2.

CHAPTER 1

GENERAL INTRODUCTION

1.1. Phosphorus – Geographic distribution and chemical properties

Phosphorus (P) is a non-metallic element with an atomic number of 15 and atomic weight of 30.97. It is the 11th most abundant element in the earth's crust at a concentration of ~1000 mg kg^{-1} (Emsley, 2011). However, it is present in much lower concentrations in the environment (0.65 mg kg^{-1} in soils, trace amounts in the atmosphere, and very low concentrations in ocean surface waters and deep waters at 1.5 μg L^{-1} and 6.5 μg L^{-1}, respectively; Emsley, 2011). First isolated in 1669 (Pierrou, 1976), elemental P does not occur naturally in the environment, but is present as an oxyanion, phosphate, which is mined around the world for use in various industrial products (e.g., fertilizers, munitions, detergents, flame-retardants, insecticides, and herbicides; Emsley, 2011). Phosphorus is a crucial molecule for all living organisms as a major component of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and adenosine triphosphate (ATP; Pierrou, 1976). Almost all forms of energy exchange within living cells involve cleaving high-energy phosphate bonds (Gulick, 1955). It also provides structural support in organisms as phospholipid membranes and hydroxyapatite (i.e., bones; Ruttenberg, 2003). Phosphorus is not directly toxic to humans and animals (Carpenter et al., 1998), but can exhibit toxicity towards plants under certain conditions (Longeragan et al., 1979).

1.2. Phosphorus in freshwater lakes

1.2.1. Sources, fate, and transport

Phosphorus is significantly less abundant in freshwater lakes relative to other biologically required elements such as carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and oxygen (O). As a result, P is usually the long-term limiting nutrient in freshwater systems, as other nutrients (e.g., C and N) have processes to adjust for deficiencies (i.e., atmospheric CO_2 input and N-fixation, respectively; Schindler, 1977; Wetzel, 1983; Litchman et al., 2003; Sterner, 2008). The average composition of atomic element ratios in phytoplankton as P:N:C are 1:16:106, respectively (Redfield, 1958). However, freshwater lakes do not appear to become N-limited until N:P <14:1, because the N:P requirements of algae vary among species (Downing and McCauley, 1992). Phosphorus enters the food chain through primary producers, which are consumed by grazers, followed by movement through trophic levels (Ruttenberg, 2003; Cembella et al., 1984a,b). Ultimately, P will either be deposited in the bottom sediments, or returned to the water column as inorganic P, where it can either be taken up again by phytoplankton or macrophytes (Robson, 2014).

Freshwater lakes receive P through only a few major pathways. Precipitation and groundwater usually contribute very little P with a range up to 100 $\mu g\ L^{-1}$ and average concentration of 20 $\mu g\ L^{-1}$, respectively (Wetzel, 1983). However, recent research has shown that atmospheric deposition of P can be significant enough to shift a system from P- to N-limited (Camarero and Catalan, 2012). Phosphorus poor areas may receive input from P rich areas, such as a transfer of P from farmland to oligotrophic lakes, in a pseudo-diffusive redistribution of atmospheric P within local systems (Tipping *et al.*, 2014). Land runoff and flowing surface waters are generally major inputs of nutrients in freshwater systems (Mortimer, 1941; Wetzel, 1983). Overland runoff and inflow can contain P from point (e.g., urban effluent and industrial discharges) and non-point sources (e.g., agricultural runoff, drainage from enriched soils; Wetzel, 1983). Concentrations of nutrients in surface water of lakes are highly correlated to the characteristics of soil in their respective drainage basins, which influence concentrations of nutrients in watershed runoff (Soranno et al., 1996). Bottom sediment can often contain large quantities of P, and can act as a P sink or source of P in overlying water (Wetzel, 1983).

The fate of P in a freshwater lake can be simplified by considering the system as three separate compartments with exchangable fluxes (Wetzel, 1983). The first compartment is the epilimnion, which is comprised of the open water and organisms. The second compartment consists of the littoral organisms, and the final compartment consists of the hypolimnion and sediment. All P will influx through the drainage basin into the epilimnion where it can be removed through outflow, become temporarily stored within organisms and sediment, or permanently buried within sediment.

Phosphorus, as dissolved or particulate fractions, can be temporarily or permanently stored within sediment (Søndergaard et al., 2001). Dissolved P is comprised of phosphate and organic P, whose diffusive movement is subject to concentration gradients of P and other compounds (Søndergaard et al., 2003). Particulate P can adsorb or chemically bind to a variety of components within the sediment (organic matter, Fe, Mn, Al, Ca, and clay particles), which are influenced by the redox potential and pH of the system (Søndergaard et al., 1996).

1.2.2. Analytical fractions

Inorganic P is regarded as the most critical compartment of P in freshwater environments due to its immediate bioavailability (Wetzel, 1983). However, the majority of P is incorporated within inert organic compounds (Wetzel, 1983). Most data regarding P in freshwater systems is reported as orthophosphate or total P (TP), which consists of unfiltered particulate and dissolved P (Wetzel, 1983). The particulate P fraction includes P in organisms, mineral phases (e.g., hydroxyapatite), and P sorbed to dead organic matter (Wetzel, 1983). Dissolved P encompasses orthophosphate, polyphosphates, organic colloids, and low molecular weight phosphate esters (Wetzel, 1983). In addition to TP, various analytically defined P fractions are often used to understand and predict algal biomass and growth rates (Bradford and Peters, 1987). Soluble reactive P (SRP) is defined as orthophosphate particles that are dissolved (<0.45 μm in diameter) and react with molybdate. Total reactive P (TRP) is the unfiltered total orthophosphate that reacts with molybdate. Total dissolved P (TDP) is comprised of all hydrolysable, dissolved P, which includes the SRP fraction (Jarvie et al., 2002).

Similar to P in water, sediment-associated P is characterized using operationally defined, analytical processes. Sequential extractions expose sediment to a sequence of various solvents, which target and extract P fractions associated with different geochemical components based on the chemical characteristics of the geochemical component (Ruttenberg, 1992). Classical methods split sediment-associated P into 3 categories: organic phosphorus (OP), apatite phosphorus (AP), and non-apatite inorganic phosphorus (NAIP; Williams et al., 1967a; Ruban and Demare, 1998; and Hiriart-Baer et al., 2011). Organic P represents all P associated with C through either C-P bonds or C-O-

P bonds. Non-apatite inorganic P is the inorganic P that is bound to non-apatite minerals, such as Al, Fe, or Mn oxides, or P from mineralized organic matter. This fraction is considered redox sensitive due to the solubility of the Fe and Mn oxides under reducing conditions. Apatite P represents all particulate P that is insoluble in water and consists of orthophosphate within the crystal lattices of apatite colloids.

The SEDEX P fractionation scheme is an alternative, modern, rigorous method, which extracts five, operationally defined, P fractions from sediment (Ruttenberg, 1992). The sequence initially extracts a fraction of loosely sorbed P, which would be subject to diffusive gradients (Ruttenberg, 1992). Subsequently, fractions of Fe-bound P, AP, and OP are extracted, with AP split into two sub-fractions. The Fe-bound P represents P bound to reducible Fe oxides (FeOOH) and Mn oxides. Apatite P is split into an authigenic carbonate fluorapatite P (CFAP) group and detrital apatite P (FAP) group (Ruttenberg, 1992). CFAP is a terminal sink for bioavailable P, whereas FAP can be mobilized to become bioavailable (Ruttenberg, 1992). Previous nomenclature, which designated NAIP and OP as conditionally bioavailable and AP as biologically inert, may underestimate bioavailable P if FAP is a major constituent of AP. Additionally, the Fe-bound P fraction is better able to predict the P pool that is susceptible to altered redox conditions. The NAIP fraction includes Al oxides, which are redox-insensitive, and may overestimate P that can be mobilized by altered redox conditions. Evaluating the quantity of P associated with various geochemical components in sediment can be used to assess the potential of a lake for internal P loading, which is the mobilization of P from sediment to overlying water.

1.3. Internal phosphorus loading

1.3.1. Mechanisms and geochemistry

Lake sediment can act as a major reservoir of nutrients and trace elements, which can be mobilized into overlying water at rates comparable to, or exceeding, external sources depending on physical, chemical, and biological conditions within the sediment (Mortimer 1941; Rossi and Premazzi, 1991).

Redox potential defines the propensity of a compound to act as an electron acceptor or donor (DeLaune and Reddy, 2005). Redox conditions influence a variety of characteristics of elements, including their valence state and solubility (DeLaune and Reddy, 2005). Redox potential is primarily considered a function of the concentration of molecular oxygen (O_2) in the given environment, but is also affected by the concentration of nitrate, Mn oxides, FeOOH, sulfate (SO_4^{2-}), and bicarbonate (DeLaune and Reddy, 2005). Within circumneutral, aerobic conditions in sediment, P will bind to positively charged, insoluble, Fe and Mn oxides, generally with greater affinity for Fe (Bortleson and Lee, 1974). The concentration of Fe governs the P sorption and retention capacity of sediment, but Mn has a greater predictive ability to determine the concentration of P in sediment (Bortleson and Lee, 1974).

Thermal stratification and/or high rates of organic matter decomposition can alter and deplete O_2 at the sediment-water interface (SWI; Mortimer, 1941). The associated decreased redox potential promotes reduction of insoluble metal oxides to soluble Fe^{2+} and Mn^{2+} compounds, which lose their ability to retain P. Phosphorus, Fe^{2+}, and Mn^{2+} are then released to overlying aerobic waters, where Fe^{2+} can rapidly be oxidized back to FeOOH, and sequester P. Manganese will remain in solution unless removal is microbially catalyzed to Mn oxides that will precipitate (Bortleson and Lee, 1974; Nealson and Saffarini, 1994). However, if the redox potential is decreased too greatly, sediment-associated SO_4^{2-} will be reduced to sulfide (HS^- or H_2S, depending on pH) by microbes (Koretsky et al., 2007). This S^{2-} can react with Fe^{2+} and precipitate as FeS, which limits the available Fe to sequester available P. This fundamental redox-dependent mechanism of P mobilization has been extensively studied (e.g., Davison and Woof, 1984; Boström et al., 1988; Ruban and Demare, 1998; Kisand and Nõges, 2003; Nürnberg et al., 2013).

Microbially-dependent P mobilization displays seasonal variation due to the direct influence of temperature on microbial activity (Jensen and Andersen, 1992; Boers et al., 1998, Søndergaard et al., 1999). Bacteria at the SWI have the ability to catalyze the mineralization of OP, take up and store P, release P under unfavorable redox conditions, release P during decomposition, convert bioavailable SRP to dissolved or particulate P, and transfer particulate P between the sediment and water (Gächter and Meyer, 1993). One study found that among the effects of temperature, NO_3^-, and pH on mobilization of P from sediment in three lakes, temperature had the greatest influence and accounted for over 70% of seasonal variation (Jensen and Andersen, 1992).

Besides these factors, pH also plays an important role in regulating P mobilization from sediment. A drift in pH away from circumneutral values can promote increased P mobilization. Phosphorus mobilization from eutrophic sediment is minimal at a pH between 4 and 7, but increases substantially when $pH > 8$ (Jin et al, 2006). Alkaline pH values, which are a function of the concentration of hydroxyl ions, are conducive to ligand substitution of hydroxyl ions for P on Fe and Mn oxides (Kim et al., 2003).

Flora and fauna can also contribute to internal P loading. Aquatic macrophytes obtain the majority of their P from the sediment, an otherwise unavailable pool, and may relay this to overlying water (Carignan and Kalff, 1980). Cyanobacteria can adjust their buoyancy, migrate downward to access the supply of P in bottom water and sediment, and then migrate back to upper water (Cottingham et al., 2015). The general influence of invertebrates on internal P loading is still not fully understood. Excessive respiration by invertebrates can decrease the redox potential within sediment, and consequently increase redox-dependent P release (Chen et al., 2016). However, bioturbation by invertebrates can also increase O_2 penetration to deeper sediment, which will maintain a greater redox potential and enable sequestration of P by insoluble Fe and Mn oxides (Chen et al., 2015).

Overall, the sediment-associated P pool can be released through a variety of altered environmental conditions, but the primary factors influencing release include warm temperatures, decreased redox potential, non-circumneutral pH, sediment resuspension, a decreased Fe:P ratio, bioturbation, mineralization and microbial processes, and the presence of submerged macrophytes (Søndergaard et al., 2003). Among these factors, decreased redox potential and increased rates of microbial activity are considered to have the greatest influence on internal P loads (Søndergaard et al., 2003). Complete elucidation of these mechanisms is required to address increasing concerns regarding the impacts of eutrophication in freshwater lakes (Brooks et al., 2015).

1.3.2. Eutrophication and algal blooms

Eutrophication is the over-fertilization of an aquatic system with nutrients, primarily P and N, which increase rates of primary production to exceed the consumptive capabilities of secondary consumers (Paerl et al., 2001). The adverse environmental implications of eutrophication extend to economic repercussions due to water-related impacts, which occurs worldwide. The U.S. loses an estimated $2.2 billion annually due to eutrophication affecting recreational water usage, waterfront real estate, biodiversity protection efforts, and drinking water quality (Dodds *et al.*, 2008). England and Wales spend $105-160 million per year to mitigate impacts of freshwater eutrophication (Pretty *et al.*, 2003), and the cost to restore the Baltic Sea to the pre-impact trophic conditions of 1960 is estimated at €210-430 million (Bryhn, 2009).

The addition of excess P into freshwater lakes, which are conventionally P-limited, can shift a lake from mesotrophic to eutrophic and render the lake N-limited (Schindler, 1978; Levine and Schindler, 1999). Nitrogen-limited lakes are undesirable as they favor cyanobacteria, which can fix biologically unavailable atmospheric N into biologically available N, and outcompete eukaryotic algae (Paerl et al., 2001). Cyanobacteria are problematic due to the potential release of metabolites and toxins that are associated with these blooms (Paerl et al., 2001). Humans exposed to sufficient concentrations of these metabolites through drinking water and recreational activity can be subject to health issues, including skin irritation, gastroenteritis, acute pneumonia, and hepatoenteritis (Falconer, 1999). Among these metabolites are taste and odor compounds, which adversely affect water quality and are both costly and difficult to treat (Smith et al., 2002; Watson et al., 2008). Some of the other metabolites have ecological implications via direct toxicity to organisms, and subsequently exerting stress on peripheral trophic levels (Paerl et al., 2001). A 37-year long-term study demonstrated that cyanobacterial algal blooms must be controlled through P-control and cannot be controlled through N-control (Schindler et al., 2008). Nitrogen-fixing cyanobacteria were able to compensate in N-limited freshwater lakes, which suggests that efforts to manage algal blooms should focus on decreasing inputs of P within the system (Schindler et al., 2008).

Efforts to restore the trophic status of freshwater lakes by reducing external P inputs, as a means to decrease concentrations of P in surface water, can be hindered for decades by internal P loading (Søndergaard et al., 1999). One shallow lake (Shagawa Lake, MN, USA) demonstrated increased concentrations of TP in surface water, from 30 $\mu g\ L^{-1}$ to 80 $\mu g\ L^{-1}$, as a result of summertime internal P loads, despite the development of a tertiary wastewater treatment plant, which had reduced external P loads by ~70% (Larsen et al., 1979). The domination of algal blooms within freshwater lakes can perpetuate eutrophic conditions through increased internal P loading. Algal blooms, whether living and respiring or as sunken decaying organic matter, can deplete large quantities of O_2 within the lake (Mortimer, 1941; Wetzel 1983). Reducing conditions at the SWI, which is due to hypoxic bottom water, can mobilize redox-sensitive P and exert O_2 stress on organisms (Winn and Knott, 1992; Paerl et al., 2001). This internal loading feedback can continue to supply P to the water column and enhance eutrophication. Furthermore, simultaneous to P, other chemicals and compounds, such as arsenic (As), can be mobilized from sediment.

1.4. Arsenic in freshwater lakes

1.4.1. Sources, speciation, and behavior

Arsenic is a trace metalloid (hereafter referred to as a metal) with an atomic number of 33 and atomic weight of 74.92 (Emsley, 2011). At a concentration of 1.5 mg kg^{-1}, it is the 53rd most abundant element in the crust of the earth (Emsley, 2011). Arsenic may be an essential element for some animals, such as chickens and rats, but this is not confirmed for humans (Pérez-Granados and Vaquero, 2011). Phosphorus and As are both group V elements, and therefore display similar chemical properties and geochemical behavior (Mucci et al., 2000). Inorganic As in freshwater lakes is usually derived from natural origins (e.g., volcanic outputs, regional bedrock composition, and volatilization from soils), but can also be added through anthropogenic sources (e.g. mining, fossil fuel combustion, and pesticides; Ferguson and Gavis, 1972; Smedley and Kinniburgh, 2002; Sharma and Sohn, 2009).

Arsenic can exist in four oxidation states (-3, 0, +3, and +5), but is predominantly found in freshwater lakes as the oxyanions arsenite (As(III)) and arsenate (As(V)) (Smedley and Kinniburgh, 2002). Concentrations of organic arsenicals are minimal in freshwater environments, but can occur through methylation reactions that convert As(V) to monomethylarsonic acid (MMA^{V}) and dimethylarsinic acid (DMA^{V}), or As(III) to monomethylarsenous acid (MMA^{III}) and dimethylarsenous acid (DMA^{III}) (Sharma and Sohn, 2009). Arsenic speciation is governed by the redox potential and pH of the environment at a given temperature, but is also dependent on adsorption to particulates (e.g. iron oxides and hydroxides, organic matter, etc.), and the concentration of HS^{-}, which influences the formation of thioarsenic species (Sharma and Sohn, 2009).

Arsenic cycling within lakes is similar to P, where As is ultimately entrained in sediment under oxic conditions (Ferguson and Gavis, 1972). As(V) and As(III) primarily bind to Fe, Mn, and Al oxides, but can also loosely sorb to particles, precipitate with monosulfides and pyrite, and form As sulfides (Keon et al., 2001). Naturally-occurring mechanisms and conditions, such as an altered redox potential or non-circumneutral pH values, can mobilize sediment-associated As and increase concentrations of As in surface water (Smedley and Kinniburgh, 2002). Within deeper anaerobic sediment, Mn oxides serve to rapidly oxidize arsenite to arsenate, followed by sorption of arsenate to Fe oxides, which have stronger sorbent surfaces than Mn oxides (Ying et al., 2012). Upon reduction and dissolution of Mn and Fe oxides, As(III) will diffuse upwards towards oxic sediment where it will either be sequestered by available sorbents (i.e., metal oxides) or diffuse to overlying water (Mucci et al., 2000). Arsenic is primarily removed from oxic waters after As(III) is oxidized to As(V), followed by sorption to clays and carbonates, or co-precipitation with newly formed Fe oxides (Ferguson and Gavis, 1972). Vertical concentration gradients of As in lakes have been observed during summer, due to high biological productivity/decomposition near the SWI, which deplete O_2 within bottom lake water (Smedley and Kinniburgh, 2002). As the redox potential decreases further, newly formed HS^- in bottom water can scavenge and co-precipitate with available arsenicals, and decrease concentrations of As in bottom water (Moore *et al.*, 1988). As(V) also is unable to sorb to sediment-associated metal oxides as pH increases, even near neutral pH values, which can lead to elevated concentrations of As in waters (Smedley and Kinniburgh, 2002). Arsenic associated with sulfides in anaerobic environments are relatively non-labile, unless sediment is suspended into oxic waters, promoting oxidation of S^{2-} to SO_4^{2-} and the release of associated As (Saulnier and Mucci, 2000). Subsequently, the concentrations of other anions (e.g., SO_4^{2-}, silicate, carbonate, and P) influence competition for available sorption sites (Ciardelli et al., 2008). At equimolar concentrations, P outcompetes arsenate for sorption sites on two common oxide minerals (goethite and gibbsite) within a pH range of 2–11 (Manning and Goldberg, 1996). Dissolved organic carbon (DOC) generally increases As mobilization via displacement of As from metal oxides in sediment, but this process depends on several factors, including the oxide mineral, DOC species, and redox potential (Grafe et al., 2001).

1.4.2. Arsenic toxicity

Arsenic poisoning has been of concern to human health throughout history. Ingestion of water contaminated with excessive As can cause a variety of adverse effects, such as carcinogenesis within the skin, liver, kidneys, or bladder, cardiovascular disease, neuropathy, and memory problems (Kapaj et al., 2006). The toxicity of As is dependent on the speciation and compound. Trivalent arsenicals are generally more toxic than pentavalent arsenicals among organisms by several orders of magnitude (Styblo et al., 2000; Ventura-Lima et al., 2011). The excretion of DMA^{V}, the metabolite of inorganic As, lead to the paradigm that methylation was a detoxification mechanism of As (Hughes, 2002). However, recent work has demonstrated MMA^{III} and DMA^{III} are more acutely and genotoxic than As(III) (Mass et al., 2001). Although trivalent and pentavalent arsenicals inhibit energy production, they operate through two distinct mechanisms of action. As(III) demonstrates preferential cellular uptake and a greater affinity for thiol groups, which can inhibit the mitochondrial-based citric acid cycle by interfering with the pyruvate dehydrogenase multi-enzyme complex (Aposhian, 1989). As(III) can also cause reactive oxygen species-mediated DNA damage (Ruiz-Ramos et al., 2008). As(V), an orthophosphate analogue, will interfere with ATP production by creating unstable esters that are hydrolyzed immediately, causing depletion of cellular cofactors (Winski and Carter, 1998).

Arsenic does not biomagnify among trophic levels in the aquatic environment (Mason *et* al., 2000), but it can bioaccumulate in invertebrates at concentrations >100x greater than that of the surrounding water (Chen and Folt, 2000). Fish consuming these As-contaminated invertebrates can be subject to As poisoning (Erickson et al., 2011). Death and decomposition of these organisms results in release of As, which can either be retained in sediment or remain in the water column depending on environmental conditions (Ferguson and Gavis, 1972).

1.5. Buffalo Pound Lake, Saskatchewan

Buffalo Pound Lake, Saskatchewan, Canada is located within the Qu'Appelle Valley of the Northern Great Plains. The lake bottom is flat and consists of eroded silts and clays (Hrynkiw et al., 2003). Originally used by First Nations people to capture buffalo, the shallow prairie lake was dammed in 1939 to stabilize fluctuating water levels and act as a source of potable water for two nearby major cities, Regina and Moose Jaw, and smaller surrounding communities (Hall et al., 1999). The lake also provides recreational and industrial use to adjacent residents and companies, respectively.

Buffalo Pound Lake (50°38'51" N, 105°30'25" W) is 29 km long, approximately 1 km wide, has an average depth of 3 m, and a maximum depth of 5.5 m (Hall et al., 1999; BPWTP, 2015). Despite being a relatively shallow lake, it develops deep-water anoxia in the late summer and throughout winter (McGowan et al., 2005). During late summer, the pH of Buffalo Pound Lake can reach values of ~9.2, and sometimes exceed this value (personal communication, Helen Baulch, University of Saskatchewan). Water flows through the Qu'Appelle arm of Lake Diefenbaker and into Buffalo Pound Lake, which maintains a residence time of 1.5 to 3 years (BPWTP, 2015). The lake also receives water inputs from groundwater and watershed runoff (BPWTP, 2015).

Buffalo Pound Lake naturally contains large concentrations of P, N and C, which support reoccurring summertime algal blooms (BPWTP, 2015). These blooms, and their associated metabolites, cause treatment challenges for the Buffalo Pound Water Treatment Plant (BPWTP; Hall et al., 1999), which spends approximately 8% of its annual budget on the treatment of taste and odor compounds (Kehoe et al., 2015). A shift in the algal bloom community in Buffalo Pound Lake has been linked to decreased N:P ratios. Although several aspects of Buffalo Pound Lake have been studied, internal P loading has not been characterized. Greater concentrations of P during summertime in shallow lakes, such as presently occurring within Buffalo Pound Lake, are indicative of internal P loading processes (Søndergaard et al, 2003). Buffalo Pound Lake and most Saskatchewan lakes contain sediment that is naturally enriched in As (Huang and Liaw, 1978). The concentration of As in treated potable water (0.4 – 0.8 $\mu g\ L^{-1}$; BPWTP, 2015) from Buffalo Pound Lake is substantially less than the guidelines value for potable water for As, which was established to protect human health (10 $\mu g\ L^{-1}$; WHO, 2011). However, historical concentrations of As in water (6.5 $\mu g\ L^{-1}$; Viraraghaven et al., 1991) and sediment (13.2 $mg\ kg^{-1}$ d.w.; Huang and Liaw, 1978) exceed Canadian freshwater guidelines established to protect aquatic life (5.0 $\mu g\ L^{-1}$ and 5.8 $\mu g\ kg^{-1}$ d.w., respectively; CCME, 2001). Additionally, the propagation of algal blooms can instigate internal As loading in shallow lakes (Martin and Pederson, 2004). If significant quantities of P are being mobilized from sediment, then As, a geochemical P analogue, may be concurrently mobilized from sediment.

1.6. Project overview and rationale

Arsenic and P are trace elements in freshwater lakes, which, in excessive quantity, are of concern for distinct reasons. Buffalo Pound Lake was used as a case study of shallow lakes, which are more susceptible to internal P loading and eutrophication (e.g., Lake Winnipeg, CAN; Lake Apopka, USA; Lake Taihu, CHN) compared to deep lakes (Søndergaard et al., 2003). This is due to the relatively greater influence of sediment in shallow lakes on concentrations of nutrients in lake water (Søndergaard et al., 2003). In addition, prairie systems often occur within nutrient rich landscapes (Allan and Williams, 1977), resulting in greater P availability. Prairie systems also tend to be Fe-poor (Allan and Williams, 1977). The limited availability of Fe reduces the P sorption capacity of bed sediment. The limited capacity for Fe sorption, relative to other systems, can be further exacerbated by relatively high concentrations of SO_4^{2-}, which occur in Buffalo Pound Lake (208 to 340 mg L-1; BPWTP, 2015). The reduction of SO_4^{2-} to HS^- in deeper, anoxic sediments acts as a permanent burial of Fe^{2+} through formation of FeS (Orihel et al., 2015). Surficial sediments that are Fe-poor are unable to effectively scavenge P that may diffuse upwards from deeper, anoxic sediments (Orihel et al., 2015). Arsenic, a geochemical analogue to P, can be mobilized in addition to P from bottom sediment to overlying water and exert toxic effects in aquatic life.

Several sites were selected within the reservoir to evaluate potential variation of As and P mobilization from sediment along the length of Buffalo Pound Lake. Sediment core incubations were used to quantitatively assess changes in P and As release rates due to altered environmental conditions (temperature, oxygen status, pH, and midge density). Sediment geochemistry was analyzed at the selected sites to support interpretation of potential differences among mechanisms of P and As release from sediment. Various water and pore water data were collected *in situ* bi-weekly for a two-month sample period during the summer. Selected environmental conditions (temperature, oxygen status, and pH), which were studied in sediment core incubations, were correlated with P concentrations in bottom water to determine mechanisms influencing potential internal P loading *in situ*.

Knowledge of the relative influence of physicochemical mechanisms affecting internal P and As loading is necessary to inform management of Buffalo Pound Lake and other prairie systems. Furthermore, the bioaccessibility of mobilized As to some benthic organisms must be evaluated to determine if there is a current, or future risk, of toxicity to aquatic organisms in Buffalo Pound Lake. In a broader context, this study will provide guidance to assess internal P loading in lakes, such as a sediment geochemical characteristics that are indicative of internal P loading, assessment of a novel internal P loading paradigm (Orihel et al., 2015), and quantitative P flux rates. It will also provide guidance to assess internal As loading, including application of an internal P loading paradigm to As (Orihel et al., 2015), quantitative As flux rates, and correlating concentrations of As in invertebrate tissue to inorganic media. To our knowledge, this study is the first of its kind in Canada to quantitatively assess internal As loading rates in a freshwater reservoir using sediment core incubations.

1.7. Goal and objectives

Using a combination of laboratory sediment core incubations, geochemical analyses of sediment, and *in situ* data, the goal of this study was to assess key biological and physicochemical mechanisms potentially influencing P and As mobilization from the bottom sediment of Buffalo Pound Lake, SK. The following objectives were devised to meet this goal:

1. Assess the influence of temperature, dissolved oxygen concentration, high pH (pH 9.3), and midge larvae (*Chironomidae spp.*) density on mobilization of P from Buffalo Pound Lake sediment quantitatively using laboratory experiments and qualitatively using *in situ* monitoring data.

    H_0: The release rate of P from sediment cores collected from Buffalo Pound Lake is not affected by temperature, dissolved oxygen concentration, high pH, or midge larvae density.

    H_0: The release rate of P from sediment cores collected from Buffalo Pound Lake does not significantly differ among sites.

    H_0: Mobilization of P from sediment from Buffalo Pound Lake *in situ* is not correlated to temperature, dissolved oxygen concentration, or high pH.

2. Assess the relative influence of temperature, dissolved oxygen concentration, and high pH (pH 9.2, observed *in situ* during summer) on mobilization of As from Buffalo Pound Lake sediment using laboratory experiments and *in situ* data.

H_0: The release rate of As from sediment cores collected from Buffalo Pound Lake is not affected by temperature, dissolved oxygen concentration, or high pH.

H_0: The release rate of As from sediment cores collected from Buffalo Pound Lake does not significantly differ among sites.

H_0: Mobilization of As from sediment from Buffalo Pound Lake *in situ* is not correlated to temperature, dissolved oxygen concentration, or high pH.

3. Characterize differences in the geochemical composition of sediment across the length of Buffalo Pound Lake.

   H_0: The concentration of TP, P fractions, total As, and other geochemistry does not differ among sites.

4. Determine the concentration of As in the tissue of midge larvae (*Chironomidae spp.*) and sediment compartments (bottom water, pore water, sediment) across the length of Buffalo Pound Lake.

   H_0: The concentration of As in midge larvae tissue is not significantly different among sites.

   H_0: The concentration of As in midge larvae tissue is not significantly correlated to concentrations of As in bottom water, pore water, or sediment as total As or HCl-extractable As.

CHAPTER 2

PHYSICOCHEMICAL MECHANISMS GOVERNING INTERNAL PHOSPHORUS LOADING FROM PRAIRIE RESERVOIR SEDIMENT, BUFFALO POUND LAKE, SK, CANADA.

Chapter preface

This chapter describes the relative influence of biological and physicochemical mechanisms that affect P mobilization from prairie reservoir sediment. Geochemical analysis of Buffalo Pound Lake sediment demonstrated that the content of Fe and Al in sediment were significantly different along the length of this reservoir, which altered P mobilization in laboratory sediment core incubations and *in situ*. Results from this research suggest that alum could potentially be used to minimize internal P loading in Buffalo Pound Lake and other shallow prairie water bodies.

This chapter is being prepared for submission as a research article to the journal *Water Research* under joint authorship with Karsten Liber (University of Saskatchewan), Lorne Doig (University of Saskatchewan), Helen Baulch (University of Saskatchewan), and Katherine Raes (University of Saskatchewan).

2.1. Introduction

Freshwater lakes worldwide are susceptible to eutrophication and the corresponding development of harmful algal blooms (HABs), which can cause an array of economic and environmental challenges (Dodds et al., 2008; Chapman, 2015). Detrimental repercussions vary among HABs and include the synthesis of neurotoxic, cytotoxic, and hepatotoxic compounds, taste and odor compounds, and oxygen depletion via bloom respiration and decomposition (Falconer, 1999). Excessive input of phosphorus (P), often the limiting nutrient for primary producers in freshwater environments (Schindler, 2008), can decrease N:P ratios and allow N-fixing algae, such as cyanobacteria, to dominate primary production (Schindler, 1977; Vitousek et al., 2002). Attempts to reduce eutrophic HABs in lakes via reduced external P input (e.g. municipal sewage or agricultural runoff) can be impeded by internal P loading, the mobilization of sediment-associated P into overlying waters (Søndergaard et al., 2001).

The internal P loading capability of a lake is poorly predicted by concentrations of total P (TP) in sediment, due to the presence of P geochemical fractions that are non-labile (Ruban et al., 1999). Within sediment, P can be associated with various sorbents, such as metal oxides (iron (Fe), manganese (Mn), and aluminum (Al)), calcium (Ca) minerals), clays, or labile and refractory organic compounds (Søndergaard et al., 2001). Because these P sorbents display different physicochemical characteristics, varying environment conditions can alter characteristics of certain P sorbents, causing release of adsorbed P. For example, reducing conditions, which are a factor of low dissolved oxygen (DO) concentrations, favor dissolution of Fe oxides and the release of associated P (Mortimer, 1941). Alkaline pH values cause ligand substitution of hydroxyl ions for P sorbed to metal oxides (Jin et al., 2006), while acidic pH values increase the dissolution of Ca-P minerals (Penn et al., 2000). Microbial activity, which is influenced by temperature, dictates the rate of redox reactions (i.e. oxyhydroxide reduction) and mineralization of organic matter, and therefore the release of associated P (Bostrom et al., 1988).

Relative to deep lakes, shallow lakes display a greater propensity to develop HABs (e.g., Lake Winnipeg, CAN; Lake Apopka, USA; Lake Taihu, CHN) due to: i) a larger ratio of the surface area of sediment to the depth of the water column, which causes sediment to exert greater influence on concentrations of P in lake water (Søndergaard et al., 2003); ii) a water column with a proportionally greater euphotic zone, which allows algae to photosynthesize while migrating downward in the water column to utilize P mobilized from sediment (Barbiero and Welch, 1992); and iii) the greater influence of warmer temperatures on shallow lakes, which promote conditions that allow cyanobacteria to dominate the algal community (Kosten et al., 2011). Additionally, Canadian prairie lakes are particularly susceptible to internal P loading due to low concentrations of Fe in sediment pore water, alkaline waters associated with sedimentary bedrock, polymictic lakes prone to transient profundal anoxia, and a naturally nutrient-rich landscape (Allan and Williams, 1977; Barica, 1993; Taranu et al., 2010, Orihel et al., 2015).

Here, using a combination of laboratory experiments and field measurements we assess the importance of four different factors in controlling internal P loads: temperature, pH, redox conditions, and bioturbation. Our work is situated within Buffalo Pound Lake, SK, Canada, a prairie-reservoir with recurrent HABs. The HABs affect drinking water treatment as well as recreational users. This study aims to understand both the hierarchy of different factors in controlling internal P load, and spatial differences in these controls along this 29-km long lake. To our knowledge, this is the first study to investigate multiple mechanisms affecting P mobilization from sediment within a Northern Great Plains lake.

2.2. Methods and Materials

Using a combination of sediment core incubations, sediment P fractionation, and *in situ* measurements, the goal of this study was to assess the relative influence of physicochemical P release mechanisms and sediment geochemistry on internal P loading. Sediment core incubations under varying temperature, oxygen status, pH, and midge larvae density were used to derive experimental release rates, which were used to compare the relative influence of different P release mechanisms. Experimental data and geochemical analyses were used to interpret *in situ* P mobilization observations.

2.2.1. Site description

Buffalo Pound Lake (50°39’N, 105°31’W), situated within the Qu’Appelle Valley in Saskatchewan, Canada, was a natural lake that was dammed in 1939 to stabilize fluctuating water levels (Hall et al., 1999). The reservoir is 29 km in length, relatively shallow (3.0 m mean depth, 5.5 m maximum depth), polymictic, narrow (~1 km wide), and has a water capacity of 87.5 x 10^6 m^3 and a residence time of 6 to 30 months (Buffalo Pound Water Administration Board, 2014). The lake’s flat bottom is composed of eroded silts and clays (Hrynkiw et al., 2003).

The reservoir receives minimal water from rain and spring runoff other than during wet years (BPWTP, 2015); instead, much of its flow is derived from upstream Lake Diefenbaker. Buffalo Pound is subject to ice-cover from November to late April. While Buffalo Pound currently provides potable water for approximately one quarter of the provincial population and is used for recreational, agricultural, and industrial purposes

(BPWTP, 2015), this shallow, polymictic lake can develop bottom-water anoxia in late summer and throughout winter (McGowan et al., 2005), and is subject to significant annual algal blooms.

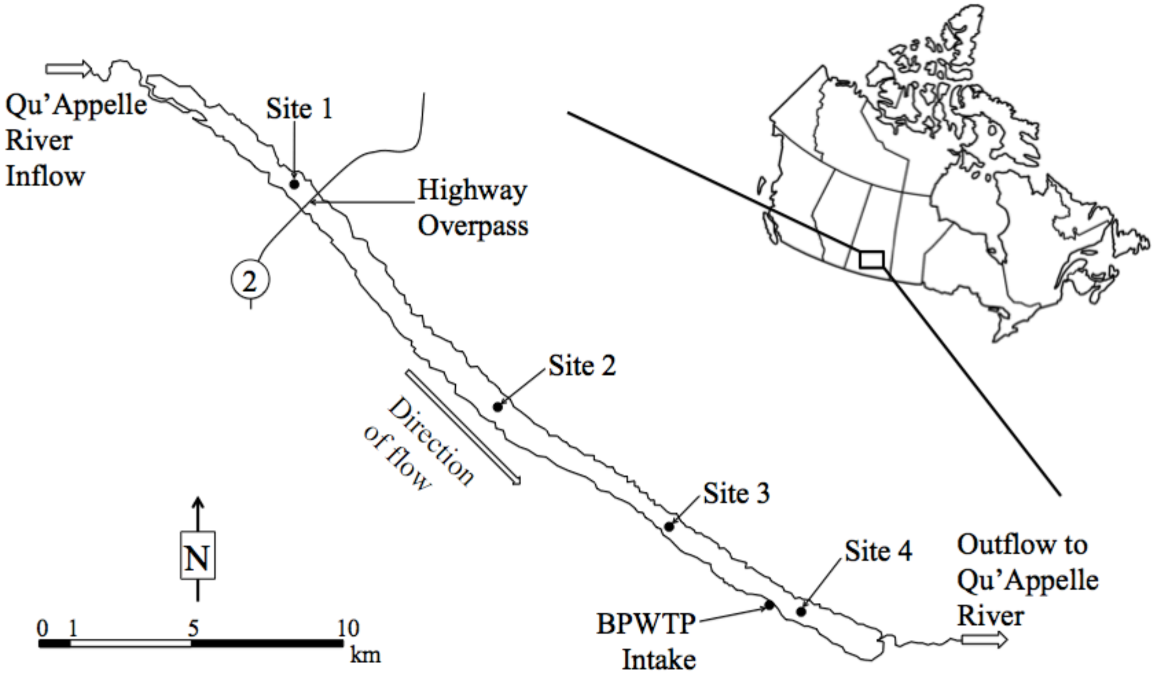

Figure 2.1. Schematic of Buffalo Pound Lake, Saskatchewan, Canada. BPWTP = Buffalo Pound Water Treatment Plant.

2.2.2. Sediment core incubations

Sediment cores were collected from Buffalo Pound Lake at four sites (Figure 2.1) over a two-year period for various experiments. To provide spatial coverage, sites were spaced 5–7 km apart longitudinally within Buffalo Pound Lake, with Site 1 located furthest up-reservoir, and Site 4 furthest down-reservoir (~600 m down-reservoir of the BPWTP water intake). Two sediment cores (~1 to 10 m spatial variation between cores) were collected at each sub-site, with three sub-sites (~50 75 m spatial variation between sub-sites) per site. Lake water was collected from Site 4 in a 50 L carboy for use in all core incubation experiments described below.

Sediment core collection and incubation techniques were based on methods described in Doig et al. (2017). Briefly, cores of sediment were collected in acrylic core tubes (61 cm height, 7.5 cm inner diameter) using a GLEW Gravity Corer (John Glew, Kingston, ON, Canada). Temperature and DO concentration were measured in the water overlying at least one sediment core per sub-site. Cores were sealed on the bottom and top with a rubber stopper and Parafilm®, respectively, and transported upright to the Toxicology Centre, University of Saskatchewan (Saskatoon, SK, Canada), for cold storage (4°C for 1 to 7 days) prior to experimental use and analyses.

Four separate core-incubation experiments were conducted to assess the effects of DO concentration (Orion Star A223 Dissolved Oxygen Portable Meter, Thermo Fisher Scientific, Waltham, MA, USA), temperature, pH, and bioturbation on P remobilization from lake sediment. Core incubations consisted of two factors, site and treatment. Excluding the bioturbation experiment, each treatment consisted of three replicate cores. Cores were standardized to ~1.5 L overlying water by removing sediment through the bottom of the core tube. Water columns were then topped up with lake water from Site 4. Lake water was filtered (8-μm filtered; Whatman Nuclepore Track-Etched Membranes, Tisch Scientific, North Bend, OH, USA) to remove invertebrates. The tops of the cores were then sealed with rubber stoppers containing two hollow glass rods to allow air or argon (Ar) inflow and outflow via a vapor lock (Figure 2.2). Vapor locks were visually monitored to assess gas flow. Core tubes were incubated in the dark to avoid photosynthetic growth.

Overlying water samples (~120 mL) were collected during the incubations (timing varied with experiment), to measure four analytically-defined, commonly reported, aqueous P fractions (total P (TP), total dissolved P (TDP), total reactive phosphorus (TRP), and soluble reactive phosphorus (SRP)), and dissolved metals (Fe and manganese (Mn); 0.45-μm filtered, polyethersulfone syringe filter with acrylic housing, VWR International, Radnor, PA, USA). Total P includes all P species. TRP consists of all molybdate-reactive P components. TDP consists of all P components <0.45 μm in diameter, and SRP consists of molybdate-reactive P components <0.45 μm in diameter. Sample and method blanks were analyzed for P fractions and metals. Core overlying water was replenished with filtered Site 4 water (8-μm; Whatman Nuclepore) to account for loss through sample collection. Temperature and DO concentrations of core overlying water were monitored every two days.

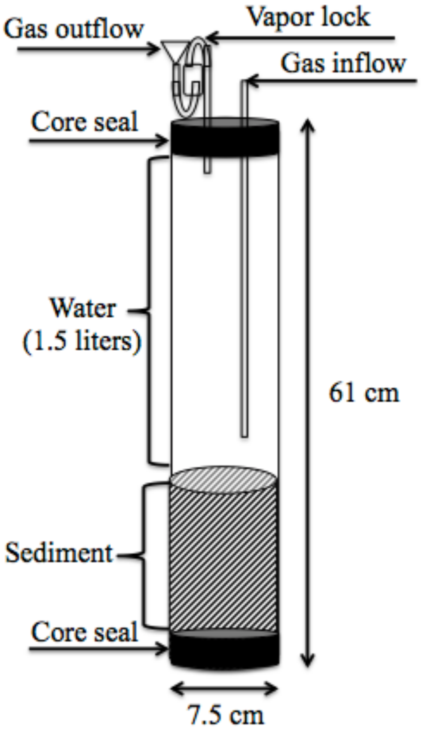

Figure 2.2. Schematic of a sediment core during an incubation experiment.

Summer anoxia incubation

A core incubation was conducted to assess the influence of oxic (8.1 ± 0.9 mg DO L^{-1}) and anoxic (0.1 ± 0.1 mg DO L^{-1}) conditions on P mobilization at a temperature representative of summer conditions (19.2 ± 0.3°C). Cores were collected in June 2014 from Sites 1, 2, 3, and 4 and incubated for 35 days. The overlying water of each core was bubbled with either air or Ar to obtain oxic or anoxic water columns, respectively. Following test initiation, overlying water samples were collected days 0, 1, 3, 8, 14, 21, 28, and 35 and analyzed for P fractions and dissolved metals.

Winter anoxia incubation

A second core incubation was conducted to assess the influence of oxygen status (oxic, 10.5 ± 3.2 mg L^{-1}vs. anoxic, 0.7 ± 0.4 mg L^{-1}) under a temperature representative of winter conditions (4.8 ± 0.2°C). Sediment cores were collected in October 2014 from Sites 3 and 4. These sites were chosen because they displayed highly contrasting P release rates in the Summer Anoxia Incubation. Core overlying water was bubbled with air or Ar to obtain oxic or anoxic water columns, respectively. These cores were then incubated for 105 days with overlying water samples collected on days 0, 1, 3, 7, 14, 21, 35, 49, 63, 84, and 105 and analyzed for P fractions and dissolved metals. The oxic treatment using Site 4 cores contained two replicates, due to the accidental loss of sediment from the third core replicate, and its subsequent removal from the incubation.

Alkaline pH incubation

A third core incubation was conducted to assess the influence of elevated pH on P mobilization. Cores were collected in September 2015 from Sites 3 and 4 and incubated for 14 days at 19.1 ± 0.1 °C under oxic (8.2 ± 0.7 mg L^{-1}) conditions. The pH of the overlying water in the control treatment was kept at a natural pH of 8.2 ± 0.2. The elevated pH treatment was adjusted to a pH of 9.2 ± 0.3, a pH value near the maximum observed in Buffalo Pound Lake during summer. The pH of the overlying water in each treatment core replicate was measured (6230N meter, Jenco, San Diego, CA, USA; 8102BN ROSS combination pH electrode; Orion, Burlington, ON, CAN) several times a day during experimentation and the adjusted pH maintained manually using additions of 1.0 M NaOH. Overlying water was sampled on days 0, 1, 3, 7, and 14 for analysis of P fractions and dissolved metals.

Bioturbation incubation

A fourth core incubation experiment was conducted to assess the influence of chironomid larvae density on P release. Sediment cores were collected in September 2015 from Sites 3 and 4 (6 cores per site), which were then frozen (-20°C) for 14 days to kill endemic invertebrates. These cores were then thawed and designated additions of 0, 1, 2, 4, 8, or 16 large-bodied chironomid larvae (*Chironomus sp.*; personal communication, Dale Parker, Aquatax Consulting, Saskatoon, SK), also collected from Buffalo Pound Lake. After the addition of midge larvae, cores were incubated at 18.3 ± 1.3°C under oxic (8.1 ± 0.5 mg L^{-1}) conditions for 14 days. Overlying water was sampled for P fractions on days 0, 1, 4, 8, and 14. Chironomids were recovered post-incubation to quantify survival rate for the experiment.

2.2.3. Sediment geochemistry

Sediment core samples for physicochemical characterization were collected in triplicate from Sites 1 to 4 in June, 2014. The top 2 cm of each sediment core were pooled, freeze-dried at -55°C (FreeZone® 1-Liter Benchtop Freeze Dry Systems 77400, Labconco, Kansas City, MO, USA) and homogenized for analysis of particle size distribution, total organic carbon (TOC) content, and P geochemical fractionation. Particle size distribution was determined using the Rapid Method (Kettler et al., 2001). Briefly, sediment is sieved to determine sand content, followed by sedimentation to determine silt content. Clay content is calculated as the remaining material. Total organic carbon of sediment was determined by combustion (LECO C632 dry combustion carbonator, LECO Corp., St Joseph, MI, USA) after HCl fumigation to remove carbonates. Sediment P geochemical fractions were determined using 0.1 g d.w. of pre-sieved (150 μm) sediment samples following the SEDEX method (Ruttenberg, 1992) to yield: (i) exchangeable, loosely sorbed P (E-P); (ii) reducible Fe-associated P (Fe-bound P); (iii) authigenic carbonate fluorapatite, $CaCO_3$-associated, and biogenic apatite P (CFA-P); (iv) igneous and metamorphic P (FA-P); and (v) organic P (OP). Total extractable P (TEP) was calculated using P fraction summation. Briefly, sediment was washed through 5 steps using increasingly harsher reagents ($MgCl_2$, citrate dithionite bicarbonate, buffered sodium acetate (NaOAc), 1 M HCl, and 550°C followed by 1 M HCl, respectively) for varied durations of time, which extract different P fractions. The extraction solvents and extraction times are provided in greater detail in the appendix (Table A1). Sample duplicates, commercially available sediment (PACS-2, National Research Council of Canada, Ottawa, ON, CAN) and method blanks were processed using the SEDEX protocol for quality assurance and quality control.

2.2.4. *In situ* monitoring

Water samples and sediment cores were collected biweekly in triplicates from Sites 3 and 4 during July–August, 2015. Water samples were collected at 1-m (top) and

2-m (middle) depths below the water surface (4.2 L Horizontal, Acrylic, Van Dorn Water Sampler, Wildoco, Yulee, FL, USA). Water from near the sediment-water interface (SWI) was collected from the sediment cores (~20–40 cm above the SWI). Water samples were analyzed for pH and TP, SRP, Al, Fe, and Mn content. Samples of surface water for metals analyses were also collected, except during the initial sample collection (2-July-2015). Top and bottom water samples were also analyzed for temperature and DO concentration. Sediment cores were sectioned at 1-cm increments to a depth of 20 cm to collect pore water samples. Sectioning was performed in a glove bag filled with Ar gas (purity > 99.998%, Praxair, Danbury, CT, USA). Sediment samples (1-cm increments) were centrifuged in 50-mL centrifuge tubes at ~206 *g* for 15 min. The pore water supernatant was collected with a 5-mL plastic syringe and filtered (0.45-μm filtered, polyethersulfone syringe filter with acrylic housing, VWR International, Radnor, PA, USA). Samples were collected to a 20 cm depth for SRP analysis, but only to a depth of 10 cm for metals (Al, Fe, and Mn) due to limited supernatant.

To calculate benthic invertebrate density *in situ* and assess benthic macroinvertebrate assemblages, three Eckman Grab (13.2 cm x 13.2 cm) samples were collected from Sites 3 and 4 in September, 2015. Samples were sieved (425 μm mesh size) and the isolated material preserved in 70% ethanol. Benthic invertebrates were isolated using the unaided eye, and separated for coarse taxonomy (chironomids, oligochaetes, small mollusks (<2 cm long), large mollusks (> 5 cm long), and other assorted taxa). Additional benthic invertebrates were collected on the same date from Site 3 using the Eckman grab sampler and transported to the Toxicology Centre for later isolation and use in the sediment core biodensity incubation experiment.

2.2.5. Chemical analyses

Total P and TDP in aqueous samples were digested using the persulfate digestion method and colormetrically analyzed using the ascorbic acid method (APHA-AWWA-WEF, 1998) at 885 nm (UV-1601PC UV-Visible spectrophotometer, Shimadzu Coorporation, Kyoto, Japan). Total reactive P and SRP in aqueous samples were directly analyzed by colorimetry (without acid digestion) using a SmartChem 170® (Unity Scientific, Brookfield, CT, USA) following protocols provided by the manufacturer (Unity Scientific, 2011). All samples collected for trace element analyses were immediately acidified using 2% HNO_3 and stored (4°C) until analysis. Aqueous samples from core incubations were analyzed for concentrations of dissolved Fe and Mn by inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 6000 series ICP spectrometer, Thermo Scientific, Waltham, MA, USA), with a method detection limit (MDL) of 1 $\mu g\ L^{-1}$. Pore water and surface water samples collected *in situ* were analyzed for Al, Fe, and Mn by inductively coupled plasma mass spectroscopy (8800 Triple Quadruple ICP-MS, Aglient Technologies, Santa Clara, CA, USA), each with a MDL of 0.20, 0.03, and 0.01 $\mu g\ L^{-1}$, respectively. Certified reference material (1640a trace elements in natural water, NIST, Gaithersburg, MD, USA), which was analyzed simultaneous to core incubation samples and *in situ* samples, remained between 80–120% of certified values.

SEDEX P fraction samples were analyzed using the ascorbic acid method as previously described. Although no certified reference material is available for P fractionation, PACS-2 was analyzed to assess TEP (88.0 ± 2.6%) versus actual TP. The first three SEDEX fractions were analyzed for Fe and Al by flame atomic absorption spectroscopy (novAA300, Analytik Jena, Jena, Thuringia, DEU), with a MDL of 0.08 mg L^{-1} and 0.70 mg L^{-1}, respectively. Certified reference materials (Magnesium single element and iron single element ICP and ICP/MS certified reference standards, VWR International, Radnor, PA, USA) were analyzed and had instrumental and method recoveries between 80–120% of certified values.

2.2.6. Numerical analyses

Experimental sediment-associated P efflux rates were interpolated with the change in P fraction mass over time in a closed environment. The Steinman *et* al. (2004) equation was amended to calculate P flux rates for each core:

$$RR_P = \frac{(V_{core})(C_2 - C_1) + (V_{sample})(C_1)}{(t_2 - t_1) \times A} \qquad [1]$$

where the phosphorus release rate (RR_P) is the release of P by sediment as mass of P per area per time (mg m^{-2} day^{-1}); C_2 (mg L^{-1}) is the concentration of P in overlying water in cores at time t_2 (day); C_1 (mg L^{-1}) is concentration of P in overlying water in cores at t_1 (day), whereby C_2 and C_1 were selected to calculate the maximum slope of the time series; V_{core} (L) is the volume of overlying water in cores; and A (m^2) is the surface area of the inner core tube. t_1 and t_2 are the initial and final points of inflection, respectively, when P mass released was plotted against time. V_{sample} (L) accounts for water removed for sample analysis. RR_{TP}, RR_{TDP}, RR_{TRP}, and RR_{SRP} correspond to release rates for TP, TDP, TRP, and SRP, respectively. RR_P is used hereafter to collectively refer to the release rates of all P fractions for a treatment.

Plots and statistical analyses were generated using Sigmaplot®, version 11 (Systat Software Inc., San Jose, CA, USA). Excluding the Bioturbation Incubation experiment, all core incubations were plotted as P mass released per area against time. Calculated RR_P

within experiments were compared via two-way analysis of variance (ANOVA) using site and treatment as factors. RRs for the Bioturbation Incubation cores were plotted against the number of chironomids that were recovered after the incubation, and then regressed using a quadratic function. Sediment geochemistry parameters were compared among sites using one-way ANOVA followed with a Tukey's post-hoc test. An $\alpha \leq 0.05$ was considered significant. Multiple linear regression analyses were conducted using DO concentrations, temperature, and pH to predict TP and SRP concentrations in Site 3 and 4 bottom waters in Buffalo Pound Lake during summer.

2.3. Results

2.3.1. Sediment core incubations

Phosphorus

All sediment cores in the Summer Anoxia Incubation (both oxic and anoxic treatments) began releasing P after a 3–8 day period and approached or reached equilibrium at incubation termination (Figures 2.3 and 2.4), with the exception of the Site 3 oxic cores, which were still releasing TP after 35 days (Figure 2.4a). Site 4 sediment released significantly less TP than Site 1, 2, and 3 sediment for both the oxic and anoxic treatments (Figures 2.3 and 2.4). For any given site, anoxic cores displayed significantly greater RR_{TP}, RR_{TDP}, RR_{TRP}, and RR_{SRP} than oxic cores (Table 2.1). Cores displayed significant differences among sites for RR_{TP}, RR_{TDP}, RR_{TRP}, and RR_{SRP} (Table 2.1). The average RR_{TP} for Site 3 was significantly greater than that of Site 2 and Site 4 (Table 2.1). Site 1 average RR_{TP} was significantly greater than that of Site 4. The average RR_{SRP} for Site 1 was significantly greater than that of Site 2 or Site 4 sediment, and the average RR_{SRP} for Site 3 was significantly greater than that of Site 4. Site and treatment displayed significant interaction for RR_{TDP} and RR_{TRP}. Under oxic conditions, the average RR_{TDP} for Site 1 was significantly greater than that of Site 2, Site 3, and Site 4. Under anoxic conditions, the average RR_{TDP} for Site 4 was significantly less than that of Site 1, Site 2, and Site 3. Under oxic conditions, the average RR_{TRP} for Site 4 was significantly lower than that of Site 1, Site 2, and Site 3.

Table 2.1. Phosphorus fraction efflux rates (mg m^{-2} day^{-1}) from Buffalo Pound Lake sediment calculated using core incubations. Values are the mean ± 1 SD (n = 3).

		Summer (19°C) P Flux		**Winter (5°C) P Flux**		**Alkaline pH P Flux**	
		Oxic	Anoxic	Oxic	Anoxic	Control	High pH
Total Phosphorus Flux (mg m^{-2} day^{-1}) (Mean±1SD) [Period of calculated P Release]	Site 1	96 ± 16 [14–21]	131 ± 36 [14–21]				
	Site 2	29 ± 6 [8–14]	78 ± 40 [14–21]				
	Site 3	95 ± 94 [21–28]	160 ± 10 [21–28]	2 ± 1 [35–63]	6 ± 1 [14–84]	4 ± 3 [3–14]	47 ± 2 [3–14]
	Site 4	11 ± 6 [8–21]	17 ± 3 [8–28]	1 ± 1 [49–63]	3 ± 2 [35–49]	4 ± 1 [7–14]	21 ± 7 [1–14]
Total Dissolved Phosphorus Flux (mg m^{-2} day^{-1}) (Mean±1SD) [Period of calculated P Release]	Site 1	54 ± 14 [14–28]	66 ± 5 [14–28]				
	Site 2	17 ± 9 [21–35]	48 ± 4 [14–28]				
	Site 3	23 ± 7 [3–35]	63 ± 9 [14–28]	2 ± 1 [35–63]	8 ± 3 [35–63]	5 ± 3 [3–14]	43 ± 10 [7–14]
	Site 4	8 ± 6 [8–28]	22 ± 8 [3–14]	0 ± 0 [35–84]	1 ± 1 [21–63]	3 ± 1 [3–14]	21 ± 8 [3–14]
Total Reactive Phosphorus Flux (mg m^{-2} day^{-1}) (Mean±1SD) [Period of calculated P Release]	Site 1	29 ± 8 [14–28]	29 ± 1 [3–21]				
	Site 2	17 ± 4 [8–28]	29 ± 3 [3–14]				
	Site 3	24 ± 5 [3–14]	31 ± 1 [3–21]	1 ± 1 [35–63]	11 ± 4 [35–49]	11 ± 7 [3–7]	64 ± 4 [3–14]
	Site 4	7 ± 6 [8–14]	29 ± 4 [3–8]	0 ± 0 [35–63]	2 ± 3 [21–35]	3 ± 1 [3–14]	27 ± 10 [3–14]
Soluble Reactive Phosphorus Flux (mg m^{-2} day^{-1}) (Mean±1SD) [Period of calculated P Release]	Site 1	21 ± 6 [14–28]	40 ± 8 [14–21]				
	Site 2	10 ± 3 [8–35]	25 ± 4 [3–14]				
	Site 3	20 ± 4 [3–14]	29 ± 2 [3–21]	1 ± 1 [35–63]	8 ± 2 [35–63]	6 ± 4 [3–14]	61 ± 5 [3–14]
	Site 4	6 ± 2 [8–14]	23 ± 6 [3–8]	0 ± 0 [35–63]	1 ± 2 [21–35]	3 ± 1 [3–14]	27 ± 11 [3–14]

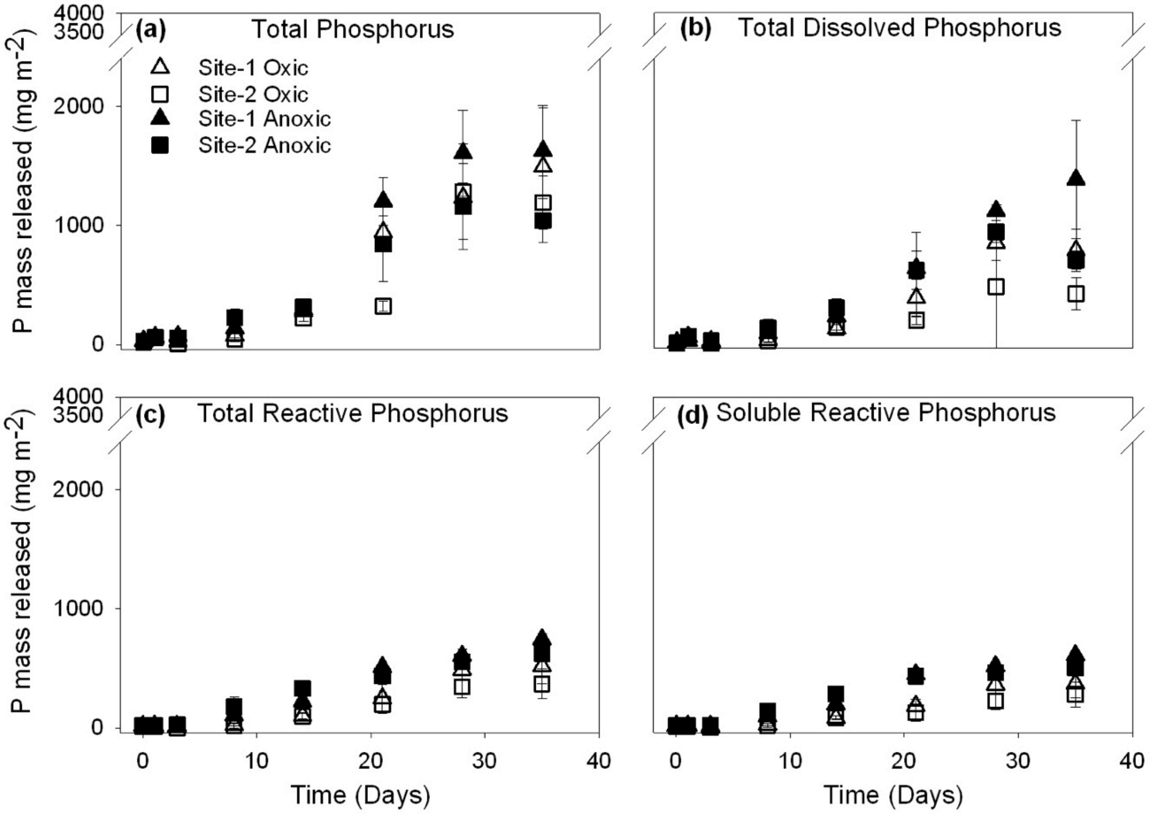

Figure 2.3. Summer anoxia experiment. Mass of (a) total phosphorus; (b) total dissolved phosphorus; (c) total reactive phosphorus; and (d) soluble reactive phosphorus in overlying water of cores per m^2 sediment versus incubation time (days) during the summer incubation experiment for Sites 1 and 2. Open symbols represent oxic cores and filled symbols represent anoxic cores. Error bars represent 1 SD (*n*=3).

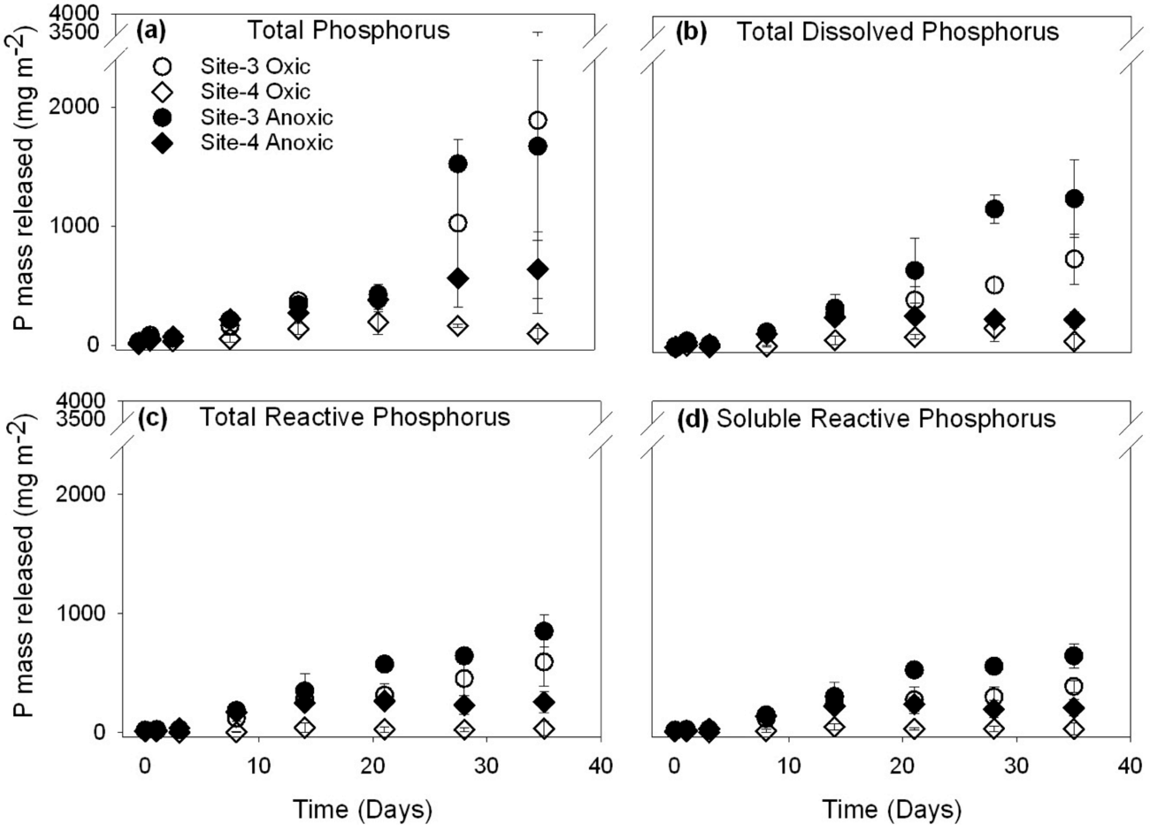

Figure 2.4. Summer anoxia experiment. Mass of (a) total phosphorus; (b) total dissolved phosphorus; (c) total reactive phosphorus; and (d) soluble reactive phosphorus in overlying water of cores per m^2 sediment versus incubation time (days) during the summer anoxia incubation experiment for Sites 3 and 4. Open symbols represent oxic cores and filled symbols represent anoxic cores. Error bars represent 1 SD (*n*=3).

In the Winter Anoxia Incubation (temperature ~5°C), sediment from Site 3 released P under anoxic conditions. A limited amount of P was released from sediment from Site 3 under oxic conditions and sediment from Site 4 under oxic or anoxic conditions (Figure 2.5). Sediment from Site 3 under anoxic conditions released TP after a 14-day period and TDP, TRP, and SRP after a 35-day period. The remaining cores released P after a 35-day period. The concentrations of the various P fractions in the overlying water of all cores reached equilibrium prior to incubation termination (105 days). For all sites, the RR_{TP}s in the oxic treatment were significantly greater than those of the anoxic treatment (p=0.026). The average RR_{TP} for Site 3 was not significantly different from that of Site 4 (p=0.055). There was no interaction between site and treatment affecting RR_{TP} (Table 2.1). There was significant interaction between site and treatment for RR_{TDP} (p=0.027), RR_{TRP} (p=0.040), and RR_{SRP} (p=0.021). During anoxic conditions, sediment from Site 3 had greater average RR_{TDP} (p=0.001), RR_{TRP} (p=0.005), and RR_{SRP} (p=0.002) than sediment from Site 4 (Table 2.1).

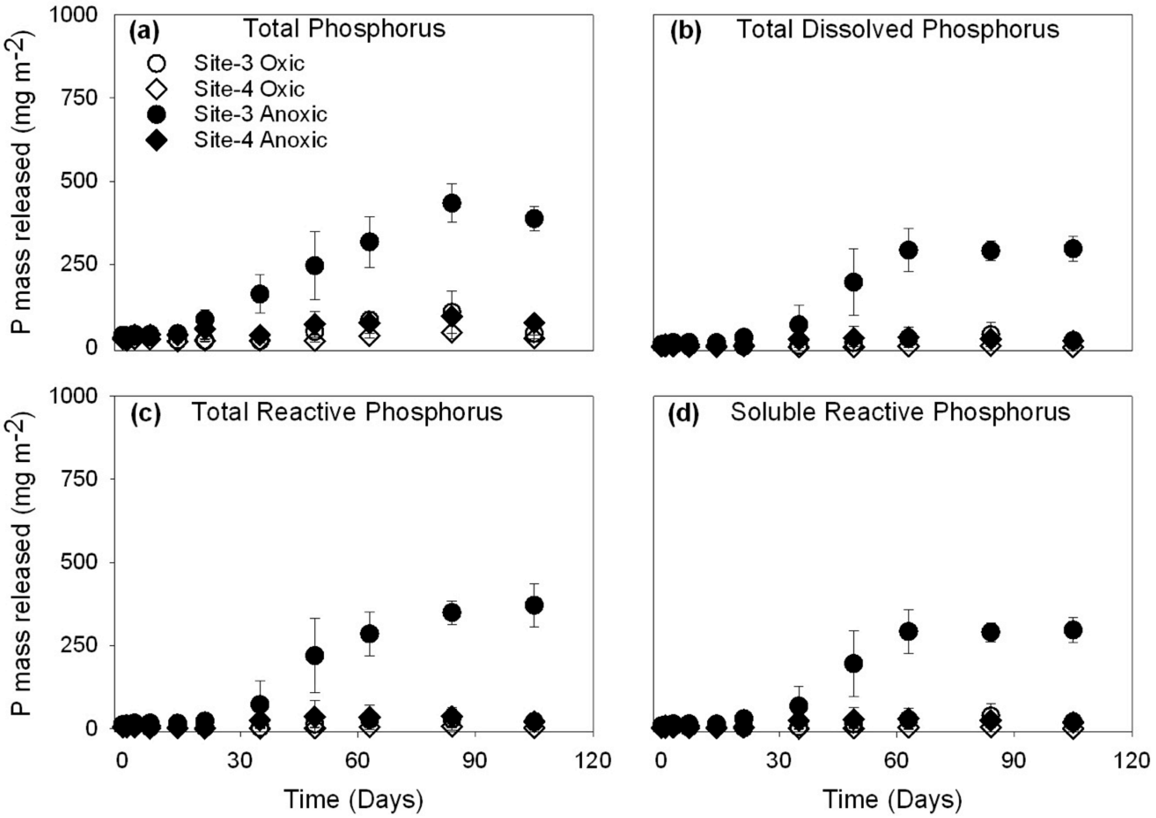

Figure 2.5. Winter anoxia experiment. Mass of (a) total phosphorus; (b) total dissolved phosphorus; (c) total reactive phosphorus; and (d) soluble reactive phosphorus in overlying water of cores per m^2 sediment versus incubation time (days) during the winter temperature incubation experiment for Sites 3 and 4. Open symbols represent oxic cores and filled symbols represent anoxic cores. Error bars represent 1 SD (*n*=3).

The high pH (9.2) treatment stimulated phosphorus release from all cores after a 1 to 3-day period, with the pH 9.2 treatment cores releasing the largest mass of P relative to the pH 8.2 control cores (Figure 2.6). Phosphorus released from control cores reached equilibrium during the 14-day experiment, whereas the high pH treatment cores did not reach equilibrium, hence higher rates and longer release may be at play at high pH. There was a significant interaction between site and treatment for RR_{TP} (p<0.001), RR_{TDP} (p=0.034), RR_{TRP} (p=0.005), and RR_{SRP} (p=0.003; Table 2.1). Sediment from Site 3 and Site 4 exposed to pH 9.2 conditions had significantly greater average RR_{TP} (p<0.001; p=0.001, respectively for each site), RR_{TDP} (p<0.001; p=0.012), RR_{TRP} (p<0.001; p=0.002), and RR_{SRP} (p<0.001; p=0.001) relative to the pH 8.2 controls (Table 2.1). Additionally, sediment from Site 3 under pH 9.2 conditions demonstrated a significantly greater average RR_{TP} (p<0.001), RR_{TDP} (p=0.004), RR_{TRP} (p<0.001), and RR_{SRP} (p<0.001) than sediment cores from Site 4 (Table 2.1).

Release rates of all P fractions demonstrated site-dependent influence by chironomid larvae density in the bioturbation incubation. Release rates of the four P fractions in Site 4 cores were significantly affected by midge density, which followed a negative parabolic function (Figure 2.7). However, phosphorus fraction release rates were not significantly influenced by midge density in Site 3 cores (Figure 2.7).

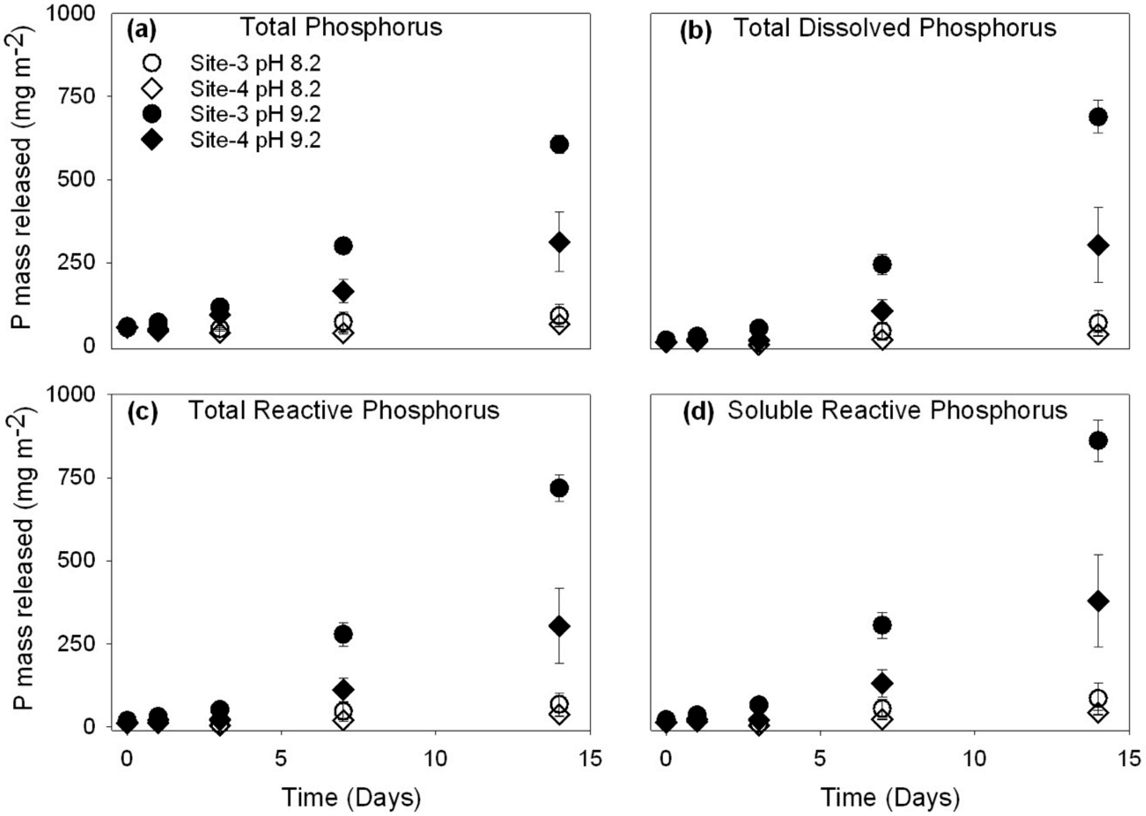

Figure 2.6. Elevated pH experiment. Mass of (a) total phosphorus; (b) total dissolved phosphorus; (c) total reactive phosphorus; and (d) soluble reactive phosphorus in overlying water of cores per m^2 sediment versus incubation time (days) during the alkaline pH incubation experiment for Sites 3 and 4. Open symbols represent control cores and filled symbols represent alkaline pH cores. Error bars represent 1 SD (*n*=3).

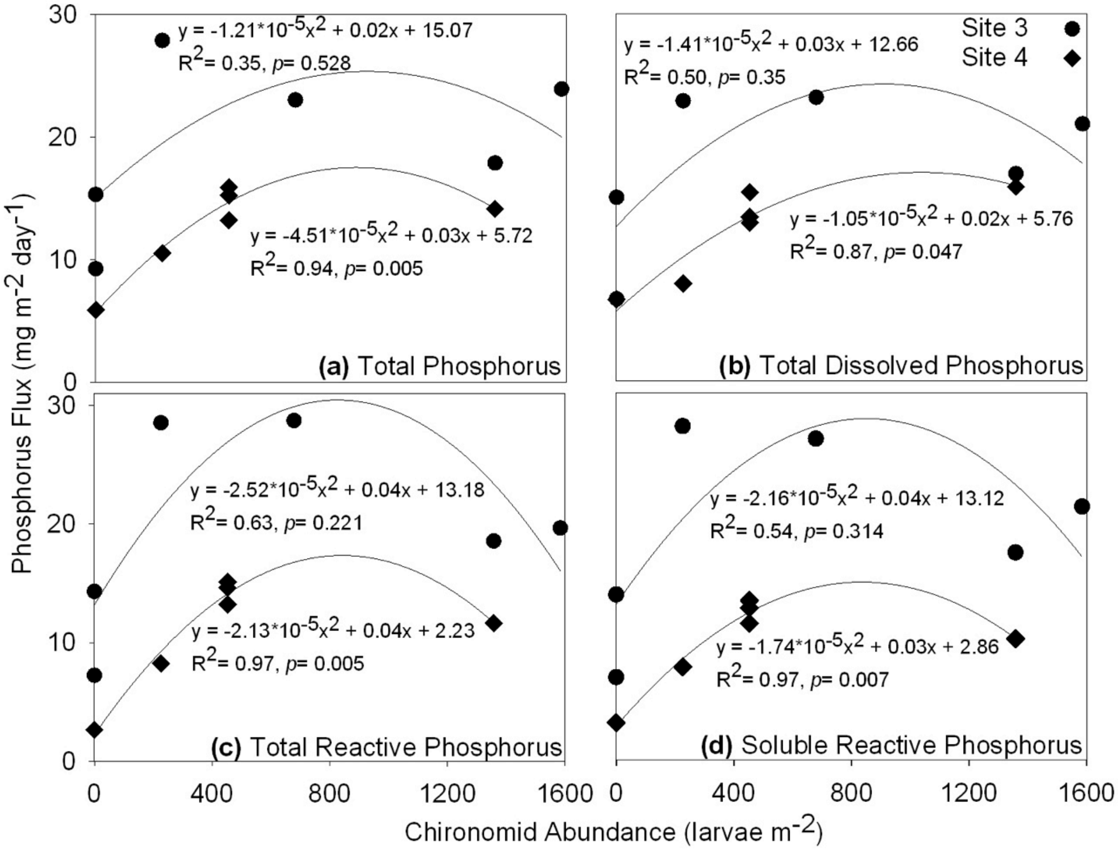

Figure 2.7. Chironomid density experiment. Flux rates of (a) total phosphorus; (b) total dissolved phosphorus; (c) total reactive phosphorus; and (d) soluble reactive phosphorus from sediment into overlying water of cores versus chironomid larvae density per core during the bioturbation incubation experiment for Sites 3 and 4. Trend lines represent a non-linear regression curve with the corresponding equation (*n*=6).

Metals

Iron was mobilized from the sediment of all sites under oxic and anoxic conditions in the Summer Anoxia Incubation (Figure 2.8a,b). From Day 0–14, the anoxic cores from all sites released a greater mass of Fe than the corresponding oxic cores. Following Day 14, oxic cores from Sites 1–3 released greater Fe mass than the corresponding anoxic cores (Figure 2.8a,b). The mass of Fe in overlying water in anoxic cores declined after Day 14. The mass of Fe in overlying water in oxic cores declined after Day 21 in Site 1 and 2 cores, after Day 14 in Site 4 cores, but did not decrease in Site 3 oxic cores throughout the incubation. In the Winter Anoxia Incubation, Fe was mobilized from all four sites and treatments (Figure 2.8c). Anoxic cores from Sites 3 and 4 released the largest mass of Fe at ~Day 35, while oxic cores released the largest Fe mass at ~Days 49–63 (Figure 2.8c). Iron concentrations in the overlying water of the anoxic cores decreased after Day 35 in the Winter Anoxia Incubation (Figure 2.8c). Overall, less Fe mass was released in the Winter Anoxic Incubation (105-day incubation) relative to the Summer Anoxic Incubation (35-day incubation). A small mass of Fe was released at the end of the Alkaline pH Incubation from Site 3 sediment in the pH 9.2 treatment (Figure 2.8d). The remaining Alkaline pH incubation cores released minimal Fe (Figure 2.8d).

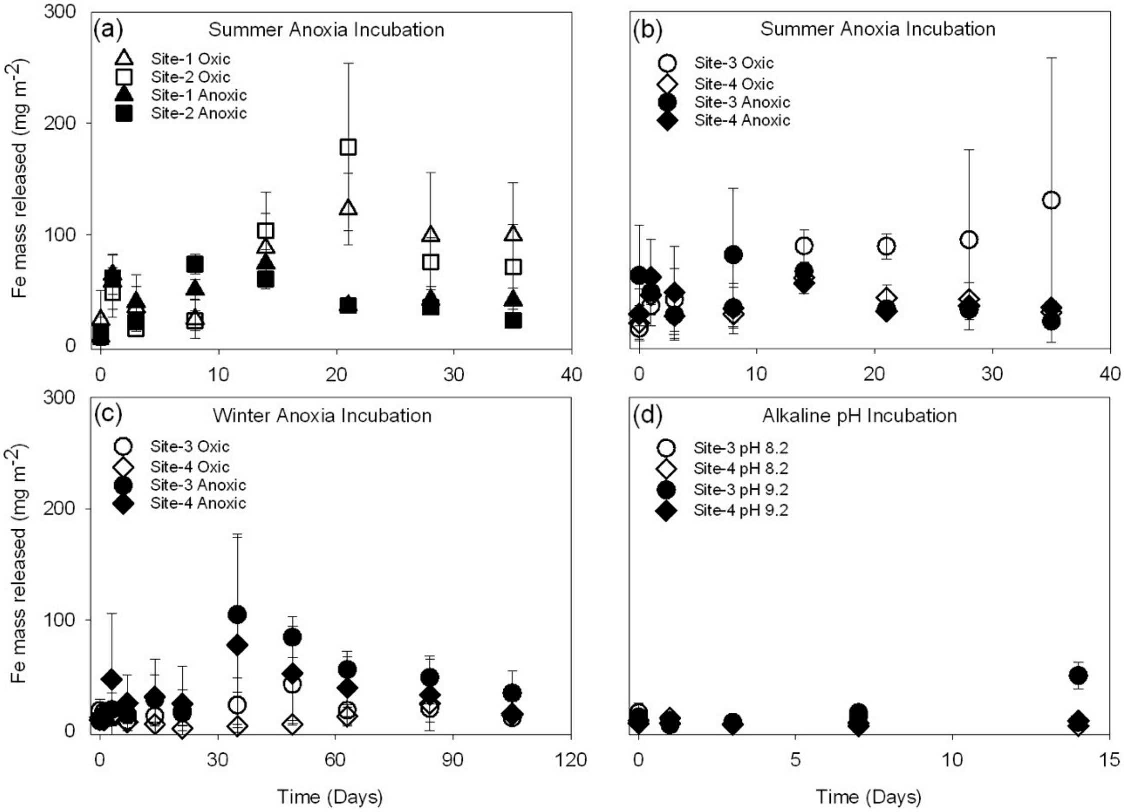

Figure 2.8. Mass of iron (Fe) in overlying water of cores per m^2 sediment versus incubation time (days) in the (a) Summer Anoxia Incubation (Sites 1 and 2); (b) Summer Anoxia Incubation (Sites 3 and 4); (c) Winter Anoxia Incubation; and (d) Alkaline pH Incubation. Open symbols represent control cores and filled symbols represent treatment cores. Error bars represent 1 SD (*n*=3).

Manganese was substantially released from sediment in all cores in the anoxic treatment in the Summer Anoxia Incubation, and Site 1 in the oxic treatment (Figure 2.9a,b). Manganese was generally released after 1–3 days, reaching equilibrium by Day 8 (Figure 2.9a,b). All cores released Mn in the Winter Anoxia Incubation after 1–3 days, with concentrations in overlying water reaching equilibrium by Day 35 (Figure 2.9c). Anoxic cores released greater quantities of Mn than oxic cores (Figure 2.9c). All cores in the Alkaline pH incubation released minimal quantities of Mn (Figure 2.9d). Temporally, sediment cores in the Summer Anoxic and Winter Anoxic Incubations cores displayed Mn release followed by Fe release, and then P release (Figures 2.3–2.5). Sediment in the Alkaline pH Incubation released P, but released limited, if any, Fe and Mn.

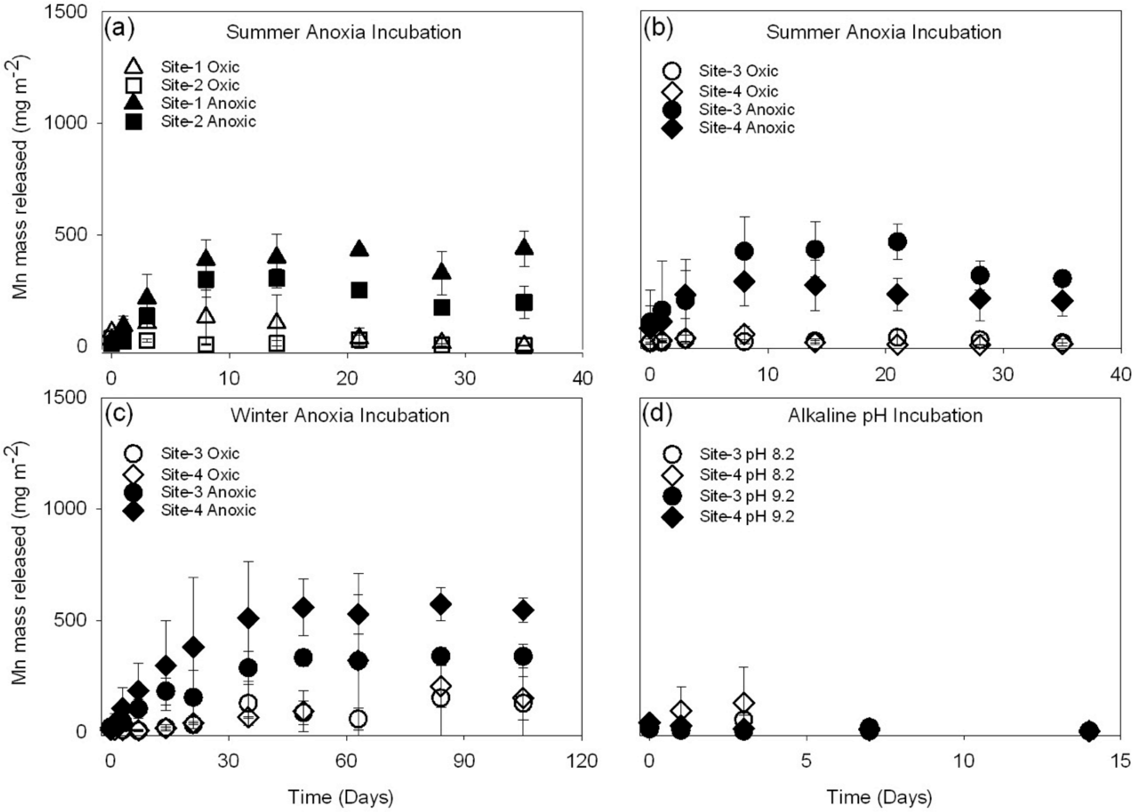

Figure 2.9. Mass of manganese (Mn) in overlying water of cores per m^2 sediment versus incubation time (days) in the (a) Summer Anoxia Incubation (Sites 1 and 2); (b) Summer Anoxia Incubation (Sites 3 and 4); (c) Winter Anoxia Incubation; and (d) Alkaline pH Incubation. Open symbols represent control cores and filled symbols represent treatment cores. Error bars represent 1 SD (*n*=3).

2.3.2. Sediment geochemistry

The physicochemical characteristics of the upper 2-cm of the sediment profile from Buffalo Pound Lake significantly differed along the longitudinal axis of the reservoir (Table 2.2). Sediment from Site 1 was composed of significantly less sand ($p<0.001$) and greater silt and clay than sediment from Sites 2–4 ($p<0.001$; $p<0.001$). Sediment from Site 1 also had significantly less TOC content than sediment from Sites 2–4 ($p=0.004$). SEDEX P fractionation demonstrated that several P fractions were different among sites. Sediment from the four sampled locations did not display significant differences in concentrations of TEP ($p=0.416$), E-P ($p=0.505$), Fe-Bound P ($p=0.220$), and CFA-P ($p=0.612$). However, the concentration of FA-P in Site 4 sediment was significantly greater than that of all other sites ($p<0.001$). The concentration of OP in sediment from Site 4 was significantly greater than that of Site 1 and 3 ($p<0.001$; $p=0.034$, respectively). The concentration of OP in sediment from Site 1 was significantly less than that of sediment from Sites 2 and 3 ($p=0.002$; $p=0.002$, respectively).

The metal content of SEDEX extracts I–III also demonstrated significant differences among sites for Fe_{MgCl2} (p<0.001), Fe_{CBD} ($p=0.023$), Al_{CBD} ($p=0.023$), and Al_{NaOAc} ($p<0.001$). Sediment from Sites 3 and 4 had significantly greater Fe_{MgCl2} content than sediment from Sites 1 and 2 ($p<0.001$), but significantly less Fe_{CBD} content than sediment from Site 1 ($p=0.023$). Sediment from Site 4 had greater Al_{CBD} content than sediment from Sites 1 and 2 ($p=0.027$ and $p=0.041$), and greater Al_{NaOAc} content than all other sites ($p<0.001$). Fe_{NaOAc} and Al_{MgCl2} content in sediment did not significantly differ among sites ($p=0.062$ and $p=0.369$). Al_{Sum}:Fe_{Sum} ($p<0.001$) and Al_{NaOAc}:$P_{Exchangeable+Redox}$

(p=0.003) molar ratios in sediment differed significantly among sites. Site 4 sediment contained significantly greater $\mathrm{Al_{Sum}}$:$\mathrm{Fe_{Sum}}$ (p<0.001, p<0.001, and p=0.002) and $\mathrm{Al_{NaOAc}}$:$\mathrm{P_{Exchangeable+Redox}}$ (p=0.006, p=0.008, and p=0.007) than sediment from Sites 1–3, respectively.

Table 2.2. Geochemistry of the upper two cm of Buffalo Pound Lake sediment represented as mg g^{-1} of sediment. Sediment samples were collected in June 2014. Solvents used for isolation of phosphorus and metal fractionation are indicated in brackets and subscripts, respectively. Benthic organisms were collected September 2015 from only Sites 3 and 4.

Parameter	**Unit**	**Site 1**	**Site 2**	**Site 3**	**Site 4**
Physical					
Sand	%	26 ± 12^{b}	82 ± 2^{a}	81 ± 7^{a}	80 ± 7^{a}
Silt	%	39 ± 7^{a}	9 ± 1^{b}	11 ± 5^{b}	10 ± 3^{b}
Clay	%	35 ± 8^{a}	9 ± 2^{b}	7 ± 2^{b}	10 ± 4^{b}
Chemical					
Total Organic Carbon	%	3.75 ± 0.16^{b}	7.01 ± 0.45^{a}	5.22 ± 1.19^{a}	6.04 ± 0.71^{a}
Phosphorus Fractions					
Exchangeable P ($MgCl_2$)	mg g^{-1}	0.12 ± 0.01	0.13 ± 0.02	0.11 ± 0.02	0.10 ± 0.04
Fe-Bound P (CBD)	mg g^{-1}	0.57 ± 0.07	0.60 ± 0.04	0.56 ± 0.06	0.40 ± 0.20
CFA-P (pH 4 NaOAc)	mg g^{-1}	0.23 ± 0.01	0.24 ± 0.06	0.27 ± 0.05	0.21 ± 0.07
FA-P (1M HCl)	mg g^{-1}	0.04 ± 0.00^{c}	0.06 ± 0.02^{bc}	0.08 ± 0.01^{b}	0.15 ± 0.01^{a}
OP (550°C – 1M HCl)	mg g^{-1}	0.19 ± 0.02^{c}	0.33 ± 0.02^{ab}	0.31 ± 0.04^{b}	0.37 ± 0.07^{a}
TEP (Sum)	mg g^{-1}	1.15 ± 0.11	1.36 ± 0.08	1.34 ± 0.11	1.23 ± 0.32
Iron Fractions					
Fe_{MgCl2}	mg g^{-1}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.06 ± 0.00^{a}	0.06 ± 0.00^{a}
Fe_{CBD}	mg g^{-1}	9.86 ± 2.74^{a}	8.73 ± 0.67^{ab}	6.94 ± 0.54^{ab}	5.42 ± 0.07^{b}
Fe_{NaOAc}	mg g^{-1}	1.13 ± 0.13	0.94 ± 0.11	1.05 ± 0.08	0.86 ± 0.11
Aluminium Fractions					
Al_{MgCl2}	mg g^{-1}	0.12 ± 0.07	0.22 ± 0.11	0.07 ± 0.06	0.17 ± 0.15
Al_{CBD}	mg g^{-1}	0.04 ± 0.07^{b}	0.14 ± 0.16^{b}	0.33 ± 0.05^{ab}	1.19 ± 0.75^{a}
Al_{NaOAc}	mg g^{-1}	0.18 ± 0.08^{b}	0.12 ± 0.11^{b}	0.27 ± 0.08^{b}	1.37 ± 0.16^{a}
Molar Ratios					
$Al_{Sum} : Fe_{Sum}$		0.07 ± 0.03^{b}	0.07 ± 0.02^{b}	0.17 ± 0.02^{b}	0.89 ± 0.29^{a}
$Al_{NaOAc} : P_{Exchangeable+Redox}$		0.29 ± 0.11^{b}	0.18 ± 0.17^{b}	0.46 ± 0.10^{b}	3.50 ± 1.41^{a}
Biological					
Chironomid larvae	organisms m^{-2}			2564 ± 1226	2009 ± 152
Mollusks, small (<2 cm long)	organisms m^{-2}			363 ± 217^{b}	1186 ± 403^{a}
Mollusks, large (>5 cm long)	organisms m^{-2}			0 ± 0	57 ± 57
Oligochaetes	organisms m^{-2}			172 ± 99^{a}	0 ± 0^{b}
Other	organisms m^{-2}			0 ± 0	421 ± 369

Values followed by the same letter are not significantly different ($p \geq 0.05$) among sites ($n = 3$).

2.3.3. In situ study

Surface water

Concentrations of TP and SRP in surface water were greater at Site 3 than Site 4 throughout summer (Figure 2.10a,b,f,g). Both sites had greater DO concentrations, pH, and temperature in the upper water column relative to bottom water throughout the field study. Variance in concentrations of TP at Site 3 bottom water was best explained by DO concentration and pH (R^2=0.57, F(3,11)=4.76, *p*=0.023), and was significantly predicted by DO concentration (*p*<0.001). Variance in concentrations of SRP in Site 3 bottom water was best explained by DO and pH (R^2=0.42, F(2,12)=4.32, *p*=0.039), and was significantly predicted by pH (*p*=0.013). Variance in concentrations of TP in Site 4 bottom water was best explained by DO and pH (R^2=0.35, F(2,12)=3.29, *p*=0.073), and was significantly predicted by DO (*p*=0.036). However, the TP model for Site 4 was not statistically significant. Variance in concentrations of SRP in Site 4 bottom water was best explained by DO and pH (R^2=0.52, F(2,12)=6.41, *p*=0.013), and was significantly predicted by DO and temperature (*p*=0.004 and *p*=0.023).

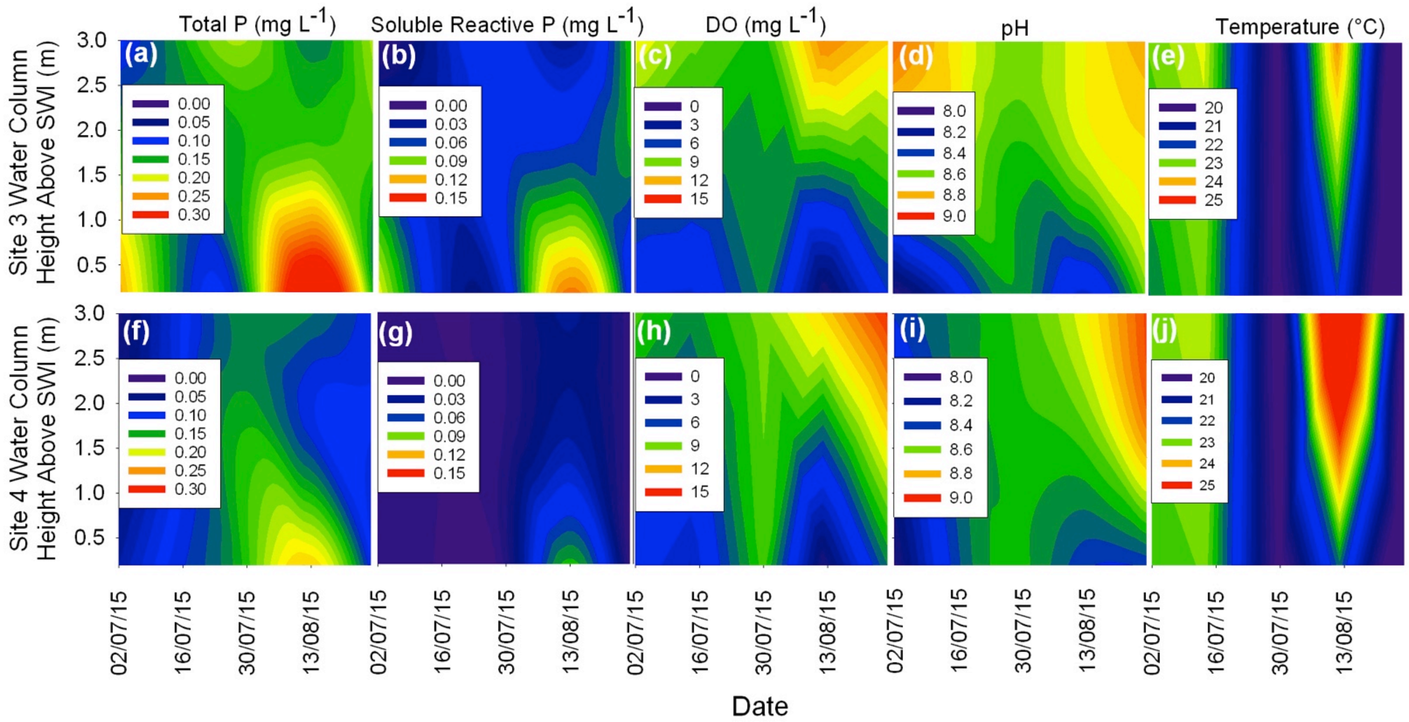

Figure 2.10. Measurements of total phosphorus (P), soluble reactive P, dissolved oxygen, pH, and temperature in Buffalo Pound Lake surface water from July 2 to August 26, 2015 at Site 3 (a–e) and Site 4 (f–j). Water samples were collected approximately every two weeks from 3 m (top), 2 m (middle) and 0.2 m (bottom) above the sediment water interface (SWI) (*n*=3).

Iron concentrations within Site 3 and 4 water columns were elevated in the early and late summer relative to mid-summer, but were homogenous through the water column each sample day (Figure 2.11). Concentrations of Mn in the water column of Site 3 were extremely variable relative to Site 4 (117 ± 117%; Figure 2.11). However, concentrations of Al in the water column at Site 3 were minimal relative to Site 4 throughout the summer (10 ± 6%; Figure 2.11). The concentration of Mn in Site 4 bottom water covaried with concentrations of TP and SRP. The concentration of Al in the water column of Site 4 was elevated mid-summer relative to early and late summer, but was homogenous throughout the water column within each sample day

Sediment pore water

The concentration of SRP was greater in pore water from Site 3 compared to pore water from Site 4 throughout the study. The concentration of SRP in pore water from Site 3 was elevated near the SWI during two sample periods, which coincided with greater concentrations of SRP in bottom water (Figures 2.10 and 2.12). Site 4 pore water SRP concentrations were minimal throughout summer. Concentrations of Fe in pore water from Sites 3 and 4 were elevated only during July, which coincided with concentrations of Fe in surface water. Site 3 and 4 displayed complex Mn pore water profiles throughout the summer, which spiked near the SWI at the start and end of summer. Site 3 pore-water Al was minimal at all depths throughout summer but Site 4 pore-water Al was greatest near the SWI at the start and end of summer.

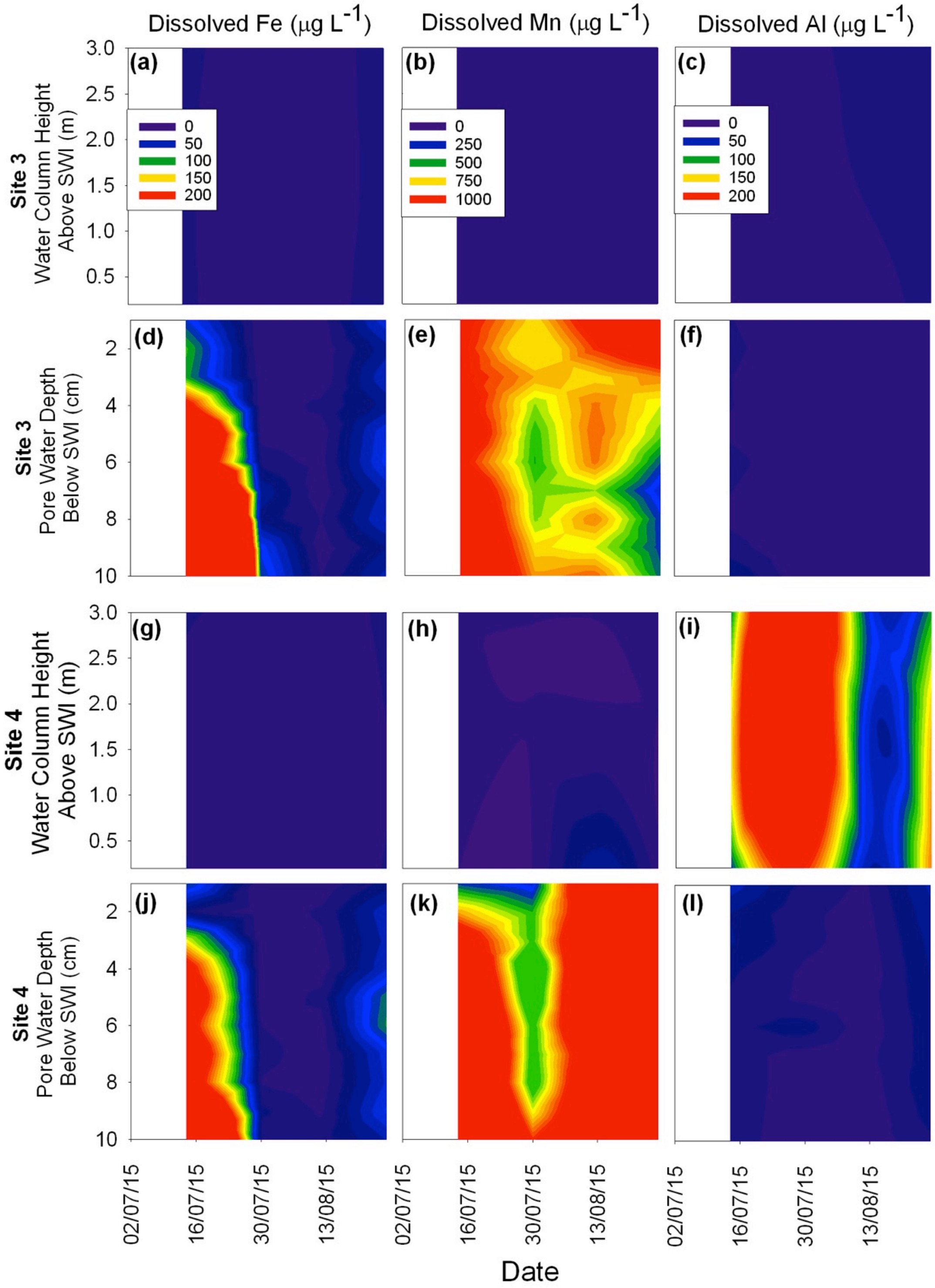

Figure 2.11. Concentrations of dissolved iron, manganese, and aluminum (μg L^{-1}) in Buffalo Pound Lake surface water (Site 3 (abc) and Site 4 (ghi)) and pore water (Site 3 (def) and Site 4 (jkl)). Samples were collected approximately every two weeks from July 14 to August 26, 2015. Surface water samples were collected from 3 m (top), 2 m (middle) and 0.2 m (bottom) above the sediment water interface (SWI). *n*=3

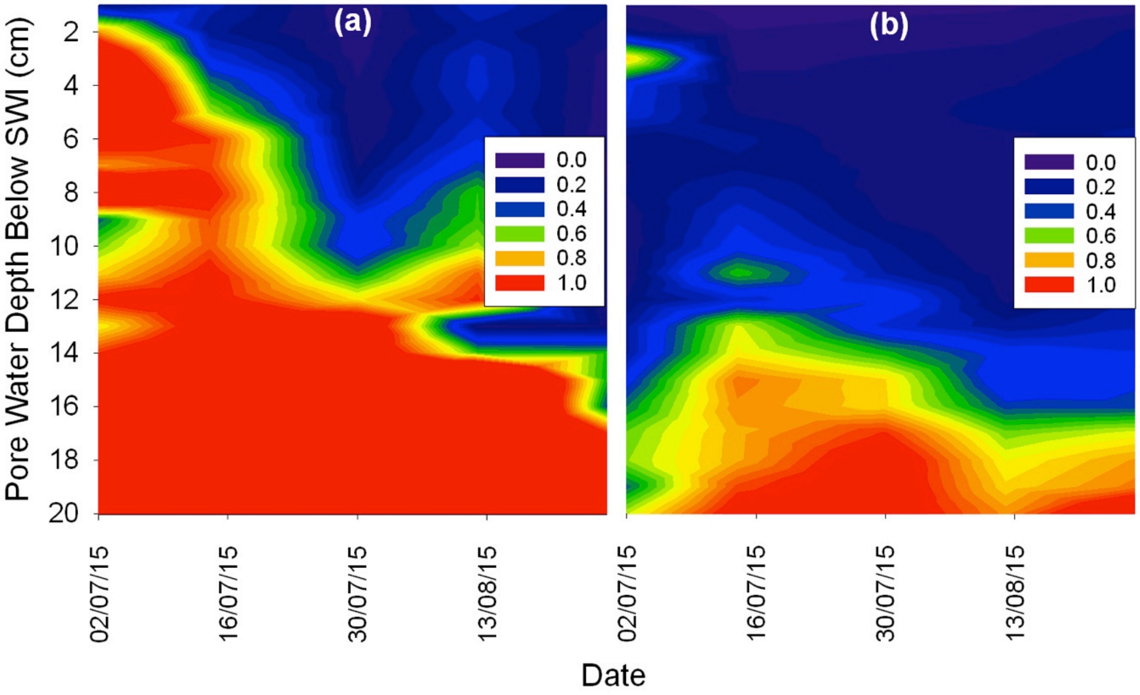

Figure 2.12. Concentration of soluble reactive phosphorus (mg L^{-1}) in Buffalo Pound Lake pore-water profiles from July 2 to August 26, 2015 at Site 3 (a) and Site 4 (b). Sediment cores were collected approximately every two weeks for pore water isolation (*n*=3).

Macroinvertebrate community assemblage

The density of chironomid larvae (*p*=0.480), large mollusks (*p*=0.159), and “other organisms” (*p*=0.119) did not significantly differ between Sites 3 and 4 during September 2015. However, the density of oligochaetes (*p*=0.040) was significantly greater at Site 3 relative to Site 4, and the density of small mollusks (*p*=0.036) was greater at Site 4 relative to Site 3 during September 2015.

2.4. Discussion

Eutrophication and algal blooms affect freshwater lakes globally. In the Canadian prairies, blooms are of particular concern due to increasing drought issues, the sensitivity of shallow lakes to develop natural (yet worsening) blooms, and regional geochemistry that encourages P mobilization from sediment. Recently, Orihel et al. (2015) demonstrated that internal P loading in shallow prairie lakes are driven by Fe-poor sediments in conjunction with polymixis, which decreases N:P ratios in surface waters and promotes bloom formation. Here, we studied how sediment geochemistry influenced rates of P mobilization from sediment under several different release mechanisms, and the occurrence of redox-sensitive P loading *in situ*, which was associated with transient stratification. Our results suggest that concentrations of Fe and Al in sediment fundamentally control internal P loading in this reservoir and possibly in other Canadian prairie systems.

2.4.1. Sediment core phosphorus mobilization

Under anoxic conditions, cores released the more reactive forms of P (i.e., TRP and SRP) for the first 21d, consistent with the accepted paradigm that P released from the sediment is largely the bioavailable orthophosphate form (Nürnberg, 1988). However, TP and TDP mass increased by >100% relative to TRP and SRP, respectively, after Day 21. Bioavailable P could have mobilized from sediment, but later sorbed to colloids from bioturbation by endogenous macroinvertebrates (Davis, 1993), which may decrease analytical detection of P as TRP and SRP. The remaining core incubations released primarily reactive P forms throughout incubation. Although SRP is used to estimate bioavailable P, it overestimates actual concentrations of orthophosphate (Ruttenberg, 2003). The Summer Anoxia Incubation RR_{TP} for sediment cores from Sites 1–3, which are large compared to regional values (Doig et al., 2017) and other lakes worldwide, are characteristic of a hypereutrophic lake (Nürnberg, 1988).

The magnitude of P release from the oxic treatment of the Summer Anoxia Incubation and control cores of the Alkaline pH Incubation was unexpected, but were likely due to warm temperatures. Dissolution of Ca-bound P and decomposition of OP can have greater influence on P mobilization than P mobilized from reducible Fe oxides (Hupfer and Lewandowski, 2008). Additionally, unsuccessful sequestration of P mobilized from subsurface sediment may have been due to the low concentrations of Fe, which are characteristic of prairie sediment (Allan and Williams, 1978). Sediment in shallow lakes, which usually contain aerobic bottom water, can only retain P if the sediment contains Fe:P $\geq$ 15:1 (by weight), and are unable to retain P if Fe:P is <10:1 (Jensen et al., 1992). Additionally, endogenous organisms were not removed from sediment cores prior to the Anoxia Incubations and Alkaline pH Incubation. The presence of benthic organisms can significantly alter RR_P as demonstrated by the Bioturbation Incubation experiment.

The Bioturbation Incubation demonstrated P mobilization following a negative parabolic function of midge larvae density. Low densities of chironomid larvae can increase P mobilization through mineralization of organic matter and excretion (Gallepp, 1979; Figure 2.7). However, increasing the density of chironomid larvae past a certain threshold can decrease P mobilization (Figure 2.7). Invertebrate tunneling increases oxygen penetration to deeper sediment, which causes oxidation of Fe(II) to Fe(III) and subsequent sequestration of available P (Chen et al. 2015). However, broad generalization regarding biodensity-dependent P mobilization should be avoided as P chemodynamics differ among macroinvertebrates (e.g. bivalves cause P release at greater densities; Chen et al., 2016).

The observed trends in Fe and Mn release are consistent with known P release mechanisms. During anoxia-mediated release of P from sediment, Mn can act as an alternate electron acceptor (i.e. the period prior to significant P release), followed by Fe reduction and the concurrent release of sorbed P (Davison and Woof, 1984), as observed in the Summer Anoxia and Winter Anoxia Incubations. Concentrations of Mn and Fe in overlying water plateaued and decreased, respectively, throughout the incubations. This was likely due to Fe sulfide formation, which was observed as a black precipitate on surficial sediment. Reducing conditions favor the microbial reduction of sulfate to sulfides, which preferentially binds Fe^{2+} relative to Mn^{2+} (Irving and Williams, 1953). The lack of Mn and Fe in overlying water in both treatments of the Alkaline pH Incubation supports the mechanism of ligand substitution. Relative to control (pH 8.2) cores, the greater concentration of hydroxyl ions in the pH 9.2 treatment cores likely substituted into phosphate-ligand compounds (Jin et al., 2006), and thereby released sorbed P without solubilizing Mn and Fe from minerals.

The significantly lower mass of P released from Site 4 cores in the majority of the core incubations was unexpected considering the limited distance between Sites 3 and 4 and the homogenous reservoir features (e.g. depth, morphometry, and land use) relative to other freshwater lakes. However, the magnitude of pH-mediated P release from sediment from Site 4 was similar to Site 3, which suggested there were fundamental geochemical differences at Site 4 relative to up-reservoir sites.

2.4.2. Sediment geochemistry

Geochemical analysis of sediment from Buffalo Pound Lake was restricted to the upper 2-cm of the sediment. However, this portion has been demonstrated to act as the primary source of P release on a short-term scale (Doig et al., 2017). Total extracted P content in Buffalo Pound Lake sediments is within the range of other Canadian prairie lakes, which range from 0.5 to 3.0 mg kg^{-1} d.w. (Table 2.2; Doig et al., 2017). Total extracted P did not significantly differ among sites, indicating RR_P variability among sites was not due to differences in TP inventory. Therefore, differences in RR_P were likely due to differences in P geochemistry. FA-P and OP are conditionally bioavailable P fractions and were the only fractions that varied among sites. FA-P and OP were both significantly greater in Site 4 sediment than sediment from Sites 1 and 3 (Table 2.2). FA-P is covalently bound P, which can become bioavailable after the mineral has been chemically weathered (Ruttenberg, 1992) and certain polyester phosphates from sediment OP can significantly contribute to the bioavailable P pool (Zhu et al., 2013). Considering P geochemistry alone, the RR_P of Site 4 sediment should be greater than the other sites due to greater sediment FA-P and OP content. Nevertheless, core incubation observations were contrary to this expectation.

The content of P sorbents in sediment was characterized using SEDEX extractants I–III, which selectively extracted Fe and Al from sediment. CBD in Extract II reduced solid Fe^{3+} to soluble Fe^{2+}, followed by chelation of Fe^{2+} by citrate. The acidity of NaOAc in Extract III solubilizes the remaining Fe. The citrate component of Extract II chelates and solubilizes Al from certain minerals and the acidity of Extract III solubilizes the remaining sediment Al (Gensemer and Playle, 1999). Sediment down-reservoir of the BPWTP intake had a significantly greater concentration of Al compared to up-reservoir sediment, likely due to BPWTP operations. Prior to 1985, alum-containing backwash from the BPWTP, was discharged directly into Buffalo Pound Lake. Following 1985, small settling ponds were constructed to minimize alum discharge to the lake, but these ponds did not fully eliminate alum discharge (personal communication, Dan Conrad, BPWTP). Sediment containing critical molar ratios of Al_{sum}:Fe_{sum} >3 or Al_{NaOAc}:$P_{Exchangeable+Redox}$ >25 can completely mitigate anoxia-induced P release from sediment (Kopáček et al., 2005). Buffalo Pound Lake sediment did not achieve these molar ratios for any site analyzed. However, the elevated Al content in Site 4 sediment likely limited anoxia-induced P release for this site, and explains the lower values for the majority of RR_P from Site 4 sediment in the Summer Anoxia Incubation and Winter Anoxia Incubation. Greater Al content in Site 4 sediment should also reduce P mobilization *in situ* relative to Site 3 sediment, as was observed in the field and discussed below.

2.4.3. Phosphorus mobilization in situ

Concentrations of TP and SRP at Site 3 were greater than at Site 4 throughout the *in situ* study period, an observation consistent with core incubation and sediment geochemistry results. Temperature and winds were anecdotally higher and lower, respectively, on days that aligned with greater internal P loading. Several days before the 30-July-2016 sampling, winds from an intense storm thoroughly mixed the water column, creating homogenous DO, pH, and temperature profiles at Sites 3 and 4. Following 30-July-2016, extended warm temperatures and calm winds allowed bottom water hypoxia to develop (Figure 2.10), which supports a new theory governing polymictic internal P loading (Orihel et al., 2015).

At both Site 3 and Site 4, bottom water TP was significantly predicted by DO concentration. This was likely due to anoxia-induced P mobilization, similar to observations in the core incubations, which was followed by P sorbing to colloids and particulates. Site 3 bottom water SRP variance was negatively correlated to pH, which was a significant predictor variable. Greater SRP concentrations may have been due to the decomposition of organic matter and OP, which can simultaneously produce acids and/or CO_2, and decrease the pH of the water (Lijkelma, 1980). Alternatively, primary productivity could have consumed SRP while photosynthetically increasing pH. DO concentration and temperature significantly predicted SRP concentrations in Site 4 bottom water likely due to greater OP content in Site 4 sediment relative to other sites. Greater temperatures increase the rate of decomposition of organic matter in the sediment profile. This would hasten the depletion of benthic concentrations of DO and increase release of iron oxide-associated P. Temperature driven, redox-induced P release is supported by trends in Mn concentration in Site 4 bottom water, and trends observed in the core incubations (Figure 2.11h). Redox-insensitive Al in sediment may have partially sequestered P mobilized during anoxic conditions at the SWI. Concentrations of SRP in Site 4 pore water were less than those in Site 3 throughout summer. This observation supports the hypothesis that Al in Site 4 sediment, which has been unintentionally added to Buffalo Pound Lake, acts as a redox-insensitive P sorbent. Application of redox-insensitive sorbent material (e.g., alum or lanthanum-modified bentonite) has been shown to mitigate anoxia-induced internal P loading in other shallow lakes (Welch and Schrieve, 1994; Spears et al., 2013), and could be purposefully applied to sediment in Buffalo Pound Lake.

2.5. Conclusions

Sediment cores from Buffalo Pound Lake demonstrated greatest P mobilization under warm temperatures, followed by alkaline pH, anoxic conditions, and intermediate midge larvae density. Interestingly, we found evidence that historic discharges of low concentrations of alum into Buffalo Pound Lake by BPWTP operations have suppressed internal P loading in down-stream areas of the lake. Episodic periods of benthic anoxia caused reduction of Fe oxides in sediment at Site 3 and Site 4, and the release of associated P. This supported a novel paradigm of P release in polymictic lakes, which hypothesizes that P is inadequately sequester by Fe-poor sediments, mobilizes from pore water into surface water by polymixis, which then decreases N:P ratios in the water column (Orihel et al., (2015). However, the greater concentration of sediment Al at Site 4, acted as a redox-insensitive P sorbent that mitigates anoxia-induced internal P loading in this region of the lake. Therefore, given ongoing issues related to recurring algal blooms in Buffalo Pound Lake, further research should investigate the spatial extent and effectiveness of historically deposited alum, or other redox-insensitive P sorbents, such as lanthanum-modified bentonite, to mitigate internal P loading.

In a broader context, to sufficiently characterize internal P loading potential in shallow lakes globally, studies should determine concentrations of TP, Fe-Bound P, total Fe, and total Al in sediment with respect to critical geochemical ratios (Jensen et al., 1992; Kopáček et al., 2005). This work also suggests that P, Al, and Fe in sediment at ratios below the identified critical thresholds can still influence the ability of sediment to sequester P under altered redox conditions.

CHAPTER 3

EXPERIMENTAL ARSENIC EFFLUX RATES AND IN SITU REMOBILIZATION FROM PRAIRIE RESERVOIR SEDIMENT, BUFFALO POUND LAKE, SK, CANADA.

Chapter preface

This chapter describes the relative influence of physicochemical mechanisms that affect As mobilization from prairie reservoir sediment. Geochemical analysis of Buffalo Pound Lake sediment demonstrated that the content of Fe and Al in sediment was significantly different along the length of this reservoir, which altered As mobilization in laboratory sediment core incubations and *in situ*. Additionally, this research provides concentrations of As in *Chironomus spp*. that were collected from a naturally As-rich reservoir. Knowledge of concentrations of As in *Chironomus spp*. from an unpolluted reservoir could be useful to environmental risk managers.

This chapter is being prepared for submission as a research article to the journal *Chemosphere* under joint authorship with Karsten Liber (University of Saskatchewan), Lorne Doig (University of Saskatchewan), and Helen Baulch (University of Saskatchewan).

3.1. Introduction

Concentrations of arsenic (As) in water bodies can be augmented by natural (e.g. soils, sediment, and volcanoes) and anthropogenic inputs (e.g. mining, fossil fuel combustion, and pesticides) to concentrations that can adversely affect aquatic organisms (Smedley and Kinniburgh, 2002). Arsenic predominantly exists in freshwater environments as the inorganic oxyanions, arsenite (As(III)) and arsenate (As(V); Smedley and Kinniburgh, 2002). Although As(III) and As(V) both interfere with energy production in living organisms, As(III) acts through a separate mechanism of action, and is generally several orders of magnitude more toxic (Aposhian, 1989; Winski and Carter, 1998; Naranmandura et al., 2007).

In addition to external inputs of As, freshwater lakes can be susceptible to internal loading of As, the mobilization of As from bottom sediment into overlying water. Sediment-associated As is primarily bound to iron (Fe), aluminum (Al), and manganese (Mn) oxides, but can also sorb to charged particles (e.g., clays, organic material) or precipitate with sulfides (Keon et al., 2001). Warmer temperatures, which influence reaction rates, elevated pH, and low dissolved oxygen (DO) concentrations can mobilize As sorbed to Fe and Mn oxides (Smedley and Kinniburgh, 2002). Arsenic sorbed to Al oxides are not affected by decreased DO concentrations, but can be mobilized by elevated pH (>8.5; Smedley and Kinniburgh, 2002). Eutrophic lakes can produce a variety of conditions at the sediment-water interface (SWI), that favor the mobilization of sediment-associated As into pore water, and subsequently into overlying water (Martin and Pedersen, 2004). However, due to varying physicochemical properties of sediments, estimating the labile and bioavailable proportion of sediment-associated As is complex

(Snape et al., 2004). Benthic organisms occurring near the SWI can accumulate As at concentrations >100 times that of the surrounding water (Spehar et al., 1980) and act as a significant route of diet-borne As exposure to fishes (Erickson et al., 2011).

Sediments in Canadian lakes are naturally enriched in concentrations of As (between 4 to 150 mg kg^{-1}; Wang and Mulligan, 2006), and uncontaminated sites can exceed the Canadian interim sediment quality guideline (ISQG; 5.9 µg kg^{-1} d.w.), or the probable effect level (PEL; 17 mg kg^{-1} d.w.) for the protection of freshwater aquatic life (CCME, 2001). Canadian prairie lakes are likely susceptible to internal As loading based on several characteristics (e.g., Fe-poor, As-rich sediments; transient anoxia; and alkaline waters; Chapter 2). However, internal loading of As, and the relative influence of mechanisms on As release rates, in Canadian prairie lakes remain unstudied. The objective of this study was to determine the relative influence of various environmental mechanisms on As mobilization from prairie lake sediment. A case study was conducted using Buffalo Pound Lake, SK, Canada, a shallow freshwater prairie reservoir. Historical concentrations of As in Buffalo Pound Lake sediment (13.2 mg kg^{-1} d.w; Huang and Liaw, 1978) exceed the current ISQG, approach the PEL guideline value (CCME, 2001), and concentrations of As observed in lake water (6.5 µg L^{-1}; Viraraghaven et al., 1992) can exceed the Canadian water quality guideline for the protection of freshwater aquatic life (5.0 µg L^{-1}; CCME, 2001). Phosphorus (P), which is geochemically analogous to As, can be mobilized from Buffalo Pound Lake sediment under different environmental conditions (Chapter 2). This study assesses whether these same mechanisms also mobilize As from sediment.

A combination of sediment core incubations and *in situ* data were used to: i) assess the relative influence of environmental variables on As mobilization from Buffalo Pound Lake sediment; ii) evaluate environmental conditions associated with As release from sediment *in situ*; and iii) assess the spatial aspects and geochemical influences on the bioaccessibility of As to chironomid larvae *in situ*. This is the first study to provide As release rates from Canadian prairie sediment, to investigate the relative influence of several mechanisms on As release rates within one system, and provide concentrations of As in chironomid tissue from an uncontaminated lake.

3.2. Methods and Materials

3.2.1. Site description

Buffalo Pound Lake (50°39'N, 105°31'W) is a shallow polymictic lake in southern Saskatchewan that was dammed in 1939 to stabilize water levels to better provide potable water to the cities of Regina and Moose Jaw (Figure 2.1; Hall et al., 1999). The lake is also used for recreational activities, including fishing, and serves as a water supply for agricultural and industrial operations. Buffalo Pound Lake contains a total water volume of 87.5 x 10^6 m^3, an average depth of 3 m, and a maximum depth of 5.5 m (Hall et al., 1999). Additional morphometric and hydrological characteristics of Buffalo Pound Lake are described in Hall et al. (1999). The relatively flat lake bottom is comprised of silts and clays (Hrynkiw et al., 2003). Buffalo Pound Lake is eutrophic, subject to oscillatory development of summertime algal blooms, and subject to transitory periods of internal P loading (Chapter 2).

Four sites, spaced 5 to 7 km apart, were sampled along the long axis of Buffalo Pound Lake to assess spatial variability of As within the reservoir. Site 1 was located furthest up-reservoir, near the water inflow of the Qu'Appelle River to Buffalo Pound Lake. Site 4 was furthest down-reservoir, approximately 600 m down-reservoir of the Buffalo Pound Water Treatment Plant (BPWTP) water intake (Figure 2.2). Three stations, spaced 50 to 75 m apart, were sub-sampled within each site to account for heterogeneity within sites.

3.2.2. Sediment core incubations

Sediment core collection and incubation techniques were based on methods described in Doig et al. (2017). Briefly, sediment cores were collected in duplicate from three stations within each site (six cores per site) using acrylic cylinder core tubes (61 cm height, 7.5 cm diameter) and a GLEW Gravity Corer (John Glew, Kingston, ON, Canada). Temperature and DO concentration were measured (Orion Star A223 Dissolved Oxygen Portable Meter, Thermo Fisher Scientific, Waltham, MA, USA) at each station in surface water and overlying water from a collected sediment core. After collection, cores were sealed at the bottom with a rubber stopper, and at the top with Parafilm®, and transported upright to the Toxicology Centre, University of Saskatchewan (Saskatoon, SK, Canada). Cores were then stored in the dark at 4°C until experimental use. Lake surface water was collected in a 50-L carboy from Site 4, upon completion of coring, and was filtered (8-µm Whatman Nuclepore Track-Etched Membranes, Tisch Scientific, North Bend, OH, USA) before use in experiments as overlying water.

Three sediment core incubation experiments were conducted to determine the influence of temperature representative of summer and winter conditions (warm and cold), low (< 1 mg L^{-1}) DO concentration, and elevated pH (pH 9.2) on As mobilization from Buffalo Pound Lake sediment. Experiments consisted of two factors, site and treatment. A sediment core from each station per site was assigned to either the control or treatment group (*n* = 3 per site). Sediment cores were adjusted to contain approximately 1.5 L of water overlying the sediment. The top of each core tube contained one port to allow air or argon (Ar) gas inflow and another port to allow air outflow through a vapor lock (S-shape airlock, E.C. Kraus, Independence, MO, USA). Rigorous air inflow was maintained to mix and homogenize the overlying water column, but to not disturb the sediment. Samples of overlying water (120 mL) were periodically collected from each core throughout the incubation period and filtered (0.45-µm filtered, polyethersulfone syringe filter with acrylic housing, VWR International, Radnor, PA, USA) to measure dissolved trace elements (As, Fe, and Mn). Sample days varied among incubations. Overlying core water was replenished with filtered Site 4 water after samples were collected. Filtered Site 4 water was pretreated to match the characteristics of control/treatment cores (i.e., temperature, DO concentration, and pH) prior to replenishment of overlying core water. Overlying water in sediment cores was monitored every two days for DO concentration and temperature (Orion Star A223 Dissolved Oxygen Portable Meter, Thermo Fisher Scientific, Waltham, MA, USA).

Experiment 1: Summer anoxia incubation

The first core incubation assessed As mobilization from sediment under high (8.1 ± 0.9 mg DO L^{-1}) and low (0.1 ± 0.1 mg DO L^{-1}) DO concentrations at a temperature representative of summer conditions (19.2 ± 0.3°C). Sediment cores were collected in June 2014 from each of the four sites, assigned to either an oxic or anoxic treatment, and incubated for 35 days. The overlying water in the oxic treatment was bubbled with air. The anoxic cores were bubbled occasionally with Ar. Samples of overlying water in cores were collected from each core tube on Days 0, 1, 3, 8, 14, 21, 28, and 35 of the incubation.

Experiment 2: Winter anoxia incubation

The second core incubation assessed the influence of high (10.5 ± 3.2 mg DO L^{-1}) and low (0.7 ± 0.4 mg DO L^{-1}) DO concentrations on As mobilization from sediment at a temperature representative of winter conditions (4.8 ± 0.2°C). Sediment cores were collected in October 2014 from Sites 3 and 4. These sites were selected for further investigation as they are close in proximity, yet demonstrated very different As mobilization trends in the Summer Anoxia Incubation. Sediment cores were incubated for 105 days in either oxic or anoxic treatments, which were bubbled continuously with air or occasionally with Ar, respectively. Samples of overlying water were collected from each core on Days 0, 1, 3, 7, 14, 21, 35, 49, 63, 84 and 105 of the incubation.

Experiment 3: Alkaline pH incubation

Sediment cores were collected in September 2015 from Sites 3 and 4. The overlying water of each core in this experiment was maintained at either the background pH of 8.2 ± 0.2 or adjusted to a pH value of 9.2 ± 0.3, representing the maximum value observed in Buffalo Pound Lake (Helen Baulch, University of Saskatchewan, personal communication). The pH of overlying water in each core replicate was monitored several times per day (6230N meter, Jenco, San Diego, CA, USA; 8102BN ROSS combination pH electrode; Orion, Burlington, ON, CAN), and overlying water in the elevated-pH treatment manually adjusted as needed using 1.0 NaOH. Cores were incubated for 14 days at a temperature representative of summertime (19.1 ± 0.1°C) oxic conditions (8.2 ±

0.7 mg DO L^{-1}). Samples of overlying water were collected from each core tube on each of Day 0, 1, 3, 7, and 14 of the incubation.

3.2.3. Arsenic mobilization *in situ*

Water column and pore water samples were collected *in situ* every two weeks between 14-July-2015 and 26-August-2015 to measure concentrations of As and other supporting variables. Water column samples were collected from three stations (spaced 50 to 75 m apart) from each of Sites 3 and 4 from 1 m (top) and 2 m (middle) below the water surface (4.2 L Horizontal, Acrylic, Van Dorn Water Sampler, Wildoco, Yulee, FL, USA). Sediment cores were also collected in triplicate at Sites 3 and 4 and the water overlying theses cores was sampled to characterize lake bottom water (approximately 0.2 m above the SWI). Upper, middle, and bottom waters were monitored for dissolved trace element content (As, Fe, Mn, and Al) and pH. Upper and bottom waters were monitored for DO concentration and temperature. The sediment cores were sectioned in a glove bag under an Ar atmosphere (purity > 99.998%). Cores were sectioned in 1-cm increments to 10 cm below the sediment surface. The individual increments of sediment were collected in 50 mL centrifuge tubes (also under an Ar atmosphere) and centrifuged at 206 g for 15 minutes. The pore-water supernatant was collected with a plastic syringe and filtered (0.45 μm) for analysis of dissolved trace element content.

3.2.4. Bioaccessibility trends *in situ*

Three Eckman Grab (13.2 cm x 13.2 cm) samples were collected from each of the four sites during August 2016 to determine concentrations of As in chironomid tissue. Bottom water, sediment, and chironomid larvae were collected from each Eckman Grab sample, which was considered a replicate. Water and sediment samples were collected into pre-cleaned centrifuge tubes (Falcon™ 50mL conical centrifuge tubes, Fisher Scientific, Ottawa, ON, CAN). Approximately 10–15 chironomid larvae (*Chironomus spp.*) were collected into pre-cleaned 1-L high density polyethylene bottles filled with pre-washed sand (150 mL, Granusil Silica Fillers – Grade 5010, Unimin Corporation, New Canaan, CT, USA) and lake water (850 mL).

Per replicate, one subsample of sediment was centrifuged (Centrifuge 5810, Eppendorf, NH, USA) at ~206 g for 10 min to collect the pore-water supernatant. Bottom water and pore water samples were filtered (0.45 µm) prior to analysis for dissolved As. The remaining sediment samples were frozen (-20°C), freeze-dried (Dura-Dry multiprocessor corrosion control freeze-drier, FTS systems™, Stone Ridge, NY, USA), homogenized, and analyzed for the concentration of bioaccessible ($\text{sediment}_{\text{HCL(1M)}}$) and total As ($\text{sediment}_{\text{Total}}$). Freeze-dried sediment (1 g) was agitated in 20 mL of 1 M HCl for 4 hours, centrifuged (described above), and the supernatant collected and filtered (0.45 µm) to estimate bioaccessible As in sediment (Snape et al., 2004). Total As in sediment was determined using microwave-assisted (MARS-5®, CEM Corporation, Mathews, NC, USA), concentrated acid digestion (H_2O_2, HNO_3, and HF) of 0.1 g sediment (digested, filtered (0.45 µm), and collected. After a 24 h gut depuration (recommended by Brooke et al. (1996)), chironomid larvae were rinsed in ultra-pure water, soaked in a 1 mM solution of ethylenediaminetetraacetic acid (EDTA; Sigma Chemical Co., St Louis, MO, USA) for 15 min, rinsed again with ultra-pure water, and oven dried (60°C) for 24 hours (Crawford and Liber, 2015). Samples of dried whole-body chironomid larvae (0.1 g) were acid digested (HNO_3, H_2O_2, and heat) to analyze concentrations of total As in chironomid larvae tissue (Crawford and Liber, 2015).

3.2.5. Chemical analyses

All samples collected for trace element analyses were immediately acidified with 2% HNO_3, and stored (4°C) for in-house analysis (Toxicology Centre, University of Saskatchewan, Saskatoon, SK, CAN). Aqueous samples from sediment core incubations were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; iCAP 6000 series ICP spectrometer, Thermo Scientific, Waltham, MA, USA). The method detection limits (MDLs) for analysis of As, Fe, and Mn using ICP-OES were 5, 1, and 1 $\mu g\ L^{-1}$, respectively. *In situ* concentrations of As in bottom water, pore water, $\text{sediment}_{HCL(1M)}$, sediment_{Total}, and chironomid tissue were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS; 8800 Triple Quadruple ICP-MS, Agilent Technologies, Santa Clara, CA, USA). The MDL for analysis of As, Fe, Mn, and Al using ICP-MS were 0.04, 0.20, 0.03, and 0.01 $\mu g\ L^{-1}$, respectively. Measured concentrations of trace elements in the certified reference materials (1640a trace elements in natural water, NIST, Gaithersburg, MD, USA; PACS-2 marine sediment for trace metals, NRC Canada, Ottawa, ON, CAN; TORT-2, NRC Canada, Ottawa, ON, CAN) were within 80–120% of certified values. Blanks, and duplicates were analyzed alongside samples to ensure quality assurance and quality control of trace element analyses.

3.2.6. Numerical analyses

Dissolved As efflux rates were calculated as the change in mass of As in a sediment core water column over time. The P release rate equation described in Chapter 2 was applied to calculate sediment As release rates.

$$RR_{As} = [(V_{core})(c_2 - c_1)+(V_{sample})(c_1)] / [(A)(t_2 - t_1)] \qquad [2]$$

where arsenic release rate (RR_{As}) values represented the positive release rate of As from sediment as mass of As per area per time (mg m^{-2} day^{-1}); C_2 (mg L^{-1}) was the concentration of As in core overlying water at time t_2 (day); C_1 (mg L^{-1}) was the concentration of As in core overlying water at time t_1 (day); A (m^2) was the surface area of sediment; V_{core} (L) represented the volume of core overlying water; and, V_{sample} (L) represented the volume of water removed for analysis. Time-points t_1 and t_2 represented the initial and final points of inflection, respectively, when As mass released was plotted against incubation time. The MDL value of 5 μg L^{-1} was used when the concentration of As at a time point were below the MDL.

Graph generation and statistical analyses were conducted using SigmaPlot®, version 11 (Systat Software Inc., San Jose, CA, USA). An $\alpha \leq 0.05$ was considered significant for all tests. RR_{As} were compared using two-way analysis of variance (ANOVA) using site and treatment for factors, followed by Tukey's post-hoc test. *In situ c*oncentrations of As in surface water at Sites 3 and 4 were analyzed using a multiple linear regression. Temperature, DO concentration, and pH were used to predict bottom water As concentrations. Within the bioaccessibility study, concentrations of As in bottom water, pore water, sediment, and chironomid tissue were compared among sites using a one-way ANOVA. Concentrations of As in $sediment_{HCL(1M)}$ were transformed using an inverse function to meet the assumption of homogeneity of variance. Pearson correlations were used to establish relationships between concentrations of As in chironomid tissue and each of the media.

3.3. Results

3.3.1. Sediment core incubations

All cores in Experiment 1 (Summer Anoxia Incubation) released As, Fe, and Mn from sediment into the overlying water during the incubation (Figure 2.8ab, Figure 2.9ab, and Figure 3.1ab). Arsenic was released from sediment beginning on Day 3, reached a maximum concentration in overlying water on Day 21, and declined until the end of the incubation (Figure 3.1ab). Compared to sediment collected from Sites 1–3, Site 4 sediment released a small mass of As during the incubation. RR_{As} were significantly influenced by site ($p<0.01$), but were not significantly influenced by treatment ($p=0.129$; Table 3.1). RR_{As} from Site 1–3 (oxic and anoxic RR_{As} combined) were significantly greater than the RR_{As} of Site 4 ($p<0.01$, $p=0.037$, and $p<0.001$, respectively). The average RR_{As} from Site 1 and Site 3 sediment were also significantly greater than Site 2 sediment ($p=0.001$, $p=0.034$). However, the average RR_{As} from Site 1 and 3 were not significantly different from each other ($p=0.350$). The mobilized Fe trends resembled mobilized As trends for all cores except Site 3 sediment in the oxic treatment (Figure 2.8 and Figure 3.1ab). The mass of Fe in Site 3 core water was largely variable throughout the incubation under oxic conditions. The content of Fe in the water of the remaining cores reached a maximum between Days 14–21, followed by a decline in mass of Fe (Figure 2.8ab). Manganese was released within the first three days from sediment in all anoxic cores and approached steady state by Day 8 (Figure 2.9ab). However, the mass of Mn in anoxic water in Site 3 cores appears to decline near incubation termination. Manganese was only released under oxic conditions from Site 1 sediment. The mass of Mn in overlying water in Site 1 oxic cores increased until Day 8, which was followed by a decline in mass and reached background concentrations by Day 28 (Figure 2.9a).

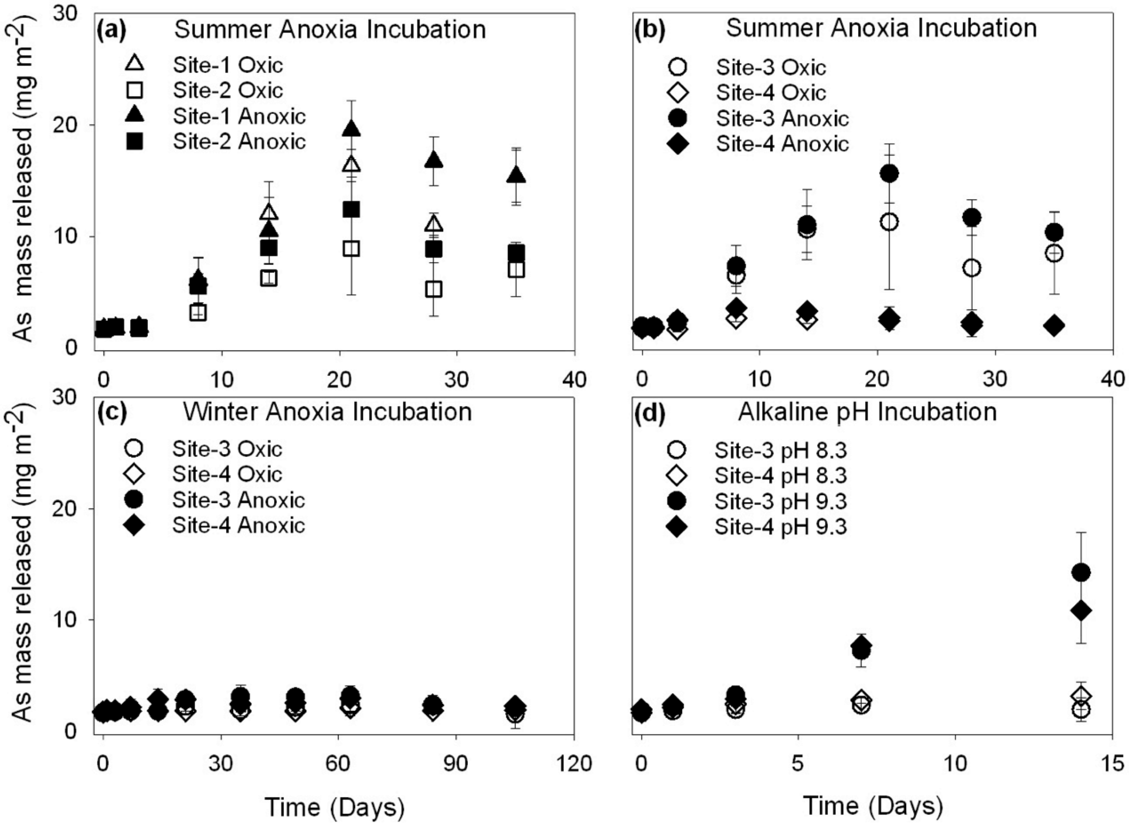

Figure 3.1. Release of arsenic to overlying water of sediment cores (mg m^{-2}) plotted against time of incubation during three sediment core incubation experiments. Open (control) or shaded (treatment) symbols represent average values (± 1 SD). *n* = 3

Table 3.1. Dissolved arsenic (As) release rates (RR_{As}) derived from sediment core incubations using sediment collected from Buffalo Pound Lake, SK, Canada. Experiments and their respective treatments are listed. Flux rates are presented as average values ± 1 standard deviation. Time interval (initial and final day) used to calculate RR_{As} are given in brackets. *n* = 3

		Experiment 1 Summer (19°C) RR_{As}		Experiment 2 Winter (5°C) RR_{As}		Experiment 3 Alkaline pH RR_{As}	
		Oxic (>8 mg O_2 L^{-1})	Anoxic (<1 mg O_2 L^{-1})	Oxic (>8 mg O_2 L^{-1})	Anoxic (<1 mg O_2 L^{-1})	Control (pH=8.2)	Elevated (pH=9.2)
Arsenic release rates (mg m^{-2} day^{-1})	Site 1	0.77 ± 0.07 [3–21]	0.95 ± 0.14 [3–21]				
	Site 2	0.39 ± 0.23 [3–21]	0.57 ± 0.15 [3–21]				
	Site 3	0.73 ± 0.15 [3–14]	0.71 ± 0.18 [3–21]	0.09 ± 0.11 [14–21]	0.18 ± 0.11 [14–21]	0.14 ± 0.24 [3–7]	1.06 ± 0.33 [3–14]
	Site 4	0.23 ± 0.05 [3–8]	0.24 ± 0.04 [3–8]	0.03 ± 0.03 [49–63]	0.13 ± 0.12 [7–14]	0.08 ± 0.15 [3–14]	1.33 ± 0.39 [3–7]

In Experiment 2 (Winter Anoxia Incubation), which assessed only Sites 3 and 4, concentrations of As in the overlying water of sediment cores were low, and did not substantially deviate from background concentrations throughout the incubation (Figure 3.1c). Average RR_{As} were not significantly affected by site (p=0.409) or treatment (p=0.181; Table 3.1). Iron was released from Sites 3 and 4 sediment under oxic and anoxic conditions on Day 35, followed by a steady decline of mass of Fe in overlying water to background concentrations by incubation termination (Figure 2.8c). Manganese was released from sediment in all cores until Day 35, followed by a plateau in mass of Mn in the water column by incubation termination (Figure 2.9c). Sediment from Site 3 under oxic conditions released a greater total mass of Mn in the Winter Anoxic Incubation relative to the Summer Anoxia Incubation. Similar patterns of release were observed for Mn from Site 4 sediment, regardless of treatment conditions.

Arsenic was released at pH 9.2 from Site 3 and 4 sediment during Experiment 3, the Alkaline pH Incubation (Figure 3.1d). At pH 8.2, the mass of As in overlying water remained at background concentrations throughout the incubation (Figure 3.1d). Sediment in the pH-9.2 treatment released As from Day 3 until incubation termination on Day 14. RR_{As} from the sediment were not significantly affected by site (p=0.539) but were significantly greater in pH-9.2 cores relative to pH-8.2 cores (p<0.001; Table 3.1). Iron was not released from sediment, except for a small mass of Fe released from Site 3 sediment under pH 9.2 conditions on Day 14. Site 4 sediment under pH 8.2 conditions released a minimal mass of Mn to overlying water during Days 1–3. The concentration of Mn in Site 4 pH-8.2 core water decreased to background concentrations from Day 7–14.

Manganese was not released from Site 4 sediment in the pH-9.2 treatment or Site 3 sediment in either treatment.

3.3.2. Arsenic mobilization and bioaccumulation *in situ*

Arsenic was mobilized from Buffalo Pound Lake sediment *in situ* on 12-Aug-2015 at Sites 3 and 4, coinciding with elevated concentrations of As in pore water near the SWI (Figure 3.2). The concentration of As in bottom water of Site 3 and 4 at this time exceeded 5 µg L^{-1}, the Canadian federal guideline for protection of freshwater aquatic life (CCME, 2001). Site 3 surface water generally demonstrated greater concentrations of As than Site 4 surface water throughout summer (1.3-fold difference), particularly during the period of As mobilization (Figure 3.2ai). However, concentrations of pore-water As near the SWI were greater in Site 4 than Site 3 during 12-August-2015, opposite to the concentration of As in overlying water at these sites. Variance in concentrations of As in Site 3 bottom water were significantly explained by DO concentration, pH, and temperature (R^2=0.962, F(3,11)=67.2, p<0.001), and were significantly correlated to pH (p=0.004), but negatively correlated to DO concentration (p<0.001) and temperature (p=0.044). Variation in concentrations of As in Site 4 bottom water were significantly explained by DO concentration and temperature (R^2=0.976, F(2,11)=181.1, p<0.001), and were significantly negatively correlated to DO concentration (p<0.001) and temperature (p<0.001). DO concentrations, pH, and temperature in overlying water at Sites 3 and 4 during the study are provided Section 2.3.3 (Figure 2.10).

Dissolved Fe concentrations were homogenous in Site 3 and Site 4 overlying water columns (Figure 3.2bj). Iron content in overlying water was greater at the beginning and end of summer, and relatively low during the middle of the monitoring period (Figure 3.2bj). Pore-water profiles at both sites demonstrated large Fe concentrations at the beginning of summer from 3 to 10 cm below the SWI (Figure 3.2fn). However, pore-water Fe content was low throughout the rest of the summer relative to the initially observed concentrations (Figure 3.2fn).

Site 3 and 4 showed contrasting patterns of Mn concentrations in overlying water and pore water. Concentrations of dissolved Mn were minimal in Site 3 overlying water (Figure 3.2c), but were greatly elevated in Site 4 overlying water (Figure 3.2k), which coincided with As mobilization from Site 4 sediment (Figure 3.2i). Site 3 pore water showed reduced fluctuations in dissolved Mn content, compared to the large dissolved Mn content in Site 4 pore water in the latter half of the summer (Figure 3.2go).

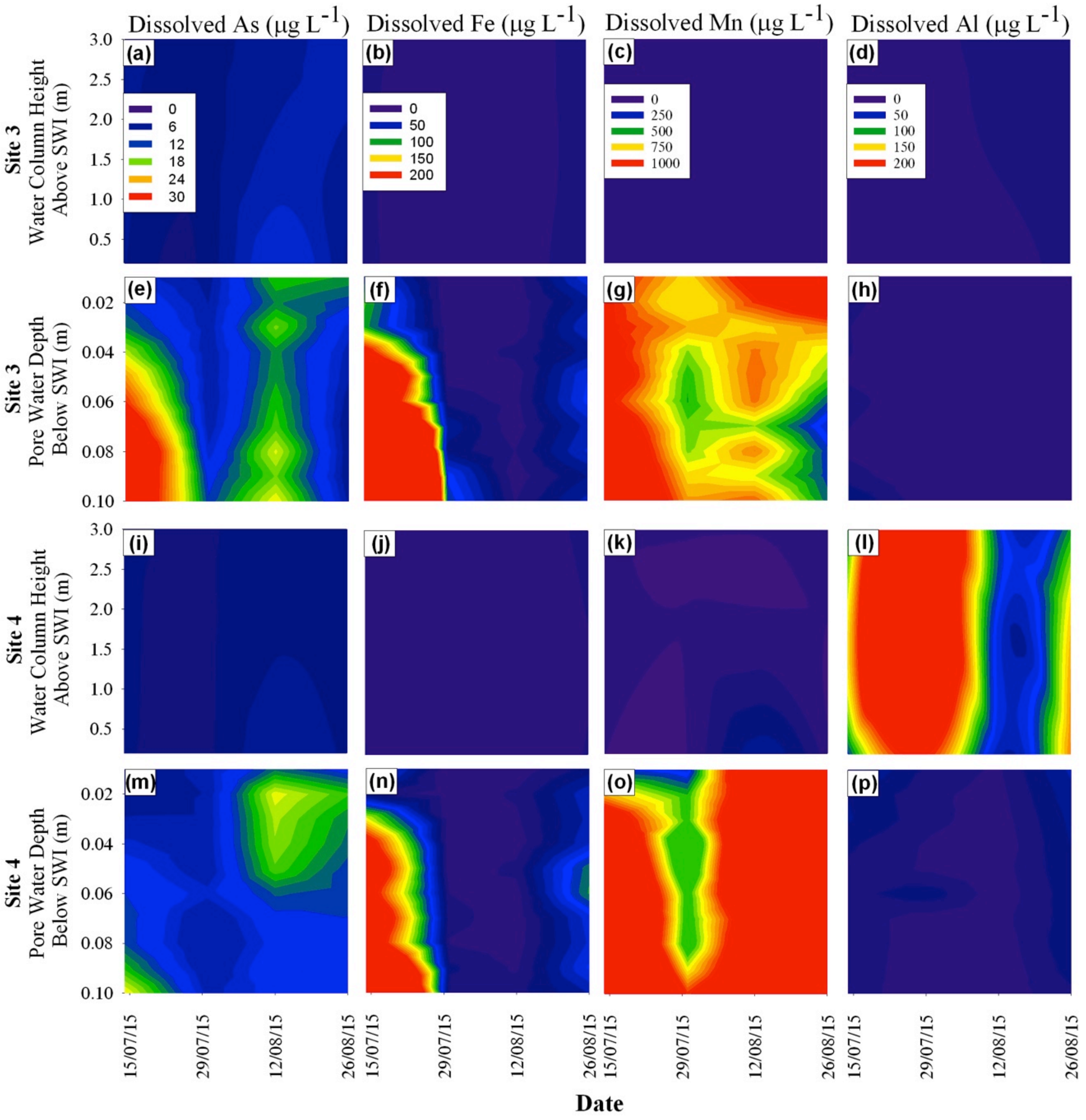

Figure 3.2. The concentrations (µg L^{-1}) of dissolved arsenic (As), iron (Fe), manganese (Mn), and aluminum (Al) in the water column (a–d; i–l) or pore water (e–h; m–p) for Site 3 or 4, respectively, Buffalo Pound Lake, SK, Canada during summer 2015. Samples of upper, middle, and bottom water and sediment cores were collected from each site in triplicate approximately every two weeks from 14-July-2015 to 26-August-2015. SWI = sediment water interface. Iron, Mn, and Al figures from Chapter 2 presented again for visual comparison with As data.

Site 4 had greater dissolved Al concentrations in overlying water throughout summer compared to Site 3 (Figure 3.2dl). The water column of Site 4 displayed elevated concentrations of Al during the end of July, which coincided with extremely low As, Fe, and Mn content (Figure 3.2ijkl). The concentration of Al in Site 4 overlying water exceeded the Canadian federal guideline for the protection of freshwater aquatic life (100 $\mu g L^{-1}$ if $pH > 6.5$; CCME, 2001) on 30-July-2015. Aluminum content was relatively low in Site 4 pore water, except for the beginning and end of summer, which demonstrated elevated Al content near the SWI (Figure 3.2p).

While determining As bioaccessibility trends *in situ*, concentrations of As in pore water ($p = 0.131$), bottom water ($p = 0.132$), and $\text{sediment}_{\text{Total}}$ ($p = 0.129$) were not statistically significantly different among sites sampled (Table 3.2). Concentrations of As in $\text{sediment}_{\text{HCL(1M)}}$ varied significantly among sites ($p = 0.004$) and were significantly greater in Sites 1 and 2 relative to Site 3 ($p = 0.004$, $p = 0.003$, respectively) and Site 4 ($p = 0.003$, $p = 0.003$, respectively; Table 3.2). Nevertheless, concentrations of As in chironomid tissue were not significantly different ($p = 0.287$) among the four sites sampled in August, 2016 (Table 3.2). In addition, concentrations of As in chironomid tissue among all sites did not significantly correlate to concentrations of As in bottom water, pore water, $\text{sediment}_{\text{Total}}$, or $\text{sediment}_{\text{HCL(1M)}}$ (Table A1).

Table 3.2. Concentrations of dissolved arsenic (As) in various media in Buffalo Pound Lake, SK, Canada during August, 2016. Value are the mean ± 1 SD (n = 3).

Media	Unit	Site 1	Site 2	Site 3	Site 4
Chironomid tissue	mg kg^{-1}	2.4 ± 1.7	0.7 ± 0.4	1.3 ± 0.8	1.1 ± 0.5
Bottom water	µg L^{-1}	5.6 ± 0.7	5.3 ± 1.5	8.6 ± 0.8	4.8 ± 3.2
Pore water	µg L^{-1}	84.1 ± 52.3	28.7 ± 23.7	43.2 ± 26.2	17.3 ± 7.7
Sediment$_{\text{Total}}$	mg kg^{-1} d.w.	14.4 ± 2.7	11.4 ± 4.4	8.3 ± 1.3	11.2 ± 0.9
Sediment$_{\text{HCL (1M)}}$	mg kg^{-1} d.w.	3.8 ± 1.0 ^{a}	4.4 ± 2.0 ^{a}	1.5 ± 0.2 ^{b}	1.5 ± 0.1 ^{b}

- Letters indicate significant ($p < 0.05$) differences among sites.

3.4. Discussion

Because sediments of Canadian prairie lakes tend to be Fe-poor and As-rich (Allan and Williams, 1978; Wang and Mulligan, 2006), they are therefore susceptible to internal loading of As. Recent studies of prairie lakes have demonstrated that internal P loading can occur under diverse environmental conditions (Doig et al., 2017; Chapter 2). However, we are aware of no studies to date that have investigated whether sediment-associated As, which behaves geochemically similar to P, will mobilize under conditions promoting P mobilization within Canadian prairie lakes. Using Buffalo Pound Lake, SK, as a case study, this investigation quantified experimental As release rates from sediment under different environmental conditions and identified the relative influence of these conditions. We also demonstrated the influence of episodic bottom-water anoxia on As mobilization from sediment in a shallow, polymictic lake. In addition, this study provides whole-body tissue concentrations of As for chironomid larvae, which are representative of an uncontaminated prairie lake. The study of As release rates from sediment due to several mechanisms, which had not been collectively investigated within one study, is the first study to do so using a Canadian prairie lake. These findings, which are elaborated upon below, suggest that further research should identify better predictors of As bioaccessibilty to benthic invertebrates.

3.4.1. Mechanisms affecting arsenic mobilization

RR_{As} for Buffalo Pound Lake sediment, which ranged from 0.03±0.03 to 1.33±0.39 mg m^{-2} day^{-1}, are relatively high for an unpolluted lake. For comparison, of two unpolluted, shallow Chinese lakes, one lake displayed an average RR_{As} of 0.08 mg m^{-2} day^{-1} and the other lake ranged from -0.00066 to 0.00067 mg m^{-2} day^{-1} (Wen et al., 2012; Wang et al., 2016). Nevertheless, RR_{As} from Buffalo Pound Lake sediment are less than RR_{As} from contaminated sediment. For example, a eutrophic, shallow, boreal lake in Canada, which served as a disposal for As-rich gold mine tailings, displayed RR_{As} ranging from 4.9 to 10.4 mg m^{-2} day^{-1} (Martin and Pedersen, 2002). This demonstrates that shallow Canadian prairie lakes, such as Buffalo Pound Lake, may be prone to significant internal As loading.

In Experiment 1 (19°C), As was mobilized from sediment under anoxic conditions, concurrent to the release of Fe and Mn, indicating a classical redox mobilization mechanism. Under anoxic conditions, Fe and Mn oxides dissolve and are mobilized along with oxide-associated As (Smedley and Kinniburgh, 2002). The mobilization of As from sediment under oxic conditions, which ordinarily maintains insoluble Fe and Mn oxides, was unexpected. The P:Fe mass ratio in Buffalo Pound Lake sediment is < 15:1 (Chapter 2), a ratio required to sequester P within sediment under warm oxygenated conditions (Jensen et al., 1992). The same ratio is likely applicable to As. Buffalo Pound Lake sediment (Fe-poor), even under oxic conditions, could not completely sequester As mobilized from deeper, anoxic sediment under warmer, summer conditions. As a result, the average RR_{As} from incubation sediment did not significantly differ between oxic and anoxic conditions for a given site in Experiment 1. However, As mobilization from sediment was dependent on temperature, occurring mainly under warm conditions.

Compared to warm conditions, RR_{As} in Experiment 2 (5°C) were greatly depressed during the 105-day incubation, regardless of treatment or site (Table 3.1; Figure 3.1c). The release of Fe and Mn from sediment under anoxic conditions is consistent with a redox mobilization mechanism, but without a substantial release of As, contrary to observations in Experiment 1. Without the necessary microbial community and adequate biological stimulation, mobilization of As under anoxic conditions can be minimal or independent of Fe mobilization (Islam et al., 2004). In this case, warmer temperatures appear necessary to induce As mobilization from Buffalo Pound Lake sediment.

Elevated pH (9.2) in Experiment 3 (19°C) promoted the greatest RR_{As}, but As mobilization occurred without the associated release of Fe and Mn (Figure 2.8d and Figure 2.9d). Therefore, As release was not due to a redox mobilization mechanism (Figure 3.1d). The ability of As to sorb to a metal oxide decreases substantially at $pH > 9$, due to ligand substitution of hydroxyl ions for arsenate ions (Smedley and Kinniburgh, 2002). Unlike the oxic cores in Experiment 1, As was not mobilized in the control (pH 8.2) cores. It is possible that Experiment 1 cores and Experiment 3 cores, which were collected in June and September, respectively, differed somewhat in pre-existing redox status, and thereby demonstrated differences in As mobility during the 14-day incubation period of Experiment 3. Although, average RR_{As} in Experiment 1 were substantially greater for Site 3 sediment compared to Site 4 sediment, the absence of different RR_{As} in Experiment 3 (pH 9.2) suggests that the geochemical association of As is different between sites. Arsenic mobilization *in situ* from sediment at Sites 3 and 4 demonstrated similar behavior to that of Experiment 1, and is discussed below.

3.4.2. Arsenic mobilization *in situ*

Based on sediment core experiments, the conditions in Buffalo Pound Lake during July and August were likely conducive to As mobilization from sediment (i.e., warm temperature, low DO concentration, and elevated pH). Accordingly, As mobilization from sediment at Sites 3 and 4 corresponded with warmer water temperature and lower DO concentration in bottom water prior to As mobilization (Figures 2.10 and 3.2). Mobilization of As therefore followed a novel mobilization paradigm of P in shallow polymictic lakes. The paradigm suggests that transient anoxia in prairie lakes promotes mobilization of P from regionally Fe-poor sediments, followed by diffusion of P into surface water during polymixis (Orihel et al., 2015; Chapter 2). Consequently, ephemeral periods of DO stratification can release both As and P in Fe-poor polymictic lakes. Although concentrations of As in bottom water negatively correlated to temperature, this is likely due to lake stratification, which resulted in bottom surface water that is cooler relative to upper surface water.

Similar to Experiment 1, concentrations of As were greater in water overlying Site 3 sediment compared to Site 4. Observed differences in As mobilization between Site 3 and 4 in both the laboratory and *in situ* were not due to differences in total sedimentary As, but were likely attributable to differences in sediment geochemistry, such as Al content. Site 4 sediment is enriched in Al compared to the other three sites, the result of long-term alum discharge from the BPWTP (Chapter 2). Pre-1985, the BPWTP released filter backwash from its water intake directly into the reservoir, which unintentionally led to the discharge of alum, a flocculation agent, into the reservoir. Settling ponds were constructed post-1985 to improve the water quality of the backwash (i.e., decrease alum content), prior to its release into the reservoir. However, high-velocity winds cause water to spill out of the settling ponds and into the reservoir (personal communication, Dan Conrad, BPWTP), which may periodically add alum to the lake. For example, elevated concentrations of Al were observed in Site 4 surface water on 30-July-2015 (Figure 3.2), which was preceded by a major storm event and high-velocity winds. Aluminum deposited in the down-reservoir region of the BPWTP, currently mitigates P release during periods of bottom water anoxia (Chapter 2). Concentrations of Al in Site 4 sediment are acting as a redox-insensitive sorbent of As, which is susceptible to elevated pH (Reitzel et al., 2013). This explains the difference in As mobilization trends between Sites 3 and 4 in Experiments 1 and 3, and differences in As trends in surface and pore water *in situ*.

Concentrations of Fe and Mn in bottom water during As mobilization *in situ* did not follow sediment core incubation trends. Unlike Experiment 1 observations, Fe and Mn were not released from sediment, concurrent to As, during low DO concentrations in bottom water *in situ*. It is possible that Fe in bottom water may have been removed from bottom water by cyanobacteria, which migrate downwards in the water column during pulse releases of ferrous Fe from Fe-poor lake sediment (Molot et al, 2014; Orihel et al., 2015). Additionally, Site 4 sediment may contain greater content of Mn oxides, which temporarily buffer redox conditions (i.e., provide buffering against Fe oxide dissolution), and delay or limit As release from Buffalo Pound Lake sediment during short periods of anoxia until Mn oxides are depleted (Oscarson et al., 1981). The reduction of Mn oxides in sediment would be associated with a release of Mn into pore water, and potentially bottom water, which was observed (Figure 3.2k). Manganese requires oxidation via a biological catalyst to precipitate out of water as Mn oxides (Nealson and Saffarini, 1994), and may be detected longer than Fe in re-oxidized bottom water after a short-lived anoxia event. Therefore, elevated concentrations of Mn in bottom water suggest bottom water anoxia led to As mobilization from sediment at Site 4 in late summer.

Concentrations of As in surface water exceeded CCME (2011) regulatory guidelines in the As mobilization study, which warranted investigation regarding the bioaccessibility of sediment-associated As using chironomids. To our knowledge, this was the first study to provide concentrations of As in chironomid tissue in an uncontaminated prairie lake. Concentrations of As in chironomid tissue were low and did not correlate with concentrations of As in other media (Table 3.2). The concentrations of As in sediment$_{\mathrm{HCL(1M)}}$, which significantly varied among sites, likely does not influence, or is a poor predictor of, As bioaccessibility to chironomids in uncontaminated sediments, contrary to Snape et al. (2004). Concentrations of As in sediment$_{\mathrm{Total}}$ nearly statistically correlated to concentrations of As in chironomid tissues ($p = 0.067$), which suggested that a different component of sediment or sub-fraction of sediment$_{\mathrm{HCl(1M)}}$ (e.g., associated to metal oxides) may better predict concentrations of As in tissues. Alternatively, although concentrations of As in surface and pore water significantly influence toxicity in chironomid larvae (Liber et al., 2011), concentrations of As in surface and pore water in Buffalo Pound Lake were likely too low and variable to significantly influence As bioaccessibility.

The concentration of As in Buffalo Pound Lake sediment, which is naturally enriched in As (Table 3.2), is less than the Canadian regulatory PEL guideline for the long-term protection of freshwater organisms (17 mg kg^{-1} d.w.; CCME, 2011). Additionally, concentrations of As in whole sediment, sediment pore water, and surface water (Table 2) were less than concentrations that cause no-observable effects to

Chironomus dilutus (< 39 ± 10 mg kg^{-1} d.w., < 420 ± 200 µg L^{-1}, and < 10 µg L^{-1}, respectively; Liber et al., 2011). Based on dose-response relationships observed in Erickson et al. (2011), the growth, survival, or reproduction of fishes is unlikely to be affected by diet-borne exposure to concentrations of As observed in Buffalo Pound Lake chironomid tissue (Table 3.2).

3.5. Conclusions

This study demonstrated that multiple environmental variables had varying influence on As mobilization from prairie reservoir sediment. In sediment core incubations (in order of importance), pH 9.2 had the greatest influence on RR_{As}, followed by warm temperature, and low DO concentration. Arsenic was not mobilized under low DO conditions in temperatures representative of winter, indicating the substantial influence of temperature on release rate. Internal As loading occurred *in situ* in the form of a transient release during a period of warm temperature and low DO concentration in bottom water, similar to trends observed during sediment core incubations. The *in situ* release of As under these conditions also aligns with a novel theory governing P mobilization within Fe-poor polymictic lakes (Orihel et al., 2015). In accordance with P, Fe-poor sediments are unable to effectively sequester As during transient anoxia, which leads to As mobilization from sediment during polymixis.

Previous work (Chapter 2) demonstrated that Site 4 sediment had greater concentrations of extractable Al, a redox-insensitive sorbent, relative to Site 3. This excess Al mitigated As mobilization from Site 4 sediment during periods of anoxia in both the core incubations and *in situ*. Despite this, both sites monitored *in situ* displayed concentrations of As in surface water that exceeded Canadian regulatory guidelines for the long-term protection of freshwater organisms. This was not due to site contamination, but to the naturally As-rich prairie sediment. Concentrations of As in chironomid tissue did not statistically differ among sites or correlate to other media, which suggested that concentrations of As in media were too low or variable to significantly influence bioaccessibility.

Further research should investigate whether alum application can modify As mobilization and bioaccessibility in Canadian prairie lakes, and factors that better predict bioaccessibility of sediment-associated As to midge larvae and other benthic invertebrates.

CHAPTER 4

GENERAL DISCUSSION

4.1. Summary of project results

4.1.1. Sediment core incubations

Phosphorus and As were mobilized from Buffalo Pound Lake sediment in laboratory experiments and *in situ*. Based on sediment core incubations, warmer temperatures (19°C) exerted the greatest influence on rates of P mobilization from Buffalo Pound Lake sediment, followed by elevated pH (9.2), and then anoxic DO concentrations (<1 mg O_2 L^{-1}). However, elevated pH (9.2) had the greatest influence on rates of As mobilization, followed by warm temperatures, and then anoxic DO concentrations. Although P was mobilized under low DO conditions in the Winter Anoxia Incubation experiment, As was not mobilized. This suggested that As mobilization was largely influenced by temperature. Average RR_P and RR_{As} from Buffalo Pound Lake sediment were significantly different among sites under anoxic DO concentrations, but were not significantly different under elevated pH. In the laboratory, dissolved Fe and Mn were released from sediment when DO concentrations were low, but were not released at elevated pH. Therefore, based on these observations, elevated concentrations of dissolved Fe and Mn in bottom water may serve as indicators of transient anoxia *in situ*. Interestingly, Sites 3 and 4, which were relatively close to each other within the reservoir, had very different RR_P and RR_{As} during the Summer Anoxia and Winter Anoxia incubations, but relatively similar RR_P and RR_{As} in the Alkaline pH Incubation experiment. Additionally, the density of chironomids in sediment significantly influenced the RR_P from Site 4 sediment by a parabolic density-dependent relationship, but did not significantly affect the RR_P from Site 3 sediment. Sediment geochemistry, which is expanded upon below, was fundamentally different among sites, and likely contributed to the varying response of P and As mobilization under different environmental conditions.

4.1.2. Sediment geochemistry

Using a sequential P extraction method (Ruttenberg, 1992), geochemical analysis of sediment demonstrated that concentrations of FA-P and OP, two conditionally labile P fractions, were spatially variable within Buffalo Pound Lake. However, FA-P and OP were significantly greatest in Site 4 sediment, which had the lowest RR_P under anoxic conditions. Additional geochemistry analysis demonstrated that Site 4 sediment contained greater extractable Al content relative to sediment from Sites 1–3. Enrichment of Al in this region of the lake is likely the result of long-term discharge of filter backwash from the BPWTP operations. Alum is a commonly used flocculation agent in water treatment plants, which precipitates as Al hydroxides in neutral or alkaline water (Welch and Schrieve, 1994). Prior to 1985, the BPWTP discharged alum-containing backwash directly into Buffalo Pound Lake. Settling ponds were constructed in 1985 to minimize alum-discharge, but this action did not fully remove alum from the discharge water. Site 4 is located down-reservoir of the BPWTP backwash discharge, and has likely received unintentional additions of alum, which have been entrained in the sediment as Al hydroxide. Aluminum hydroxide ($Al(OH)_3$) can act as a redox-insensitive sorbent of P and As, and the presence of $Al(OH)_3$ likely mitigated P and As release from bottom sediment during the Summer Anoxia Incubation and Winter Anoxia Incubation experiments. However, $Al(OH)_3$ did not appear to mitigate P and As release from Site 4 sediment under elevated pH conditions (Smedley and Kinniburgh, 2002; Jin et al., 2006), as evident by the lack of significant differences in the average RR_P and RR_{As} among Sites 3 and 4 in the Alkaline pH Incubation. Therefore, if low DO concentrations mobilize P and As from sediment *in situ*, we would predict that concentrations of P and As in bottom water should be greater at Site 3 relative to Site 4 under similar conditions. In addition, bottom water concentrations of Fe and Mn should also be elevated at both sites, the result of reductive dissolution of Fe and Mn oxides. *In situ* data supported these laboratory-based predictions and are expanded upon below.

4.1.3. In situ P and As mobilization

Warm temperatures and calm winds persisted for a two-week period in early August, 2015, which encouraged the development of low DO concentrations in Buffalo Pound Lake near the SWI. Bottom water concentrations of As and P during this time period were elevated relative to upper portion of the water column, and relative to the entire water column during other time intervals. These observations are consistent with the novel paradigm of Orihel et al. (2015) that describes internal P loading in shallow lakes as a function of Fe-poor sediment. Briefly, they state that shallow prairie lakes often contain Fe-poor sediment, which cannot effectively sequester P during transient anoxia, and releases large concentrations of P to overlying water during polymixis (Orihel et al., 2015). Based on the *in situ* data, the P mobilization framework of Orihel et al. (2015) can also be applied to As mobilization in Fe-poor shallow lakes. However, Al can also play a role in P and As mobilization in certain circumstances, such as those at Site 4 in this study. Bottom water concentrations of As and P were lower at Site 4 than Site 3, likely due to sequestration of P and As by redox-insensitive Al hydroxides in the bottom sediment at Site 4.

4.1.4. Arsenic Bioaccessibility

Although sites demonstrated differences in As mobilization from sediment during laboratory experiments and *in situ* monitoring, this did not significantly affect As bioaccessibility. Concentrations of As in chironomid tissue were low (0.7±0.4 to 2.4±1.7 mg kg^{-1}) and not significantly different among sites. Concentrations of As in chironomid tissues did not correlate to concentrations of As in bottom water, pore water, or sediment as total As or HCl-extracted As. This suggests that As bioaccessibility was not influenced by these variables at the observed concentrations of As. Alternatively, a different sediment parameter may better predict bioaccessibility of sediment-associated As.

4.2. Integration of project results

The goal of this study was to assess the influence of several environmental mechanisms on P and As mobilization from bottom sediment in a shallow prairie lake. The investigation provided information that can inform management of shallow prairie lakes and potentially other freshwater systems.

Internal P loading in Buffalo Pound Lake occurs during ephemeral anoxic events, a mechanism recently proposed for polymictic, Fe-poor, lakes (Orihel et al.; 2015). In addition, As is mobilized from sediment in shallow prairie lakes following this same framework (during transient anoxia), which to our knowledge, has not yet been identified in peer-reviewed literature. Underpinning this paradigm is sediment geochemistry.

Conceptually, insoluble, redox-sensitive Fe oxides retain P in sediment. Under anoxic conditions, the Fe oxides are likely reduced and soluble Fe and P are released to overlying water. Redox-insensitive Al oxides and irreducible Fe minerals can bind and mitigate P that is released during anoxic conditions (Hupfer and Lewandowski, 2008). A variety of sequential P extraction schemes have been developed to characterize labile P in sediment (Williams et al., 1967a; Ruttenberg, 1992; Ruban and Demare, 1998; and Hiriart-Baer et al., 2011). However, investigation efforts should also focus on the concentrations of P sorbents (i.e., Fe and Al oxides), which directly influence sediment-associated P dynamics under altered redox conditions. Sediment must contain a Fe:P mass ratio of >15:1 to retain P under oxygenated bottom water conditions (Jensen et al., 1992). Additionally, sediment can also effectively retain P under anoxic conditions if molar concentrations of Al:P or Al:Fe exceed 25:1 or 3:1, respectively (Kopáček et al., 2005). Considering that As behaves geochemically similar to P, there are likely concentration ratios of Al:Fe, Al:As, and Fe:As, indicative of effective mitigation of As mobilization from sediment under altered redox conditions. These ratios, not evaluated herein, should be studied to determine key geochemical ratios to improve management of polymictic lakes that are contaminated with As (e.g., tailings ponds; Martin and Pederson, 2004). If concentrations of Fe in sediment are insufficient to sequester P and As under oxidized conditions, Fe salts could be applied to mitigate mobilization of P and As (Orihel et al., 2015). Considering that low DO concentrations were observed at the SWI in Buffalo Pound Lake, it is recommended to use a redox-insensitive sorbent, such as alum to better immobilize P under a wider range of environmental conditions. Greater Al content in Site 4 sediment, relative to sediment from Sites 1 to 3, mitigates P and As mobilization in this region of Buffalo Pound Lake. Alum dosing could be applied more broadly to Buffalo Pound Lake to decrease concentrations of P and As in the water column, and is discussed in detail in section 4.4.2.

Detecting ephemeral periods of anoxia may be difficult in shallow, Fe-poor polymictic lakes, unless there is dedicated monitoring equipment. However, elevated concentrations of dissolved Mn in bottom water may serve as an indicator of bottom water anoxia (Chapter 2 and 3). Iron and Mn oxides in sediment, which are common sorbents of As and P, may dissolve under reducing conditions, and can be released to bottom water. A pulse release of Fe can be rapidly taken up by Fe-deficient cyanobacteria (Molot et al., 2014; Orihel et al., 2015), and may not be detected using periodic sampling. Mobilized Mn may persist longer than Fe in bottom water, as it requires a biological catalyst to reform relatively insoluble Mn oxides (Nealson and Saffarini, 1994). Therefore, dissolved Mn may remain in solution when bottom water is re-oxygenated, serving as an indicator of episodic anoxic events at the SWI.

4.3. Improvements and recommendations

The various core incubations proved useful in assessing the influence of different environmental mechanisms of P and As release. Nevertheless, technical aspects of the sediment core incubations, sediment geochemistry analysis, and *in situ* monitoring could be improved.

The water overlying sediment in the cores can form vertical concentration gradients of solutes during incubation if the water is not adequately mixed (Dadi et al., 2015). Here, the water overlying sediment in cores was bubbled with air or Ar to mix the column of water. However, under oxic conditions, rigorous stirring is required to ensure oxygen penetrates into subsurface sediment and increase depth of the redox boundary (Sweerts et al., 1989). As an alternative to the approach herein, an adjustable magnetic stir system could be used to ensure a well-mixed water column and potentially increase oxygen penetration into sediment profile (Dadi et al., 2015).

Additional data could have been collected to improve interpretation of each core incubation experiment. The concentration of acid volatile sulfides (AVS) is an easily measureable parameter, and is fundamentally important to Fe and As mobilization during anoxia events (Ferguson and Gavis, 1972). Quantifying the concentration of AVS in overlying water in cores from the Summer Anoxia Incubation and Winter Anoxia Incubation would have aided in interpretation of Fe and As profiles. AVS can precipitate with available Fe and As (Ferguson and Gavis, 1972; Søndergaard et al., 2003), and likely decreased concentrations of Fe and As in overlying water of anoxia treatment cores. Determination of AVS trends throughout those incubations would have suggested whether the hypothesis was valid. Measuring concentrations of sulfate in overlying water in sediment cores could have alternatively been used to evaluate this hypothesis. If concentrations of sulfate were decreasing in overlying water, it would infer the reduction of sulfate to sulfide.

Within the Alkaline pH Incubation, two procedural changes are suggested to increase environmental realism, preferably in conjunction. Increasing the pH might better have been accomplished by CO_2 stripping. This is a more environmentally relevant mechanism for altering pH (decreases alkalinity), compared to additions of NaOH, which increases alkalinity (Boers, 1991). Under elevated pH, P desorption can increase with greater alkalinity (Boers, 1991). Therefore, a potential artifact of NaOH addition is that experimental RR_Ps may overestimate actual RR_P. The second recommendation would be the use of a pH-probe linked to either an automated titrator or gas input. In this manner, the pH of overlying water would have been more precisely monitored and manipulated. Lastly, the effects due to different environmental conditions (e.g., temperature, DO concentration, pH, and bioturbation) should all be attempted at once. Cores within this study were collected at different times of the year, and therefore had a potential artifact of variable baseline geochemistry. The multi-mechanism incubation could be limited to one site for logistic reasons; however, temporal variability can also complicate site comparisons.

Geochemical analysis of sediment was an essential component of this study, which explained P and As mobilization differences observed among sites and experiments. Although the SEDEX P fractionation method (Ruttenberg, 1992) can characterize five different P-geochemical associations, the protocol is labor intensive and time-consumptive. The solid-phase extraction manifold (SPExMan) was designed to decrease SEDEX time of analysis, and reduce error associated with sample handling (Ruttenberg et al., 2009). Despite its practicality, parts and assembly of the SPExMan are costly. Therefore, if a large (>100) number of sediment samples are to be analyzed for geochemistry, it is recommended that the SPExMan approach be used to reduce analytical time and error. Additionally, analysis of metals content in SEDEX extracts I–III assumed the relevant metal content was extracted (Chapter 2). In future work, it is recommended that Raman spectroscopy or X-ray diffraction be used to analyze the mineralogy of sediments, which can aid in characterization in the type of metal oxides present. For example, we assumed all Fe oxides were amorphous Fe oxyhydroxides, which may not have been the case.

Periodic collection of sediment cores and surface water samples was an effective means to characterize P, As, Fe, Mn, and Al dynamics in sediment pore water and the water column *in situ*. However, this approach also had several limitations. It was time consuming and labor intensive to collect and process core samples. Sectioning sediment cores on a cm-scale can be too coarse to provide the necessary resolution to characterize the heterogeneity of pore water, which might require a mm scale (Stockdale et al., 2009). Furthermore, only the top few cm of sediment are relevant when assessing short-term P dynamics (Doig et al., 2017). Lastly, periodic collection of sediment cores may not capture short-lived mobilization events and makes assumptions regarding water chemistry trends between sample dates. Diffusive gradients in thin films (DGT) samplers can be used to circumvent some of the problems associated with using sediment cores to measure pore water (Zhang et al., 1998). DGT samplers are well-established passive sampling devices used to determine the bioavailable fraction of elements in various media, including pore water and surface water (Zhang et al., 1998). Several DGT samplers could be deployed into the sediment at a sample location, and retrieved one-by-one over a predetermined time scale (e.g., alternating weeks). Trace elements are eluted from mm-long, sectioned strips of the DGT gel, and the solutions are analyzed to create a high-resolution pore water profile (Wang et al., 2016). Although time must still be set aside for sectioning the device, field sampling time would be greatly reduced. The most notable feature, with regards to this thesis, is that the DGT sampler will capture any short-lived mobilization events of the trace elements, which cannot diffuse out of the

DGT gel unless the binding agent is saturated (Zhang et al., 1998). However, DGT samplers also have several disadvantages. Chemicals are eluted from the gel resin prior to analytical measurement, which, depending on the analyte, may dilute the concentration of the chemical below the limit of detection. Additionally, deployment and retrieval of DGT samplers may pose difficulties (e.g., buoys are often used to mark DGT samplers, but may be subject to tampering by the public). Lastly, DGT samplers measure contaminants as a mean concentration over a period of time. If a sampler is deployed for several weeks, pulses of a contaminant at magnitudes large enough to cause acute toxicity may be misinterpreted as a lesser average concentration value recorded by the sampler.

4.4. Future research

Good science should not cease after having simply answered the questions originally posed, but rather advance and address new questions arising from unexpected results. Although there are several topics that could be further explored based on this research, two major topics stood out and are elaborated upon below.

4.4.1. Alum application to mitigate redox-induced internal phosphorus loading

Alum sulfate is commonly used in water treatment plants, but has also been applied to eutrophic lakes to manage concentrations of P in surface water (Welch and Schrieve, 1994). Within neutral or alkaline water, alum sulfate will precipitate to the SWI as Al hydroxide, which is a positively charged, redox-insensitive sorbent that can bind oxyanions such as P and As (Welch and Schrieve, 1994). A decreased concentration of P in surface water of freshwater lakes is paramount to controlling algal blooms (Schindler et al., 2008). Alum application within shallow lakes can decrease surface water concentrations of TP by 50–80%, for a period up to five years (Welch and Schrieve, 1994). Given the success of alum treatment in decreasing internal P loading in the Site 4 down-reservoir region of Buffalo Pound Lake (Chapter 2) and in many American and Danish shallow lakes (Welch and Cooke, 1999; Jensen et al., 2015), further investigation is needed to establish whether alum additions can be used to manage internal P loads in other shallow prairie lakes that contain Fe-poor sediment. It is particularly important to assess the mechanism influencing internal P loads prior to alum application, because Al oxides do not efficiently sequester P outside of a circumneutral pH range.

In addition to beneficial outcomes, alum application to a reservoir can also cause problems, and caution should be taken. The presence of macrophytes may decrease the effectiveness of alum application and instead, increase internal P loading (Welch and Schrieve, 1994). Alum application may also have unintended toxicity, such as lysing of cyanobacterial cells and subsequent release of intracellular cyanotoxins into surface water (Han et al., 2013). Additionally, Al is mobilized outside a pH of 6 to 8.5, which may exert Al toxicity in aquatic organisms (Reitzel et al., 2013; Zamparas and Zacharias, 2014). From an economical standpoint, application of alum costs \$50,000 km^{-2} to \$100,000 km^{-2}, but is generally effective for at least five years (Welch and Schrieve, 1994). Therefore, alum application within Buffalo Pound Lake (area = 29 km^2) would cost \$290,000 yr^{-1} to \$580,000 yr^{-1} every five years for repeat applications.

Further research and pilot studies are recommended to further assess whether alum application can effectively decrease internal P loads within eutrophic shallow prairie lakes and reservoirs, and whether alum application itself causes adverse environmental effects. Such research would identify whether alum application is an environmentally and financially viable option to manage internal P loads in shallow eutrophic prairie lakes in Canada.

4.4.2. Arsenic speciation in Canadian prairie lakes

This research demonstrated that many Canadian prairie lakes are likely susceptible to internal As loading under low DO concentrations, which may intermittently increase the risk of As toxicity to aquatic organisms in As-contaminated systems (Chapter 3). Under low DO concentrations, sediment-associated As(V) is reduced to As(III), which may exert toxicity on aquatic organisms (Chapter 3). Although As(III) can be removed from solution after oxidation to As(V), the oxidation process can take several weeks to months without adequate biological activity (Smedley and Kinniburgh, 2002). Elevated concentrations of As(III) are concerning due to its toxicity, which is several orders of magnitude greater than As(V) in majority of organisms (Sharma and Sohn, 2009). Additionally, eutrophic lakes (i.e., lakes having elevated primary productivity) encourage biotransformation and methylation of inorganic arsenicals to organic arsenicals (Sohrin et al., 1997). Among most organisms, MMA^{III} and DMA^{III} are more toxic than As(III), which would further increase the risk of As toxicity in the aquatic environment (Sharma and Sohn, 2009). Further research should investigate the seasonal dynamics of As speciation in shallow eutrophic prairie lakes, and apply this understanding to contaminated systems to better characterize the risk of toxicity to aquatic organisms.

4.5. Conclusions

Whether in laboratory experiments or *in situ,* Buffalo Pound Lake sediment is capable of releasing significant concentrations of P and As to the overlying water column under different environmental conditions. RR_P in sediment core incubations, which differed among sites, were influenced the greatest by temperature, followed by elevated pH, and then low DO concentration. However, RR_{As} were influenced the greatest by elevated pH, followed by temperature, and then low DO concentration. Concentrations of P and As sorbents (i.e., Fe and Al) varied among sites, and modified P and As mobilization. Phosphorus and As mobilization *in situ* occurrs during short-lived episodes of bottom water anoxia. Relative to up-reservoir sites, Site 4 sediment contained significantly greater concentrations of Al, an artifact of filter backwash discharge, which mitigated P and As release under low DO concentrations during core incubations and *in situ*. The study suggested the importance of characterizing geochemical sorbents when evaluating P and As mobilization from sediment. Further investigation is recommended to assess the use of redox-insensitive agents (i.e. alum) in Canadian prairie systems to mitigate P and As mobilization from sediment during transient anoxia near the SWI.

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APPENDIX

Table A1. Sediment extraction (SEDEX) scheme, based on Ruttenberg (1992), used to characterize operationally-defined phosphorus fractions.

Phosphorus phase extracted	Solvent	Time	Volume (mL)
Exchangeable P	$MgCl_2$ (pH 8.0)	2 hr	10
	$MgCl_2$ (pH 8.0)	2 hr	10
	H_2O wash	2 hr	10
	H_2O wash	2 hr	10
Fe-Bound P	CDB (pH 7.6)	8 hr	15
	$MgCl_2$ (pH 8.0)	2 hr	10
	H_2O wash	2 hr	10
Carbonate Fluroapatite P	Acetate Buffer (pH 4.0)	6 hr	10
	$MgCl_2$ (pH 8.0)	2 hr	10
	$MgCl_2$ (pH 8.0)	2 hr	10
	H_2O wash	2 hr	10
Fluroapatite P	1M HCl	16 hr	10
Organic P	Ash at 550°C	2 hr	–
	1M HCl	16 hr	10

Table A2. Correlation coefficients, p-values, and sample numbers of Pearson correlations between concentrations of As in chironomid tissue and other environmental media. Samples were collected August, 2016.

	Concentration of As in chironomid tissue correlated to concentrations of As in:			
	Bottom Water	Pore Water	Sediment (Total)	Sediment (HCl-extractable)
Correlation coefficient	0.178	0.177	0.544	-0.0239
p	0.581	0.582	0.0673	0.941
n	12	12	12	12