Seasonal and Diel Changes in Phosphorus Transport and Retention in an Intermittent Agricultural Stream

A Thesis

Presented in Partial Fulfillment of the Requirements for the

Degree of Master of Science
with a
Major in Water Resources
in the
College of Graduate Studies
University of Idaho
By
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December 2021

Abstract

Phosphorus (P) is an essential nutrient for an aquatic ecosystem, however, excess contributions of P from anthropogenic sources, mainly from agricultural land use, can lead to poor water quality, impair aquatic beneficial uses and, in extreme cases, can lead to the development of toxic algal blooms. P is a commonly studied element in agriculture streams, nevertheless, there is still a lack of understanding about the geochemical, and biological processes driving the retention, release, and transport of P. Geochemical pathways consist of metal-P complexes, and biological pathways consist of direct uptake of soluble reactive phosphorus (SRP). Diel SRP patterns have been observed at Missouri Flat Creek (MFC), a stream flowing through the Cook Agronomy Farm in Pullman, Washington. This suggests potential dynamic P retention and release processes at MFC. The purpose of this research is to assess which of the two pathways drive SRP diel cycling at MFC. Understanding stream P release and retention in stream ecosystems can provide insight into the impacts of management and climate on P export, and lead to realistic restoration goals of these agroecosystems. The objectives of this study were to: (1) Monitor seasonal and diel changes in stream temperature, DO, pH, Soluble Reactive Phosphorus (SRP) concentration and dominant forms of extractable P bound to metals in bed sediments six times throughout the water year (Fall, Spring, and Summer), (2) Quantify seasonal variability in the proportion of soluble and particulate P loading transported in the stream six times throughout the water year (Fall, Spring, and Summer), (3) Quantify the extent to which diurnal and seasonal variation in pH, temperature, DO, flow, stream SRP, and dissolved metal concentration in streams, drive SRP adsorption pathways for each of the 6 sampling days. The results of this study indicate that during the cooler months, Ca/Mg-SRP is the dominant metal-P complex found in sediments, with peak concentration occurring at midday. Ca/Mg-SRP complexes gradually decreases in the warmer month as Fe/Mn-SRP and assimilation becomes more dominant, likely due to increased DO concentration and temperature. In June, low DO concentrations are observed concurrently with higher SRP concentrations and lower sediment Fe/Mn-SRP complexes. Diel cycling of SRP, pH, DO, and temperature was also observed in the spring and summer, making biological assimilation of P a plausible retention pathway.

A second, interdisciplinary goal of the project, was to increase the knowledge and understanding of the role stream ecosystems play in watershed management of high school students. This goal was addressed by working with local high school teachers on developing hands-on, stream chemistry and ecology curriculum that can be implemented in the classroom. This outreach effort increased student knowledge and interest in stream chemistry.

Acknowledgments

First, I would like to acknowledge my advisor, Erin Brooks for helping me with this thesis. I would also like to acknowledge my committee members Sarah Roley, Aline Ortega-Pieck, and Jodi Johnson -Maynard for continuously helping me become better scientists. Their commitment to my project has greatly improved my thesis. I would also like to thank Alex Crump and the Brooks Lab Group, specifically Zach Smith, Julia Reese, Jaz Ammon, and Gerrit Bass, for helping me with laboratory question and my diel sampling.

Next, I would like to acknowledge the Water Resources program, and LTAR for funding this research. This research was funded by a joint Non-Assistance Cooperative Agreement between the USDA-ARS Cook Agronomy Farm and the University of Idaho (Agreement #58-2090-8-079).

Finally, I would like to acknowledge all my friends and family who helped support me through this process.

Dedication

This thesis is dedicated to Holly Davis-Lowery and the members of Ophelia’s place for encouraging me throughout this process. I would also like to dedicate this thesis to Isabelle Horvath, Erin Cuddihy, Mikayla Call, Julia Reese, Jaz Ammon, and Zach Smith for supporting me throughout this process.

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Chapter 1: Literature Review of Phosphorus in Agricultural Ecosystems

Introduction

Phosphorus (P) is an essential nutrient for organisms, however, there is a tipping point where too much P modifies ecosystem function (Mallin & Cahoon, 2020). Fertilizer, which contains P, is applied to agricultural lands surrounding streams and will eventually be transported to the stream (Mullins, 2009). Terrestrial P at the highest elevation in the watershed travels to the lowest point of the watershed, which is typically a lake or a stream. As water travels from high elevation to low elevation, more P is accumulated (Johannesson, 2015). This excess P loading into surface water can cause significant issues for the water quality through eutrophication (Caraco, 1993; Mallin & Cahoon, 2020). Eutrophication occurs when the water body (i.e. stream, lake, ocean) becomes excessively rich with nutrients, leading to excess algae and/or harmful algae blooms (Kleinman et al., 2011; Wurtsbaugh et al., 2019). Algae are photosynthetic eukaryotic organisms that thrive in the presence of nutrients, such as P and N (Vidyasagar 2016). P is especially important, as it is generally the limiting nutrient in most streams, making it a vital element for algal growth (Correll, 1999). However, increased algae death decreases the concentration of dissolved oxygen (hypoxia), which in turns has a negative effect on the survival of aquatic organisms (fish, crabs, zooplankton, etc.) (Beeton & Edmondson, 1972; Shukla et al., 2008). Eventually, aquatic ecosystem will experience a loss of biodiversity, which includes a decrease in the number and variety of species (Amorim & Moura, 2021; Reid et al., 2019). Algae blooms, however, affect more than the ecosystem health.

P pollution can also affect the local/regional economy and human health. When water is polluted with nutrients, humans must limit their access to water bodies (Berdalet et al., 2016). Algae can be toxic to humans and pets if exposed either by swimming, drinking, or eating fish (Berdalet et al., 2016). Certain bodies of water are sources of drinking water for nearby towns. When contaminated (e.g., by microcystin), water can cause economic and health effects for those residents (Azanza & Taylor, 2001; Granéli & Turner, 2006). Besides the health risk of eutrophication, the local economy can be hurt by poor water quality as well. For example, if a body of water is green and/ or toxic, fewer people want to live or visit the surrounding towns (Nicholls & Crompton, 2018). Fewer residents and recreation opportunities put local businesses might be put at risk (Larkin & Adams, 2007). Therefore, understanding P cycling is critical to address and mitigate the negative effects of excess P on ecosystems and human populations.

P enters aquatic ecosystems through fertilizer runoff, soil erosion, and weathering of rocks (Vaccari, 2009). Unlike Nitrogen (N) or Carbon (C), P is a unique element as it tends to accumulate due to a lack of a gaseous phase and remains mostly bound to minerals. P is released from rocks through mineral weathering and transported through soils and into nearby streams via runoff, soil erosion, or subsurface artificial drainage. Soil P is used by plants and crops, or moves deeper in the soil profile and is eventually transported to a stream (Schlesinger & Bernhardt, 2013; Sharpley & Syers, 1979; Vaccari, 2009). The inorganic and soluble form of P is phosphate ($PO^{3-}{}_4$), which is readily available for organisms to uptake. Eventually, the phosphate dissolved in streams and lakes may travel to oceans (Schlesinger & Bernhardt, 2013). However, P undergoes biogeochemical transformations as it travels through streams (Schlesinger & Bernhardt, 2013). P can either stay in dissolved from as

PO^{3-}_4, remain as suspended sediment, be taken up by organisms, or sorbed to ions in the sediment through redox or pH sensitive pathways. Each stream ecosystem will consist of different surrounding landscapes (i.e., mountains or fields), streamflow measurements, and amount of sunlight and precipitation. Likewise, stream metabolism, consisting of respiration and respiration, is influenced by these abiotic conditions. Essentially, these abiotic conditions and stream metabolism will whether P is retained or released, as well as the P travel time through the system (Schlesinger & Bernhardt, 2013).

P is known to exhibit biogeochemical cycling once in the stream, however little research has been focused on understanding the impacts of stream metabolic processes on biogeochemical cycling. This study aims to understand the seasonal biotic and abiotic conditions that drive P diel variability in small, temperate, semi-arid agricultural streams. Identifying the specific metals in the bed sediments that bind phosphorus and the factors driving adsorption and release of phosphorus over time will lead to improved understanding of internal P loading dynamics in these small agricultural streams. Furthermore, given that the forms of stream P (particulate or dissolved) can be affected by seasonal changes in abiotic and biotic conditions (Wojciechowska et al., 2018), understanding the seasonal conditions that lead to the release and retention of P may improve our knowledge on internal sources and impacts of future management practices.

Background Information

Stream Metabolism

Stream metabolism is an important indicator of ecosystem function and is integrated with photosynthesis and respiration. Photosynthesis converts carbon dioxide (CO_2) to hydrocarbon, and therefore releases oxygen. Eventually the oxygen will be consumed, and the hydrocarbons will be converted back to CO_2 during respiration (Hoellein et al., 2013). Ecosystem respiration (ER (g O_2 /m^2*d)) is the amount of energy/biomass consumed via respiration, whereas gross primary production (GRP (g O_2 /m^2*d)) is the amount of biomass produced (Hoellein et al., 2013). Net ecosystem production (NEP) is the difference between ER and GRP (Hoellein et al., 2013). If NEP is negative there is net production, whereas if NEP is positive there is net consumption (12/6/21 3:04:00 PM). Stream metabolism can indirectly and directly affect sediment nutrient retention and assimilation in plants (Cohen et al., 2013). Any change in climate (i.e. storm events), chemical (i.e. nutrient concentrations), physical (i.e. canopy cover), and biological factors (i.e. organic matter) can affect metabolism (Brighenti et al., 2018; Marzolf & Ardón, 2021). This in turn affects dissolved oxygen, and P retention and release (Cohen et al., 2013; Hoellein et al., 2013). During photosynthesis, plants release dissolved oxygen into the stream and uptake carbon dioxide, resulting in higher pH (Diaz et al., 1994; Hoellein et al., 2013). During respiration, dissolved oxygen decreases, carbon dioxide increases, which can lead to a decrease in pH. All the aforementioned factors affect P retention, assimilation, and release in bed sediments and by autotrophs. P retention and release refers to the mass of soluble reactive phosphorus (SRP) released into the water column, assimilated by stream biota or retained in bed sediments.

Stream metabolism and equilibrium of P concentration between bed sediments and overlying water, are important factors controlling whether P is absorbed or released (Kim et al., 2004; Stumm & Morgan, 1996).

Chemical and Biological Release of Phosphorus

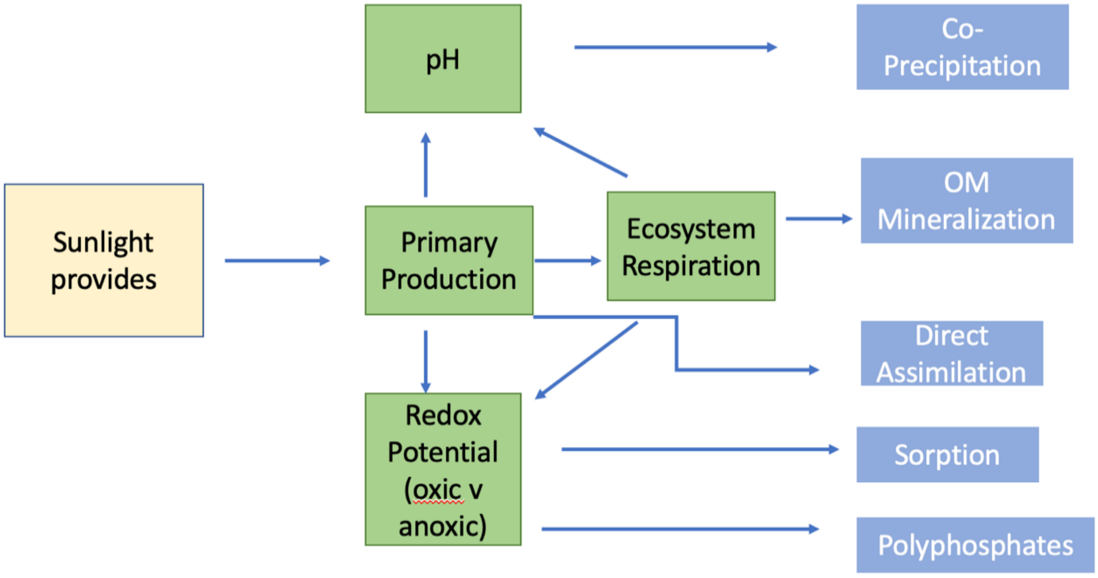

Figure 1.0.1: Primary abiotic and biotic factors that affect release/retention of P in stream ecosystems. Modified from Cohen et al., 2013

CO_2 can be transformed and exchanged within an environment through plant, algae, or phytoplankton metabolic activity leading to subsequent release or sorption of inorganic phosphorus. Inorganic P can be released whenever a) there is an increase of pCO_2 b.) a decrease in pH c.) an increase in temperature, or d.) with the supersaturation of Calcium (Ca) that results in the precipitation of Ca carbonate (Effler et al., 1987; House, 1990). Calcium carbonate is polymorphic, and can therefore be preset in different forms, such as calcite or aragonite (Dabb, 1971). Co-precipitation can occur in two different ways: a.) adsorption where an element, such as magnesium (Mg) or Ca, adsorbs to another element (e.g., P) on the surface or b.) mixed crystals form and the *"micro component diffuses through the interior of the solid phase"*(Otsuki & Wetzel, 1972; Walton, 1967). Calcite equilibrium saturation can also change throughout 24 h. Typically, calcite is at equilibrium during the night and supersaturated during the day (de Montety et al., 2011). During the day photosynthesis and respiration consume and replenish bicarbonate, which affects pCO₂, pH and calcite equilibrium (de Montety et al., 2011) (Figure 1.0.1). Higher amounts of autotrophs can a.) decrease the partial pressure of CO_2 (PCO_2) and b). increase pH (Figure 1.0.1) (Diaz et al., 1994). Equation 1.1 describes the precipitation/dissolution reaction of Ca carbonate in water. If the pH of stream water becomes more basic, Ca carbonate will most likely precipitate, and P will be retained in the sediment.

$$CaCO_{3(s)} + H_2CO_{3(aq)} \leftrightarrow Ca^{2+}_{(aq)} + 2HCO^{-}_{(aq)}$$

$$CaCO_3 - PO_4^{-3}{}_{(s)} \Leftrightarrow \mathrm{Ca}^{2+}_{(aq)} + CO^{-2}_{(3)(aq)} + PO^{-3}_{4\,(aq)}$$

Equation 1.1

Temperature is another driving factor of Ca carbonate precipitation and dissolution. Inorganic P and Ca carbonate can be released when temperature decreases since cooler temperature evade CO_2 to the atmosphere, which breaks down carbonic acid (Oyeneyin, 2015). Other biological and physical mechanisms may also affect calcium carbonate dissolution/precipitation. Any CO_2 released into the atmosphere from microbes or mineralization, increases organic acids due to decomposition, and decreases the amount of sorption activity, indirectly favor Ca/Mg-P dissolution (Cohen et al., 2013; Cornelissen et al., 1997; Gächter & Meyer, 1993; Wu et al., 2012)).

Similar to calcite, P can co-precipitate with Mg carbonate, however, there has been little research on this mechanism (Cohen et al., 2013) It is understood that Mg, will affect the form of $CaCO_3$ present (Dabb, 1971; Diaz et al., 1994; MÜller et al., 2006). These unstable forms of $CaCO_3$ requires less energy to precipitate and dissolve (Dabb, 1971; Diaz et al., 1994; MÜller et al., 2006).

In oxic environments, iron (Fe) (III) and manganese(Mn) (IV) oxides are insoluble, P sorption is favorable, and P release is limited (Smith et al., 2011). Conversely, in anoxic conditions, Mn (IV) oxides, Mn (IV) phosphate, Fe (III) oxyhydroxides and Fe (III) phosphate can dissolve via microbial activity, releasing P into the water column (Parsons et al., 2017). The Fe and Mn oxidation states are dependent on dissolved oxygen concentration, and they release P based on the redox potential (Figure 1.0.1). Redox potential is the measure of a chemical species' ability to lose or gain electrons. A higher redox potential (more positive value) indicates oxidizing conditions, whereas a negative value indicates reducing conditions. Both Fe (III) and Mn (IV) have a higher redox potential than Fe (II) and Mn (II), respectively. Mn (IV) oxides release and absorb P similarly to Fe, however, Mn can become reduced and release P more rapidly than Fe (Smith et al., 2011). Fe is also oxidized at quicker rates than Mn (Giles et al., 2016). Fe also adsorbs to phosphate easier than Mn and is less soluble, meaning P is more likely to remain sorbed to Fe(III) (Bortleson & Lee, 1974). Under highly aerobic conditions, Fe and Mn are oxidized to their higher states (Fe III and Mn IV) and eventually precipitate as a P-metal hydroxide solid. In reducing environments, metals precipitate and release phosphate (Kim et al., 2004)). Under basic conditions, Fe (III) complexes have less room for binding with both phosphate and hydroxide ions (Huang et al., 2005). Consequently, both ions must compete for binding with ferric iron. This will ultimately lead to increased release of dissolved phosphorus (Huang et al., 2005). Temperature may also indirectly affect Fe and Mn reduction/oxidation reactions. Higher temperature increases microbial activity, which lowers the redox potential of sediments, potentially favoring P release from Fe (Jensen & Andersen, 1992). Lastly, Fe-P reactions may have interactions with sulfide. If the redox potential of the sediment becomes too low, Fe may precipitate as an FeSx product, leading to more phosphate release into the stream, and further preventing Fe-P re-precipitation (René Gächter & Müller, 2003; Wilfert et al., 2020).

Al oxides ($Al(OH)_3$) are relatively stable in anoxic and oxic conditions, providing P with a stable metal to bind to in the sediment. If the water is anoxic P will be released from Fe oxides, however, since aluminum is stable in anoxic conditions, it can absorb the excess P (Kopáček et al., 2005). However, P is more likely to bind to Fe first, as P has a greater affinity to Fe over Al (Pa Ho Hsu, 1976). While aluminum oxide is stable under all oxygen conditions, it can be controlled by the pH of the water. Al oxides are stable under circumneutral pH, however, if the pH increases above 8, Al oxides will dissociate, releasing P (Jan et al., 2015; Kopáček et al., 2005; Reitzel et al., 2013).

Organic matter (OM) mineralization is a biological adsorption pathway that may increase inorganic P. Organic matter mineralization occurs when organic nutrients are oxidized into soluble inorganic nutrients, such as phosphate (Bridham & Ye, 2013). P mineralization transforms organic P into inorganic phosphate, which is released and readily available for plants. Organic matter can release P into the environment directly, from sediments that have mineralized organic matter, and indirectly, through mineralization affecting the calcite saturation state (Cohen et al., 2013). After a certain amount of organic matter is mineralized, the calcite saturation state decreases. This enables aqueous Ca to precipitate along with P (Cohen et al., 2013). Factors affecting P mineralization include temperature and OM inputs. Furthermore, the higher the temperature and OM inputs, the faster the OM mineralization rates (Cardoso et al., 2019; Cohen et al., 2013)

The shortest P pathway is direct assimilation which is the amount of P directly used by autotrophs (Cohen et al., 2013; Reddy et al., 1999). Autotrophs are organisms able to form nutritional substances using light, water, and carbon dioxide, while phosphorus supports the growth of these organisms (Graneli et al., 1999). Examples of autotrophs are plants, algae, cyanobacteria, and phytoplankton. Direct assimilation does not directly depend on oxic conditions, pH, or respiration, but depends on primary production, light, and temperature (Figure 1.0.1) (Stewart & Alexander, 1971). Autotrophic pathways of P assimilation may be detected through diel SRP measurements as biota can release and retain SRP (Cohen et al., 2013). Assimilation rates are typically higher during peak growing season (e.g. spring) due to warmer temperatures (Reddy et al., 1999; Wilkins, 1987).

Diel Patterns

Diel patterns are clear changes over 24 h. Patterns of diel variation can be observed for pH, DO, and water temperature, and other water quality parameters in rivers and streams (Nimick et al., 2003), and several nutrients and metals (e.g. Fe, Al, Ca) can also exhibit diel cycling (Nimick et al., 2003). Diel changes of water quality parameters may indicate biogeochemical cycling (Cohen et al., 2013; Hoellein et al., 2013). Phosphorus diel cycling are increasingly being studied. As each ecosystem is unique, P retention and release diel patterns may be related to physical (surface area), chemical (pH, DO), and biological (plant) conditions (Cohen et al., 2013).

Past research at MFC has found diel patterns of SRP The daily release of SRP from sediments is known as internal loading and represents the recycling of P between sediments and the water column (James, 2016). Internal loading can increase the probability of eutrophication and decrease ecosystem health (James, 2016). Phosphorus retention and release has been studied on a larger annual and seasonal scale to better understand P cycling and fate in an aquatic ecosystem (Martí et al., 2020). However, the analysis of diel P cycle can provide a finer understanding of the effect of P retention and release (Martí et al., 2020). In agricultural systems that have a similar soil chemistry and geology at MFC, diel patterns observed in this research may behave similarly to other semi-arid agricultural ecosystems

Problem statement

Despite P being a ubiquitous element in streams draining agricultural basins, little is understood about the relative contribution of biogeochemical processes on P dynamics on a diel scale. This research will address this knowledge gap by measuring the seasonal abiotic and biotic conditions that contributes to P release and retention over a 24 h period in a stream located in a semi-arid dry agricultural region. Diel cycling of SRP and abiotic conditions (i.e., DO) has been observed in agricultural streams, however, there is a lack of knowledge on abiotic factors that may control this P release on a high temporal resolution. New information on seasonal and diel changes of these abiotic conditions can indicate main internal loading sources (i.e., sediment P bound to Ca). Internal loading describes the process of P being readily exchanged between bed sediment and overlying water. This is extremely important when managing water quality (James, 2016). Hence, appropriate management practices can be recommended to reduce internal loading or P- adsorbing techniques can be implemented to reduce P release from sediments (James, 2016). This research will provide insight in the processes and mechanisms that drive internal loading and improve water quality in the small agriculturally dominated streams.

Chapter 3: Educational outreach

In 2012, science, technology, engineering, and mathematics (STEM) literacy score of high-school students in the United States was approximately 10 points below the average of other developed countries (Boylan, 2014; Mihelich et al., 2016; Schleicher, 2007; "Science and Engineering Indicators 2016," 2016). Typically, students lose interest in STEM out of fear they do not fit the stereotype of a scientist, belief that science is too hard, and/or lack of engagement by teachers (Hasni & Potvin, 2015; Kennedy et al., 2018; Lei et al., 2019). In order to improve student's STEM literacy scores, educators must better prepare their students, while maintaining their interest in the subject. Previous students revealed science topics related to social issues and real-life situations were more likely to maintain student's interest (Mandler et al., 2012; Mihelich et al., 2016). The overarching goal of this outreach program was to develop a lesson plan incorporating real life problem into the chemistry curriculum.

Objectives

Chapter 2:

1. Monitor seasonal and diel changes in stream temperature, DO, pH, Soluble Reactive Phosphorus (SRP) concentration and dominant forms of extractable P bound to metals in bed sediments six times throughout the water year (Fall, Spring, and Summer).
2. Quantify seasonal variability in the proportion of soluble and particulate P loading transported in the stream six times throughout the water year (Fall, Spring, and Summer).
3. Quantify the extent to which diurnal and seasonal variation in pH, temperature, DO, flow, stream SRP, and dissolved metal concentration in streams, drive SRP adsorption pathways for each of the 6 sampling days.
4. Compare SRP release and retention from anoxic and oxic stream water conditions in one controlled lab experiment.

Chapter 3

1. Create a lesson plan aimed at teaching high schoolers about Environmental Chemistry and Stream Ecology

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Chapter 2: Seasonal and Diel Changes in Soluble Reactive Phosphorus in Stream Water and Bed Sediments in an Intermittent Agricultural Stream

Abstract

Phosphorus (P) is deposited in agricultural streams from soil erosion. P can either be in the particulate form and be bound to the sediment, assimilated by autotrophs, or be in a dissolved form in the stream. P may exchange between particulate and dissolved forms at any time depending upon abiotic and biotic conditions within the stream system which could ultimately improve or degrade stream water quality. In the Palouse, soluble reactive phosphorus (SRP) may enter waterways through tile drains as sediment-bound P, and SRP exhibits diel cycling. However, little is known about the geochemical cycling of P once SRP is in the stream. The main goal of this paper was to monitor and analyze different metals and forms of SRP within the stream water and bed sediments under seasonal and diel varying dissolved oxygen, pH, temperature, saturation states, and concentrations of ions. Depending on the abiotic conditions SRP may be released from these sediments, ultimately increasing stream SRP concentration. Furthermore, this may contribute to algae blooms. Based on this research, SRP was predominantly bound to calcium (Ca) and/or magnesium (Mg) minerals throughout the season, albeit these minerals gradually decreased as the year progressed. In the spring, iron (Fe)/manganese (Mn)-SRP increased, most likely attributed to high oxic conditions and the buildup of a Fe/Mn-SRP surface oxic layer. Summer, however, consisted of decreased Fe/Mn-SRP most likely due to decreased dissolved oxygen (DO) levels. Both spring and summer consisted of greater diel cycling of stream SRP, DO, pH, and temperature, indicating the stream is more biologically active. Ultimately, vegetation P uptake is a likely P pathway during warmer months.

Introduction

Phosphorus (P) is a common nutrient found in agricultural and aquatic ecosystems. Fertilizer runoff, soil erosion, subsurface artificial drainage, weathering of rocks, and internal loading are common external and internal sources of P to nearby streams (Mullins, 2009)). P has a strong affinity to soil, particularly clay, and therefore the major source of P transport in streams occurs as particulate P, which may be bound to soil particles. Hence, there is often a relationship with the turbidity of the stream and particulate phosphorus (Stutter et al., 2017).

There are four major fates of P once delivered to the stream. 1) P may be released as the dissolved form of P (phosphate, PO_4^{-3}), which is the bioavailable form of P and referred to soluble reactive P (SRP) (Ballantine et al., 2009; Sharpley et al., 2013). 2) SRP may be utilized and released by aquatic life (Reddy et al., 1999; Triska et al., 2006). 3) SRP may be retained by bed sediments through sorption, and 4) P may remain as particulate phosphorus sorbed to suspended sediment (Ballantine et al., 2009; Sharpley et al., 2013). Under certain environmental conditions P may be released from sediments, which is known as internal loading (Lannergård et al., 2020).

P can be retained by sediments for as long as centuries and is often described as legacy P (Sharpley et al., 2013). Legacy P is an accumulation of deposited sediment enriched with P from a long history of upland erosion and scour, particularly in agriculturally dominated watersheds (Sharpley et al., 2013).Different stream morphologies and varying flow conditions will have different effects on the release and retention of legacy P (Sharpley et al., 2013).and management practices such as dredging, or harvesting vegetation may promote the release of sediment P into the overlying water (Lannergård et al., 2020; D R Smith & Pappas, 2007; Douglas R. Smith et al., 2006). In addition to physical changes, stream metabolism may alter chemical and biological P retention and release pathways (Cohen et al., 2013).

Excess P released into the water column may further impair water quality and ecosystem function through eutrophication. In turn, increased algal biomass leads to a decrease in biodiversity (through the depletion of oxygen with algal die offs), which may negatively impact the economy and human welfare (Kleinman et al., 2011). Studying the pathways of P retention and release is important to understand dominant internal sources of P, which could contribute to a nutrient rich environment.

Background

Internal loading refers to the processes of P release from sediment into overlying water as PO4-3 and P retention as particulate P in the sediment (Lannergård et al., 2020; Paytan et al., 2017)). While there are certain physical properties of the stream that may release P such as the streamflow and morphology; some geochemical pathways can contribute to internal loading. One of the most common geochemical pathways is co-precipitation. P can bind to calcium (Ca) carbonate, magnesium (Mg) carbonate, and mineral lattices in sediment. Calcite is the most stable form of Ca carbonate, however, as Ca carbonate is polymorphic, there are multiple forms of Ca carbonate (i.e., aragonite). Under low mineral saturation states, typically in the evening, Ca carbonate dissolution is favored (de Montety et al., 2011; Simpson et al., 2019)). Ca carbonate, however, reaches peak saturation states during the day, precipitating easily (Cohen et al., 2013; de Montety et al., 2011; Simpson et al., 2019). Acidic pH, along with higher concentrations of Ca ions, will likely result in the release of Ca-bound P (Figure 2.0.1) (Diaz et al., 1994). Alternatively, basic pH (above 8.5) with high concentrations of Ca can lead to precipitation of calcite (Figure 2.1) (Diaz et al., 1994; Effler et al., 1987; House, 1990; Wu et al., 2012).Lower temperatures may also favor the dissolution of Ca minerals and most Mg minerals, releasing any phosphate and Ca ions in the overlying water (Diaz et al., 1994; Effler et al., 1987; House, 1990; J. Li & Li, 2019; Wu et al., 2012). Conversely, increased temperatures may decrease the sorption capacity of sediments and increase organic matter decomposition, producing organic acids that may indirectly favor Ca/Mg-P dissolution (Cornelissen et al., 1997; R Gächter & Meyer, 1993; Wu et al., 2012).

Although studies on Mg co-precipitation are limited, Mg is known to influence the formation of Ca carbonate (Dabb, 1971). Consequently, as Mg concentration increases or decreases, less stable forms of Ca carbonate developed, and may dissolve or precipitate with less energy (Dabb, 1971; Diaz et al., 1994; MÜller et al., 2006). Another common pathway includes the release and retention of iron (Fe)/manganese (Mn) phosphate, and Fe-oxides, and Mn-oxides (see Figure 2.0.1). This sorption complex is extremely redox sensitive, meaning that the presence of oxygen will alter the state of Mn and Fe phosphates (L. Smith et al., 2011). If Fe(III)-phosphates are in anoxic sediments, Fe III becomes Fe II, and phosphate is released into the sediments. If the stream is oxic, this reaction can occur in reverse. Eventually an oxic microlayer (with Fe(III)-P) may build up. Under anoxic conditions and warmer stream temperatures, this Fe-P may be released in the streams (Lannergård et al., 2020; Penn et al., 2000; Wu et al., 2012). Conditions such as organic matter concentration Fe and P concentrations, pH, and sulfide production, all affect the concentration of Fe-P in the sediments (Asomaning, 2020; René Gächter & Müller, 2003; Huang et al., 2005a; Wilfert et al., 2020; Wu et al., 2012). The last metal-P complex of interest is release and retention of aluminum (Al) oxides bound to P. Al oxides have been mostly studied in wastewater treatment plants due to their capacity to sorb and remove P. Al oxides can temporarily remove P from the overlying water. Al is not redox sensitive, meaning slight changes in oxygen may not alter the reaction (Kopáček et al., 2005; Rydin & Welch, 1998). Al oxides are, however, slightly pH sensitive; this compound is stable in the precipitate form from pH of 6 to 8 (see Figure 2.0.1) (Jan et al., 2015; Kopáček et al., 2005; Reitzel et al., 2013). However, if the pH falls of this range, Al oxides dissociate, and any phosphates bound to this complex are released. Understanding the dominant P sorption complex in sediments from small agricultural streams could increase our knowledge of seasonal changes of internal P loading. Figure 2.0.1 summarizes the different P release/retention pathways under varying abiotic conditions.

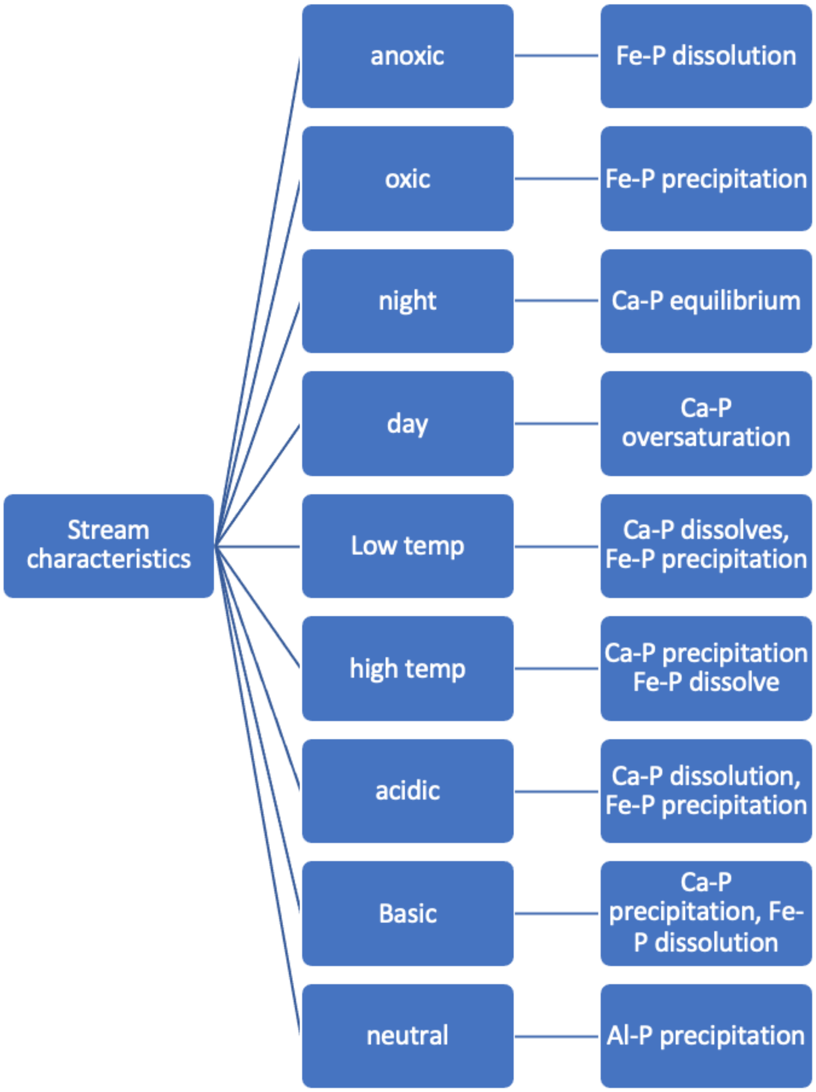

Figure 2.0.2: Typical P form (i.e., dissolved or bound to bed sediment) under different abiotic factors

In semi-arid agricultural ecosystems, SRP may enter nearby streams through subsurface flow (Ortega-Pieck et al., 2020; Reid et al., 2012). Specifically, SRP in drain tiles was found to be primarily from P landscape hotspots, which typically occurred around the baseline of the slope (Ortega-Pieck et al., 2020). The P entering the stream from these hotspots may be retained and released from sediment and autotrophs over the course of a year.

Previous research indicates that P concentration varies seasonally and in a diel fashion (Cohen et al., 2013; L. Smith et al., 2011). Diel patterns of variation are clear patterns of abiotic factors over the course of 24 hours. Past studies have reported diel patterns of temperature, CO_2, pH, and oxygen, due to respirations and photosynthesis (Nimick et al., 2003). which may influence SRP dynamics. Previous studies have shown diel cycling of P in streams due to changes in temperature, pH, redox conditions, and direct assimilation (Beck & Bruland, 2000; Cohen et al., 2013; Kurz et al., 2013; L. Smith et al., 2011; Tobias & Böhlke, 2010). While these abiotic factors are known to vary seasonally, there are management practices that could also affect the drivers of P release and retention. For example, the canopy of riparian vegetation can increase shade, cool water temperatures, and affect the aforementioned pathways (C. Kelley & Krueger, 2007). Additionally, the application of lime to increase soil pH in fields (Anderson et al., 2013) may affect the stream pH and therefore P is release and retention.

Despite P being a ubiquitous element in streams draining agricultural basins, little is understood about the relative contribution of geochemical and biological processes on P dynamics in the stream. Previous studies have examined the main agricultural external sources of P and stream cycling of P; however, little is known about geochemical factors that may retain and release legacy P. Diel cycling of SRP is evident in semi-arid agricultural systems, but there is a knowledge gap about the specific pathways that may control to diel changes of P. P can be bound to sediments for decades before being released, however, without knowing what metals SRP is being released from, little can be done to address internal loading sources. Therefore, the overarching goal of this study was to better understand P retention and release in small agricultural streams across seasonal and daily scales through a water year.

The objectives of this research are:

1. Monitor seasonal and diel changes in streamflow, stream temperature, DO, pH, Soluble Reactive Phosphorus (SRP) concentration and dominant forms of extractable P bound to metals in bed sediments six times throughout the water year (Fall, Spring, and Summer).
2. Quantify seasonal variability in the proportion of soluble and particulate P loading transported in the stream six times throughout the water year (Fall, Spring, and Summer).
3. Quantify the extent to which diurnal and seasonal variation in pH, temperature, DO, flow, stream SRP, and dissolved metal concentration in streams, drive SRP adsorption pathways for each of the 6 sampling days.
4. Compare SRP release and retention from anoxic and oxic stream water conditions in a controlled lab experiment.

Methods

Study area

The study area is located near Pullman, in Eastern Washington and is a part of the Missouri Flat Creek Watershed in the semi-arid Palouse River Basin. The study took place in

Missouri Flat Creek (MFC), a headwater stream flowing by the Cook Agronomy Farm (CAF), a USDA Long-Term Agroecosystem Research (LTAR) site (Figure 2.0.2).

Crops grown at the CAF are winter wheat, spring wheat, and chickpeas (C. J. Kelley et al., 2017)). The CAF has well-studied artificial subsurface drainages, which deliver high nutrient and dissolved organic matter concentrations to the stream (Bellmore et al., 2015; C. J. Kelley et al., 2017). (Shaljian, 2017) investigated seasonal variation of anion and cation loading from an artificial drain from an upstream no-till field at the CAF. During this period, the majority of the cations present in the drain line effluent were Mg and Ca and the dominant anions was bicarbonate. Other potentially dominant cations in the stream are Fe, Al, and Mn (Shaljian, 2017)During the summer, the evaporation fraction of MFC is between 20%-40%, with more evaporation happening from August to October (Moravec et al., 2010). The dominant soils in the region are Palouse and Thatuna silt loam soils (Donaldson, 1980). The mean annual precipitation is 517 mm/yr, with most of the precipitation happening in the winter (WRCC,2021). The main source of streamflow is precipitation during the winter season (Keller et al., 2008; C. J. Kelley et al., 2013). The winter (October-March) mean precipitation (1980-2010) is 340.36 mm and the summer (April-September) mean precipitation (1980-2010) is 176.53 mm ("Western Regional Climate Center," 2021). The mean temperature from October to March (1980-2010) is 2.69 ºC and 14.71 ºC from April to September (1980-2010) ("Western Regional Climate Center," 2021).

LTAR research focuses on assessing the health of agroecosystems to assure they are productive in the future, provide an area for studying agricultural systems and interconnected regional and local policies, and addressing any educational needs for farmers and stakeholders (LTAR CAF, 2021.). LTAR sites were also established to facilitate the sharing of research findings with producers and stakeholders. Specifically, the CAF LTAR site is focusing on long term research on precision agriculture and cropping systems (no-till and conventional tillage practices). No- till is an agriculture practice where seeds are planted in the residue of the crop, without the soil being disturbed (Keller et al., 2008). Excessive erosion has affected this region since farming first began and has continually been an environmental issue (Kok et al., 2009). Hence, conservation tillage practices such as no-till are utilized to reduce erosion and consequently sediment bound P to nearby streams (Kok et al., 2009; Ortega-Pieck et al., 2020). However, despite the adoption of no-till site practices SRP concentrations in subsurface drains periodically exceed regional stream water quality standards (0.1mg/L) (Ortega-Pieck et al., 2020).

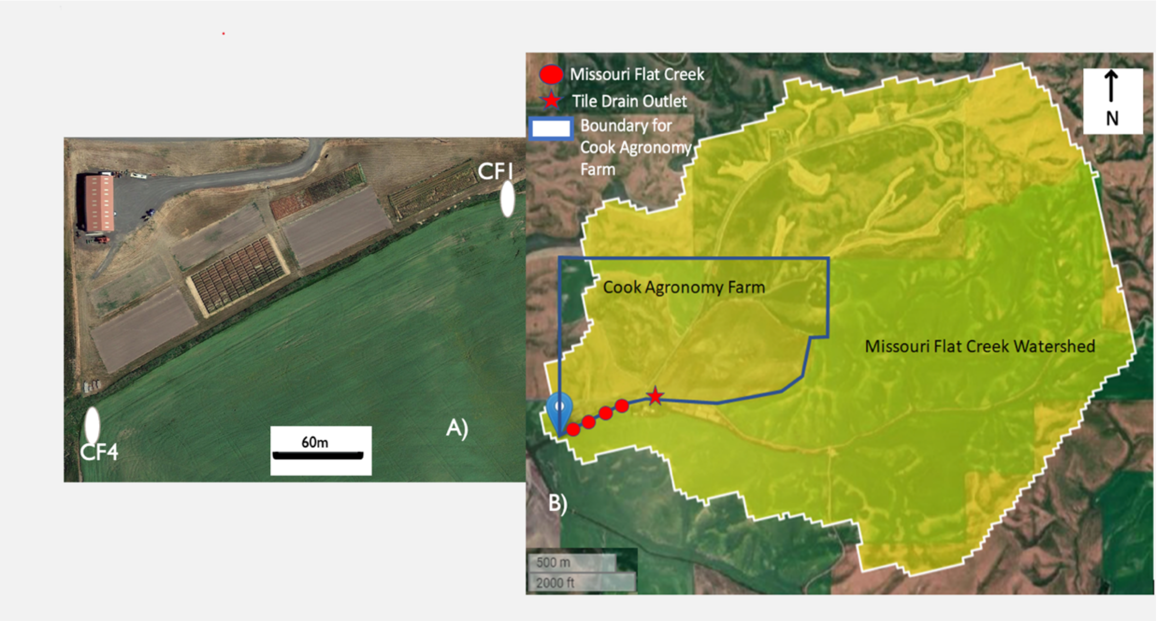

Figure 2.0.3: A) Map of Missouri Flat Creek sampling sites (CF4 and CF1) along Cook Agronomy Farm. B) Map of the Missouri Flat Creek Watershed. Red dots represent MFC and where samples were collected, and the red star represents the tile drain outlet. The yellow boundary represents the Missouri Flat Creek Watershed, and the blue polygon represents CAF. The CF1 and CF4 represent the two sampling sites where sediment and water samples were collected

Sampling strategy (Objective 1)

This project focused on documenting diel cycling of dissolved oxygen (DO), pH, temperature, and phosphorus variables within a 355 m stream reach of Missouri Flat Creek at the CAF (Figure 2.0.2). Initially two different sampling locations, 355 m apart, were identified along Missouri Flat Creek. At the downstream location (46.725476/-117.009555) a complete automated stream water quality station took high frequency (15 minute) measurements of pH, specific conductance, dissolved oxygen, turbidity, and water temperature using a multi-parameter probe (Hydrolab HL&, OTT Hydromet, Loveland, CO). Water level was measured using a pressure sensor (OTT PLS Pressure Level Sensor, Hydromet, Loveland, CO). All the data was logged by the OTT Hydromet XLink-100.

Stream SRP and dominant dissolved metals in the stream water and the top 10 cm of sediment and SRP was monitored manually over a 24-hour period on specific sampled dates during winter, spring and summer stream conditions. Stream bed sediment samples were taken every 1-2 hours to ensure diel changes would be captured. All stream samples collected consisted of surface water, with minimal biological components (i.e., vegetation, organic matter, and algae). All sediment cores were extracted from the bed sediment using a small pipe (1ft long, 2in wide) and immediately placed in an air-tight bag. All samples were collected facing upstream to avoid any displacement of sediment from settling on the sample. Bed sediment cores were limited to the top 10 cm as the majority of P bound to metals are found near the surface (Kinsman-Costello, 2019). MFC is typically dry from the summer to early fall. The first sample collection was on November 17th, 2020. Sediment and water were collected at four sites every other hour from 12am-8pm (Figure 2). However, only the 6 h frequency samples from CF4, the furthest downstream station over the stream reach, at the location of the automated stream gage station, were analyzed in the study. As all the sediment samples had to be analyzed within a week of collection, further resources were needed to analyze 24 samples from across four different sampling sites. The second sample collected was on January 20th, 2021. Sediment and water were collected at CF4 every two hours from 12am-12am. In the analysis January and November sampling dates are referred to as winter samples due to the similar environmental conditions on these dates. Samples were also collected on April 5th, April 14th, and April 27th at CF4, every two hours, and are referred to as spring sample dates. The final sampled collection date was on June 1st, which is referred to as the summer sample. Although June is technically still in the spring according to the accepted calendar date, due to the dry spring and warm temperatures during the 2021 water year, the stream characteristics during this time were more typical of summer conditions in Missouri Flat creek.

At each sampling site, sediment cores were extracted from the 0-10 cm surface sediment layer at each location during each sampling hour. Care was taken not to extract cores from previous sampled locations in the stream bed. Samples were stored in air-tight zip-lock bags and placed in a N_2 filled bag and stored in a fridge to avoid changes of oxygen content. Freezing was avoided as thawing a sample can lead to lysis of microbial biomass.

Every hour dissolved oxygen, specific conductance, pH, and temperature, were measured using the multiparameter and pressure probes described above. Discharge was determined using a stage-discharge relationship. One hundred- and twenty-five-mL water samples were manually collected every sampling hour from the water column.

In addition to water quality analysis and soil chemical analysis of bed sediment samples, a lab-based incubation of the stream-bed sediments was conducted to determine the relative amount of P released from sediments under anoxic and oxic conditions. All analytic methods are described below and included in Appendix A and B.

In this study ’stream SRP’ refers to the SRP concentration measured in water samples. ‘Stream metal concentration’ (i.e. [Fe], [Mn], [Al], [Ca], [Mg]) refers to the concentration of metals determined for each water samples. ‘Sediment metals’ (i.e. [Fe], [Mn], [Al], [Ca], [Mg]) refers to concentration of metals measured in the extracted soil cores, and Fe/Mn-SRP, Ca/Mg-SRP, and Al-SRP refers to extractable P bound to metals in the bed sediment samples, which were determined through a sequential extraction procedure described below. ‘Loosely bound-SRP' refers to the water extractable P in the bed sediments.

Laboratory Analysis

Water Quality Analysis (Objective 1 and 2)

Soluble Reactive Phosphorus was measured using the method in Appendix A. Every sample was subsampled and filtered through a 0.45um membrane filter within 48 hours after collection. A color reagent using sulfuric acid, Ammonium Molybdate, Ascorbic Acid, and Potassium Antimonyl Tartrate was made within 8 hours of analysis. 0.4mL of this color reagent were used to react with any SRP in each sample. After allowing the color to develop for 13 minutes, the absorbance on a spectrometer was recorded at a wavelength of 830nm. After the SRP analysis, both the filtered and original sample were preserved with a few drops of trace metal grade nitric acid. The filtered preserved samples were later analyzed for trace metals in the stream on the Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES, Agilent 5110). Metals measured were Ca, Mg, Fe, Al, and Mn. The detectable elemental wavelength frequencies used for analysis on the ICP-OES were Ca (317), Al (308), Mg(280), Fe(238), Mn(257). Between 5-9 unfiltered water samples per day were sent to a commercial lab (Anatek Laboratories, Moscow, ID) to be analyzed for total P (TP) using EPA method 200.7. Samples were selected to capture the full range of variability in TP based on observed variability in stream SRP. P loading was calculated by multiplying flow by concentration.

P Sequential Extraction Analysis of Streambed Sediments (Objective 1)

The sequential extraction procedure was developed to measure the mass of P bound to sediments by increasing affinity. The following order of the extracts is from weakly to strongly bound P complexes: 1. Loosely-bound P (water extractable), 2. Redox sensitive bound P (sodium bicarbonate and sodium dithionite (BD) extractable) 3. Non-Redox sensitive bound P (Sodium hydroxide (NaOH) extractable), and 4. pH sensitive bound P (hydrochloric acid (HCl) extractable). The adapted method used is in Appendix B.

After the samples were collected, streambed sediment samples were stored in a refrigerator for 24 h. On day one of the experiment, each sediment sample was homogenized by squeezing the Ziplock bag and then 1g (or ~5mL) of the sample was manually weighed out into a centrifuge tube. The centrifuge tubes were stored at 4 °C in a N_2 filled bag. The first and second day of analysis include the loosely bound and BD fraction, respectively. The first fractionation is the loosely bound P-H_2O (i.e., water extractable SRP). Twenty-five mL of deoxygenated grade water was added to each sediment sample and the samples were shaken for 1 h on high and then centrifuged at 4,200 rpm for 12 min. The supernatant was filtered using a 0.45um syringe. Twenty-five mL of de-oxygenated water was added to the centrifuge tube to rinse the pellet. The sediment was mixed to resuspend the pellet and then centrifuge at 4,200rm for 22 min. The new supernatant was added to the supernatant from the first step. 1mL of 1M sulfuric acid was added to the H_2O-P extracted, for a total of 51mL in each centrifuge tube. The H_2O-P extractants were stored in the refrigerator until analysis. SRP of the first extractant was measured using the colorimetric method within two weeks, as the sulfuric acid preserved the sample. The leftover sediment pellets were sealed in a N_2 filled bag stored at 4 °C.

The next fraction measured was the phosphate bound to redox-sensitive materials and were stored in a N_2 filled bag (BD fraction). This fractionation was completed very early the second day to limit any oxygen exposure. 25mL of deoxygenated sodium bicarbonate-sodium dithionite reagent was added to the sediment pellets remaining from the H_2O-P extraction step. The sediments were resuspended and shook for 1 h on high and then centrifuged for 22 min. The supernatant was poured in a 125mL bottle. This step was repeated one more time. 25mL of deoxygenated water was added for a final rinse of the sediments. The total 75mL of sample was filtered using A/E filters and vacuum filtration. Once the samples were filtered, they were aerated for at least one hour at a strong rate using an aquarium bubbler or air vent. Finally, 4.7mL of 1M sulfuric acid was added to each BD-P fraction tube. It is important that sulfuric acid is added to each fractionated after aeration is complete to avoid creation of elemental sulfur. 50mL of the aerated and acidified samples were stored in a refrigerator and analyzed for SRP within two weeks and Fe and Mn concentrations any time in the future. The remaining pellet was stored at 4 degrees Celsius. The rest of the fractionation steps are not oxygen sensitive.

The next fraction measured was the phosphate bound to aluminum oxides (NaOH Fraction) 0.25mL of NaOH were added to the remaining sediment and shook for 16 h on high and then centrifuged at 4,200 rpm for 22 min. The supernatant was poured in a 125mL bottle. This was completed in duplicate. 25mL of deionized (DI) water was added to the sediment for a final rinse. Finally, the 75mL of supernatant was filtered using an A/E filter.

Similar to the other samples, sulfuric acid preserved these fractionations. The NaOH-P samples were refrigerated for SRP and Al analysis.

The next fraction measured was the phosphate bound to pH sensitive materials using hydrochloric acid (HCl). The addition of HCl reacts with Ca carbonate and causes it to dissociate. When Ca carbonate dissociates, Ca ions and inorganic P is released. 25mL of 0.5M HCl was added to the remaining sediment and shook for 1 h on and centrifuged for 22 min at 4,200 rpm. The supernatant was poured in separate centrifuge tubes. This was completed in duplicate. Like the other fractions, HCl-P extractants were analyzed for SRP and Ca and Mg concentration.

The analysis of the SRP in the BD, NaOH, and HCl extractant fraction had to be diluted either 10x or 30x and individual standards had to be created for each fractionation. When creating the BD-P fraction standards it is important to aerate for longer than an hour to create more accurate standards. Aside from the standards, SRP was analyzed using the colorimetric method in Appendix A. The grab water samples were analyzed for SRP as well, however, these samples were not diluted.

The BD, NaOH, and HCl extractant fraction were also analyzed on the ICP for the following elements: Ca (317), Al (308), Mg (280), Fe (238), Mn (257), and P (213). The P detected on the ICP was any residual P on each sample. The TP for that sample/metal was calculated by adding the SRP and residual P.

The SRP concentrations from each sediment extractant were normalized for the dry weight using the equation below (Equation 2.1):

$$C_u * D = \frac{(C_d * L)}{W_d} = C_{sd} \qquad \text{Equation 2.1}$$

Where C_u (mg/L) is the concentration of the diluted sample not corrected by the dilution factor, D is the dilution factor, C_d is the concentration of the corrected sample (mg/L), L is liters of the extractant solution used, w is the dry weight of the sample, C_{sd} is the concentration corrected for the dry weight (mg/g). The dry weight was calculated by recording approximately g or 5mL of a sediment sample in a tin container. As the November and January samples had more pore water the 5mL sample was used. Both samples were then dried for 48 h at 105 ºC. The dry weight was then recorded. The dry weight for the 5mL sample was 0.698 g and a1 g wet soil sample was composed of 0.624 g of dry soil (i.e., a gravimetric soil water content of 0.60 g/g). Once all the sediment concentrations were corrected, percentages of different SRP-Metal concentrations were compared seasonally and then diurnally.

Internal P Loading Rates (Objective 4)

Sediment cores were incubated to measure the change in SRP between bed sediment and overlying water over 24 h to quantify the relative difference in P release from bed sediments in anoxic vs oxic conditions. The purpose of this experiment was to develop the magnitude of SRP released from the sediments. Two sediment cores were collected from the field and kept in a cool environment upon returning from the lab. The core samples were placed in an environmental dark chamber and a temperature matching the environment. Water from the stream was added to each of the two cores. Next, one core was exposed to oxic and anoxic treatments. For the anoxic treatment, the water column was exposed to slow bubbling N_2 with 100 CO_2 ppm to buffer pH gas for 24 h. At hours 0, 1, 2, 4, 6, 8, 12,14, 16,18, 20, 24, and 28, 5mL of water was removed from the sediment cores with a syringe and filtered through a 0.45um membrane filter. These samples were analyzed within 24 h. The following equation was used to calculate the P release flux:

$$P_{rr} = \left(\frac{(C_t - C_0) * V}{A}\right) \qquad \textit{Equation 2.2}$$

Where P_{rr} is the release of retention rate/ unit surface area of the sediment (mg P/m^2/h), C_t is the concentration of SRP at a given time (mg/L), V is the volume of the water (L), A is the planar surface area of the incubated sediment (m^2), and C_0 is the initial concentration of P (mg/L). The initial volume of the water was 0.412 L and the surface area of the sediment was 0.00202 m^2

Data Analysis

The diel response in both the stream samples and sediment samples were analyzed by season. Analytes expressing the most dynamic response were considered most prominent in the sediment. Therefore, the analytes that exhibited greater diel variation and higher concentrations compared to other analytes in the sample were a main component in P cycling for that sampling day and season. Seasonal variation in analytes was determined by observing changes in the magnitude of diel cycling and the overall concentration of the analyte. Calculating significant correlation coefficients revealed potential abiotic factors that influence changes in analytes.

Statistical Analysis (Objective 3)

The relationship between abiotic factors and SRP adsorption, SRP in streams, and stream metal concentration was evaluated using a Kendall Tau correlation analysis (Kendall, 1938) within the R software package, specifically the ggpairs function in the ggally package.

Kendall Tau is a correlation coefficient that evaluates the strength of the association between two variables and indicates whether the two variables are positively or negatively related. The closer the value is to 1 or -1, the stronger the relationship (Kendall, 1938). The Kendall Tau approach provides an indication of the significance of a relationship based on p value. Figure 2.4 summarizes the dominant abiotic drivers and possible responses by P and metals that were investigated in this study.

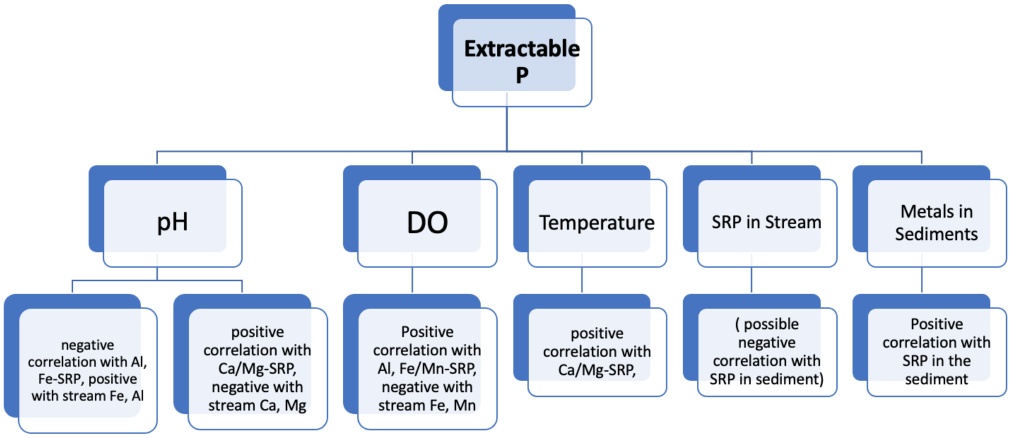

Figure 2.0.4: Expected correlations and indicators between abiotic factors and sediment and stream samples at Missouri Flat Creek

Results

Water Quality Parameters Across Sampling Dates

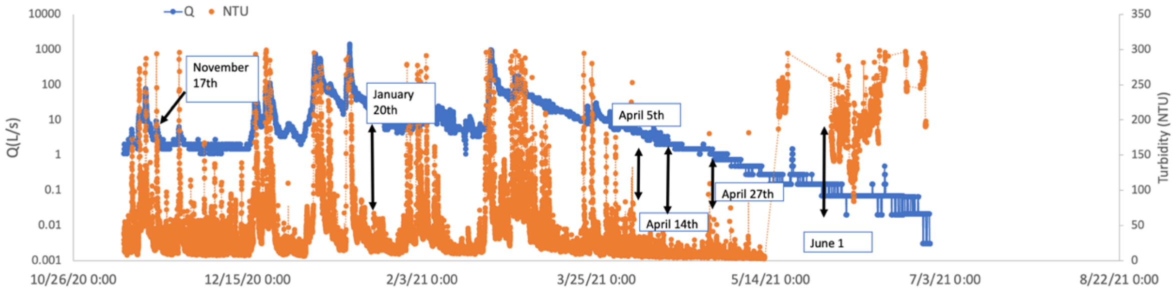

Figure 2.0.5: Streamflow (L/s) and Turbidity (NTU) over the course of the 2020-2021 Water Year at Missouri Flat Creek. The streamflow y axis is on a logarithmic log scale and the turbidity is on a regular scale. The high turbidity in May and June are likely due to algae.

The region experienced near record low rainfalls during the 2020/2021 water year. According to precipitation records collected at the Palouse Conservation Field Station (Pullman 2NW COOP weather station) the total observed precipitation in March, April, and May of 2021 was the second driest record and 111 mm (4.38 inches) below normal (Barry 2021). Typical for streams in the region, streamflow peaked in the months of January and February. Streamflow exceeded 100 L/s on 15 days (December 21, January 2-5,7, 12-13, February 22-24, and March 1-3)(Figure 2.5). On January 13th, the highest flow was greater than 1,000 L/s November and January sampling days had the highest flow (Table 2.0.1). June 1st had the lowest flow of all the sampling days. Flow gradually decreased from late February to the end of the water year. Turbidity exhibited similar patterns to streamflow but was elevated at the end of May and June, likely due to disturbance in the streambed. All samples were deliberately collected between storm events to avoid collecting data when diel patterns were obscured by increased runoff from upland influences.

Table 2.0.1: Range and average readings for pH, specific conductivity, temperature, dissolved oxygen and streamflow for each sample date. The average of the measurements is provided within the parentheses.

Date	pH	Specific conductance (mS/cm)	Temperature (ºC)	Dissolved Oxygen (mg/L)	Turbidity (NTU)	Streamflow (L/s)
November 17th	6.98-7.15 (7.07)	0.271-0.286 (0.277)	5.1-6.5 (5.75)	9.11-9.67 (9.42)	18.8-139.8 (41.94)	2.7-6.4 (4.14)
January 20th	5.82-7.11 (6.58)	0.322-0.341 (0.332)	0.5-3.2 (1.82)	12.15-12.84 (12.51)	13.8-67.1 (24.78)	9.17-19.07 (15.13)
April 5	7.33-8.99 (8.20)	0.352-0.365 (0.358)	3.6-13.7 (7.18)	10.15-14.82 (12.10)	8.1-252.8 (24.45)	4.28-6.43 (5.03)
April 14	7.25-9.77 (8.53)	0.346-0.363 (0.354)	1.8-16.8 (7.89)	9.37-15.85 (12.60)	5.0-56.1 (11.47)	2.03-3.41 (2.51)
April 27	7.08-9.97 (8.66)	0.33-0.354 (0.344)	3.7-20.6 (10.72)	8.36-14.99 (11.72)	4.2-180.2 (18.38)	0.74-1.51 (1.07)
June 1st	8.98-9.99 (9.32)	0.312-0.336 (0.324)	10.7-29.3 (19.49)	2.63-11.03 (6.94)	148 - 2931 (557.46)	0.07-0.15 (0.104)

The onset of streamflow was in mid-November, with the first sampling date occurring on November 17th. The stream temperature was relatively low (less than 7 ºC), with little diel cycling, the pH was circumneutral with little diel change, the DO indicated the stream was well oxygenated, and with an average flow of 4.14 L/s. On January 20th, stream temperatures were low (less than 4 degrees C), pH was circumneutral (6.58), the water was well oxygenated, and flows were relatively high compared to other sampling dates. On April 5th, the pH was basic (8.20) with high diel variation, the temperature had clear diel changes, the stream was still well oxygenated, and the flow was still high, but lower than that recorded in January (5 L/s). On April 14th, the pH was basic (8.53), the stream temperature varied substantially, the stream was still oxic, and there was low flow (2.5 L/s). On April 27th, pH was basic (8.66) with high variability, the stream temperature varied from 3.7-20.6 ºC, the water was still oxic, and exhibited low flow (1L/s). The last sampling day was on June 1st. The pH was extremely basic (9.32), temperatures were very high with less variation, water was less saturated with oxygen, and flow was minimal (0.1L/s). The water temperatures during the late spring and early summer were well above those measured at MFC, during the 2020 water year (max temperature around 16 ºC-data not shown). This was likely due to the dry warm spring weather conditions but could also be due to stream dredging occurring approximately 800 m upstream of the study stream reach. This dredging removed all vegetation (e.g., reed canary grass and cattails) and shading of the creek.

Diel Stream P and Stream Dynamics

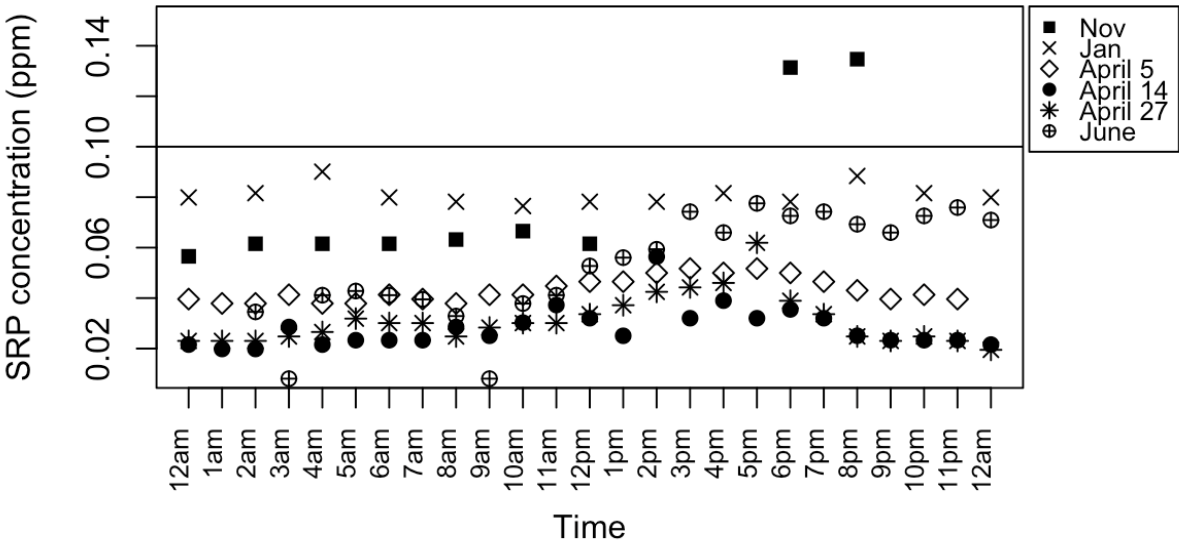

Figure 2.0.6: Diel SRP Stream Concentration (no sediments) for each month

There was evidence of diel cycling and seasonal changes of SRP concentration in the stream. In the winter season sampling events (November 17th and January 20th), there appeared to be little change over the course of the 24 hours. The winter SRP stream concentrations tended to be higher than spring and summer concentrations. In spring, there was a small peak concentration of phosphate in the mid-afternoon for all three sample days, albeit, the concentrations were all lower than those measured in winter months. In the summer, the morning stream SRP samples were similar concentrations as the spring samples, however, by noon the concentrations rose to those that were similar to winter months. There was little variation in the June samples after 3pm. The greatest stream SRP variation occurred in April.

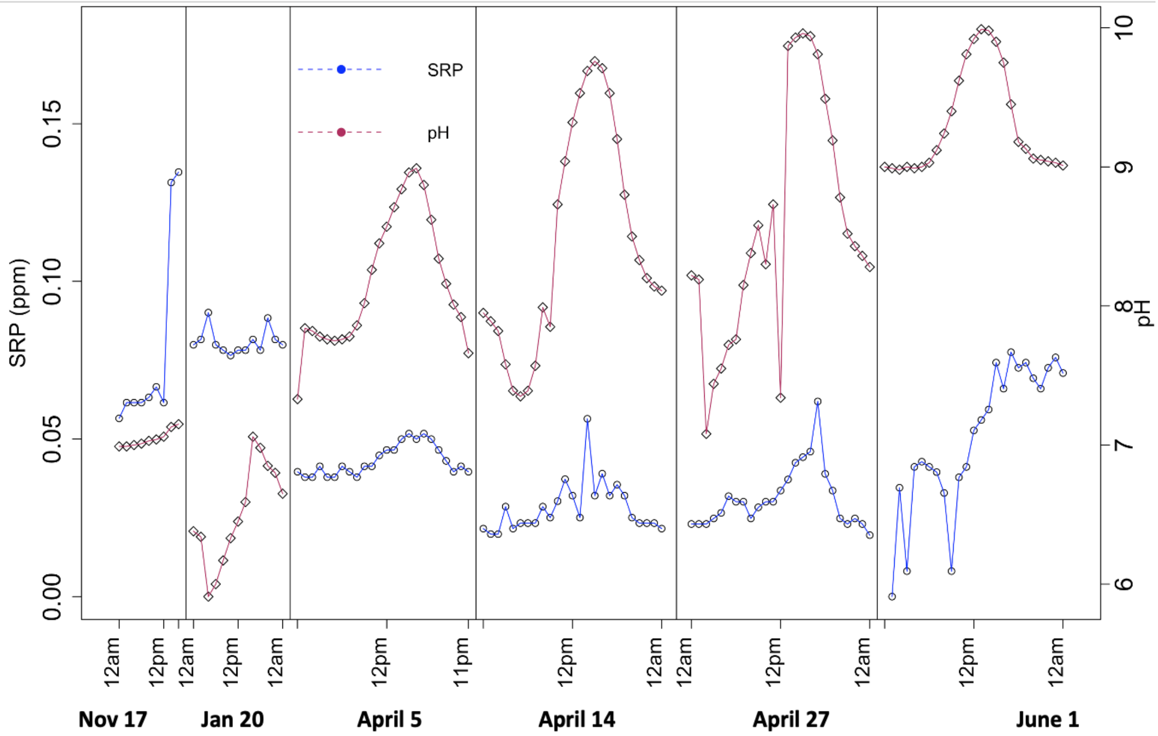

Figure 2.0.7: pH and SRP Concentration on 6 days representative of 3 seasons (winter, spring, and summer) at Missouri Flat Creek.

The stream also experienced consistent diel pH variation patterns. The pH of the stream water was more acidic and exhibited less diel variation in the winter. During the April and June sampling days, the pH became increasingly basic. With exceptions in November and June, SRP concentration in the stream water was generally higher with more acidic pH and lower with more basic pH (Figure 2.0.6). The pH values reported for June are likely too high due to calibration issues. The drift during June could have been as much as one unit high (i.e. instead of pH measurements between 9-10 it is likely the measurements were between a pH of 8-9). However, as the temperature in the stream was substantially higher than previous years, pH may change more drastically as there would be less CO2 in the stream. In the 2020 water year the max temperature in April was 14 ºC (data not shown).

Likewise, any slight drift in pH would not drastically change the results as the pH of the stream would be extremely basic.

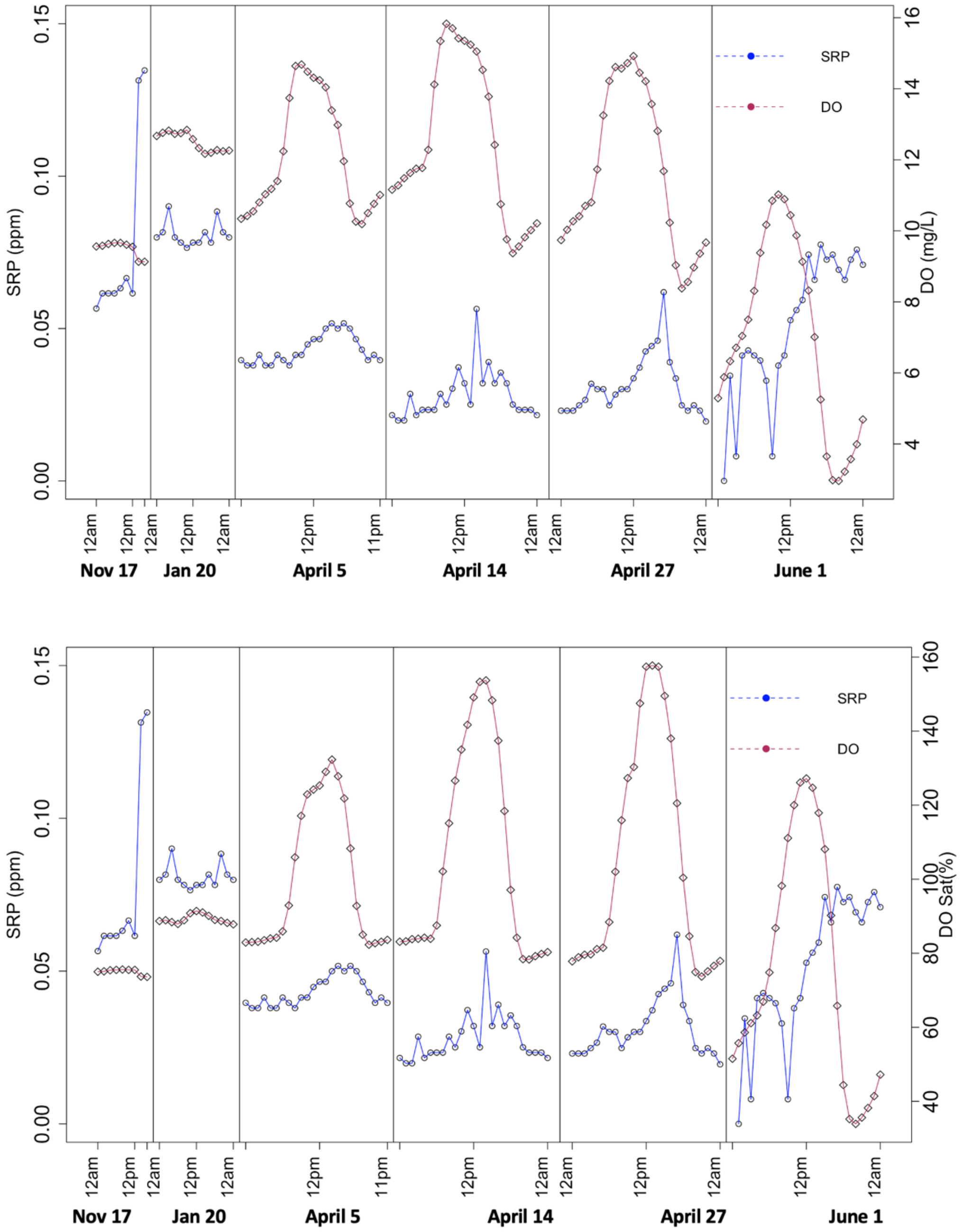

Figure 2.0.8: DO Saturation (%) and DO Concentration (mg/L) and SRP concentration on 6 days representative of 3 seasons (winter, spring, and summer) at Missouri Flat Creek. A SRP reading of 7 ppm at 12 am on June 1 is not shown.

Very similar to pH, DO exhibited consistent diel patterns particularly during warmer months. On the November 17th and January 20th sampling dates the DO was near 100% saturation (between 9-13 mg/L), however through the spring and summer sampling dates the DO consistently reached super-saturated conditions (15-16 mg/L) during the middle of the day (Figure 2.0.7). In June, the DO levels dropped below 4 mg/L. The DO reaches the peak concentration before the SRP peak concentration.

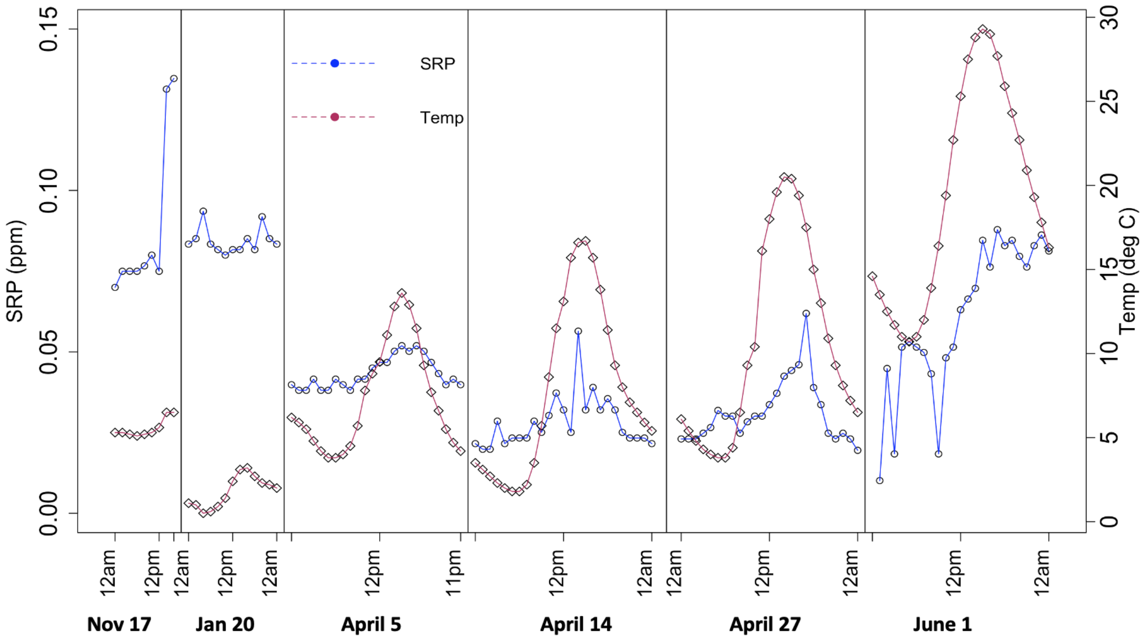

Figure 2.0.9: Water Temperature (Temp) and SRP concentration on 6 days representative of 3 seasons (winter, spring, and summer) at Missouri Flat Creek.

Similar to DO and pH, water temperature showed consistent diel variation and became more prominent as the water year progressed. The water temperature increased as the air temperature warmed during late April and early June (Figure 2.0.8)

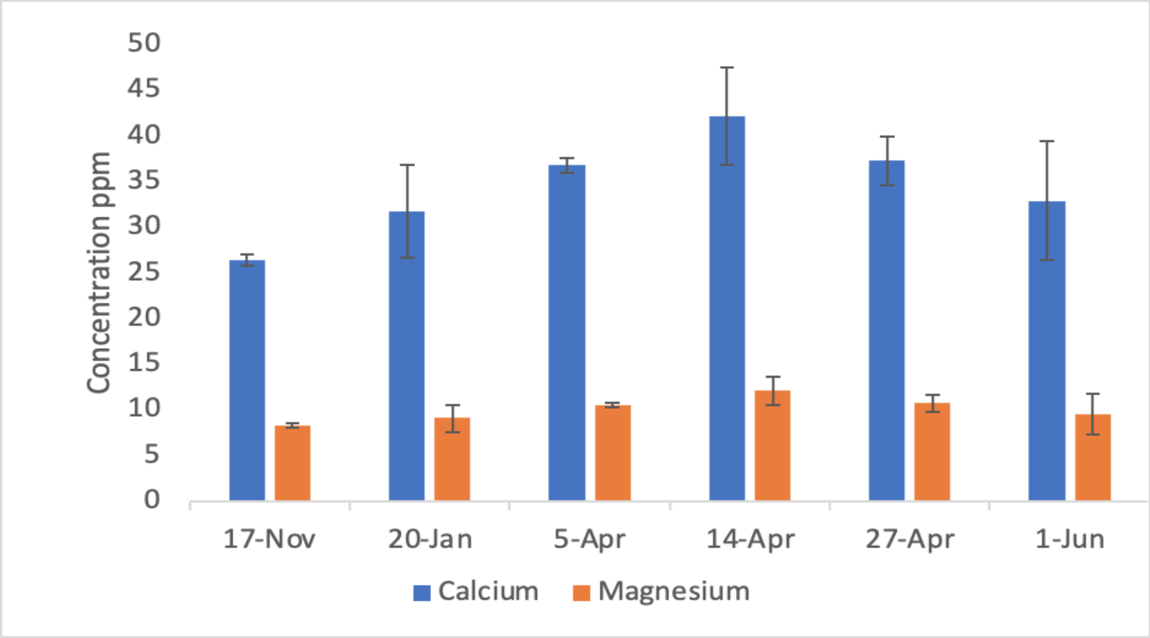

Figure 2.0.10: Daily average concentration of Calcium (Ca) and Magnesium (Mg) in water samples collected from Missouri Flat Creek on the 6 sampling dates. Error bars represent the standard deviation of the measurements over the sampling day.

The Ca and Mg concentrations were substantially higher than all other ions analyzed in the stream (Figure 2.0.9; 2.0.10). The Mg concentration was over 60 times greater than Mn concentrations. The Ca concentration was approximately 3.5 times greater than the concentration of Mg. There were seasonal changes in both Ca and Mg concentration, however, there were more distinct seasonal changes in Ca. The diel changes in metal concentrations of the stream water are provided in Appendix C.

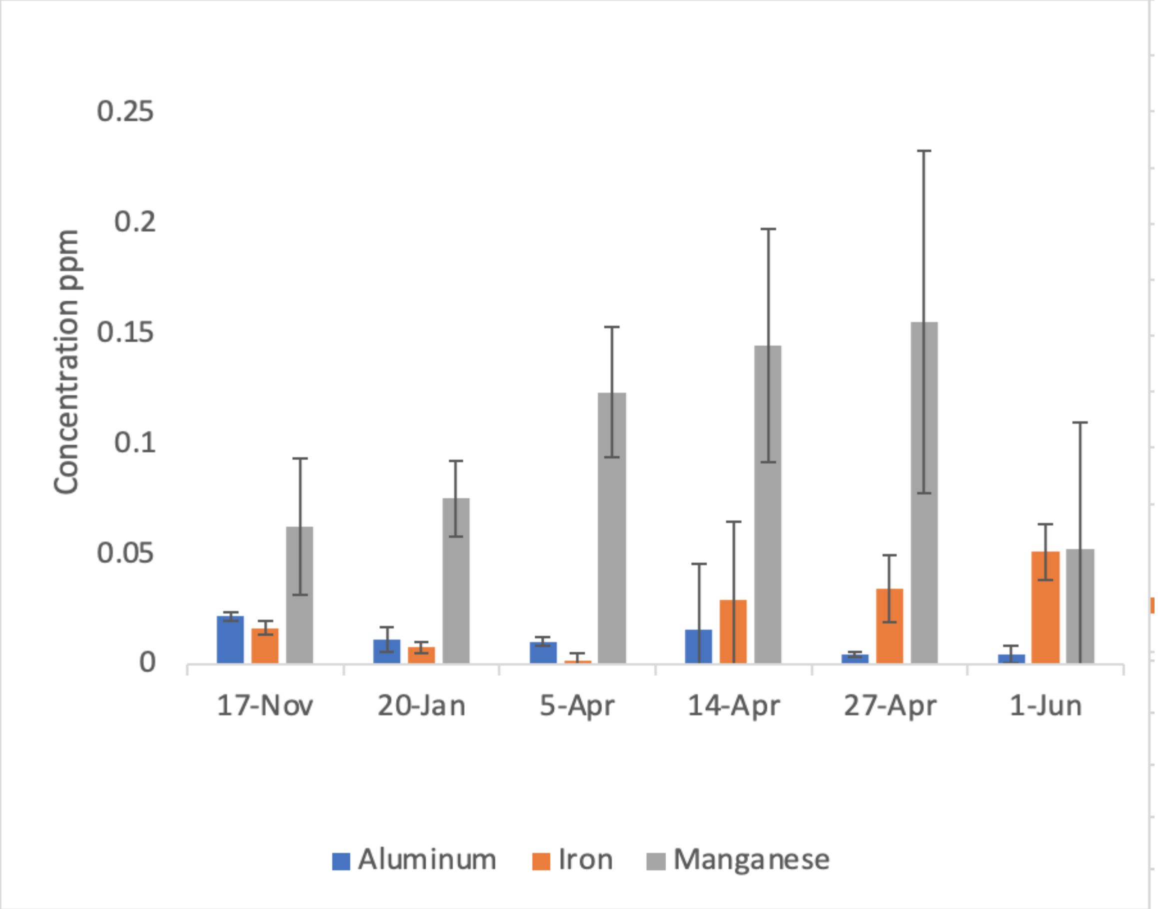

Figure 2.0.11: Daily average concentration of Al, Fe, and Mn in water samples collected at Missouri Flat Creek on the 6 sampling dates. Error bars represent the standard deviation of the measurements over the sampling day.

Similar to the concentrations of Ca and Mg, there was evidence of daily and seasonal changes in Al, Fe, and Mn concentrations in the stream water (Figure 2.0.10). Mn had the highest concentration of these three metals. Mn and Fe exhibited the greatest seasonal changes (Figure 2.0.10). The diel changes in metal concentrations of the stream water are provided in Appendix C.

Bed Sediment P Dynamics

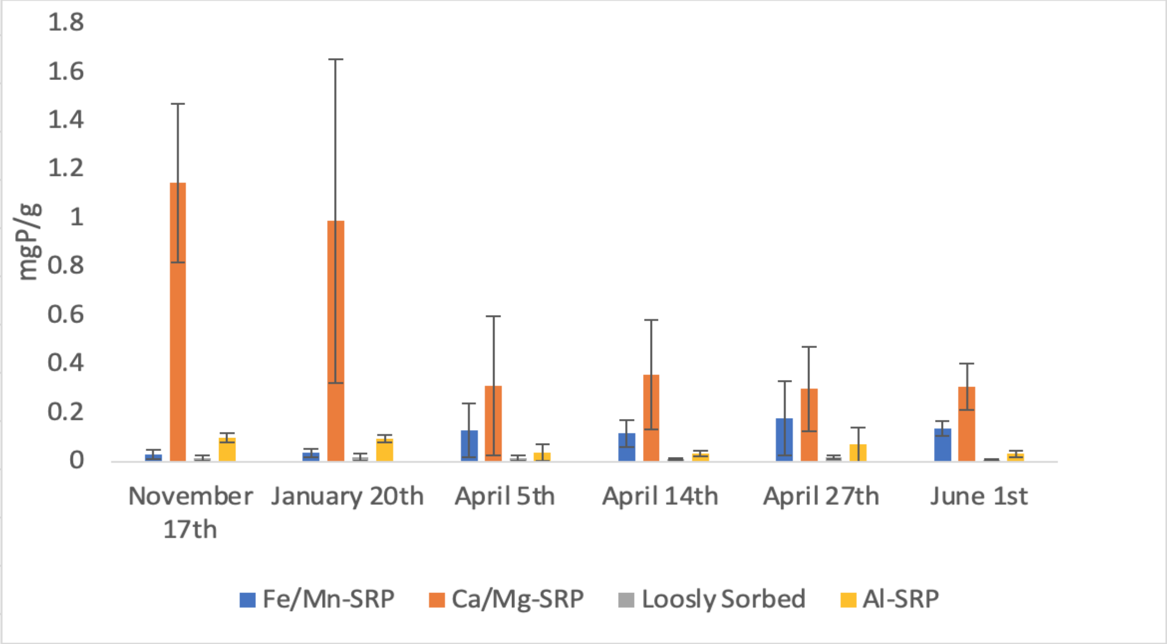

Figure 2.0.12: Extractable soil P from specific types of metals within streambed sediments sampled from Missouri Flat Creek throughout the 2021 water year. Error bars represent the standard deviation of the measurements over the sampling day. Fe/Mn-SRP indicates extractable P bound to Fe and Mn, Ca/Mg-SRP indicates extractable P bound to Ca and Mg, loosly bound indicates any P in the pore water, and Al-SRP indicates all extractable P bound to Al.

Similar to the observed metal concentrations in the stream water, the extractable SRP in the stream bed sediments were predominantly associated with Ca and Mg. In November and January, P bonded to Ca or Mg minerals were highly prevalent in sediments (Figure 2.0.11). There was also evidence of diel cycling of P bound to Ca or Mg minerals. However, over the course of the season, phosphate bound to these pH sensitive materials becomes less dominant. As the year progresses, the concentration of SRP bound to redox sensitive minerals (e.g., Fe, Mn) became more prevalent (Figure 2.0.11). While diel variation was present in all sorption P complexes in sediments, diel cycling was present with calcite/magnesite materials in the winter and then appears more in redox sensitive materials in the spring.

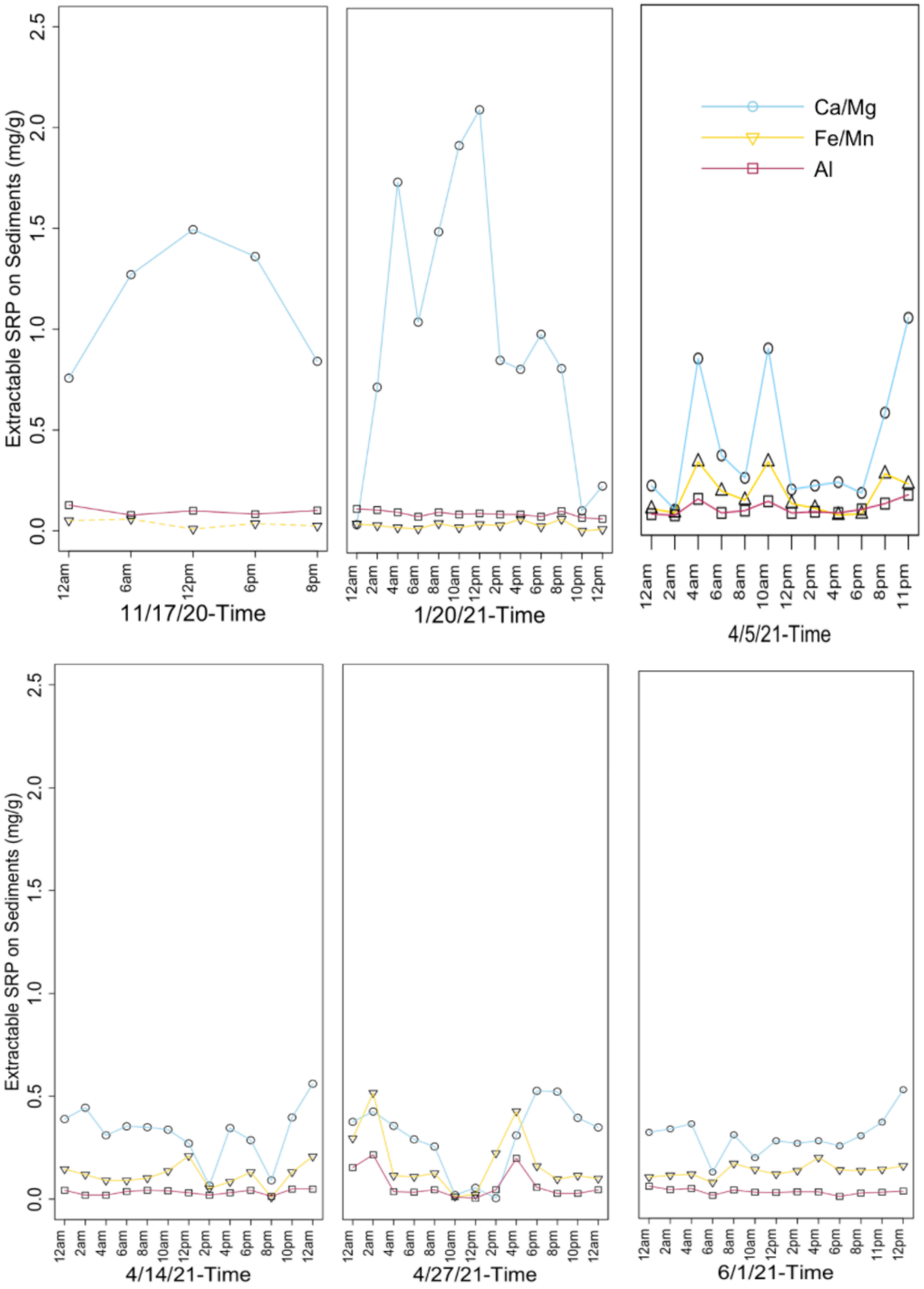

Figure 2.0.13: Diel cycling of Extractable SRP bound to different metals during from November 17th, 2020, to June 1, 2021 at Missouri Flat Creek.

In November and January any SRP bound to Fe (or possibly Mn) and Al, varied very little over the course of 24 h. In contrast, any SRP bound to pH sensitive materials (i.e., Ca and Mg minerals) varied substantially over the course of 24 hours (Figure 2.0.12). In the winter the daily average of SRP bound to Ca is almost 30 times higher than the daily average of SRP bound to Fe. The magnitude of Ca/Mg-SRP diel cycling changed, however, during the spring season. (Figure 2.0.12). While Ca/Mg-SRP diel cycling was still present in the spring, the Fe/Mn-SRP complex became more dominant during the spring season. All the SRP-Ca, SRP-Fe, and SRP-Al sorption complexes were still present in sediments in June, however, overall P sorption has less diel variation in June compared to previous sampling dates.

Loosely bound P (e.g., water extractable soil P) was present in the sediments throughout the year, however, the diel and seasonal concentration changes were minimal compared to the other P complexes. The magnitude of diel changes did not vary extensively between seasons. The concentration values of any P loosely sorbed to sediment are in Appendix D (Figure D.1).

Fe/Mn-SRP, Ca/Mg-SRP Ratio in bed sediments

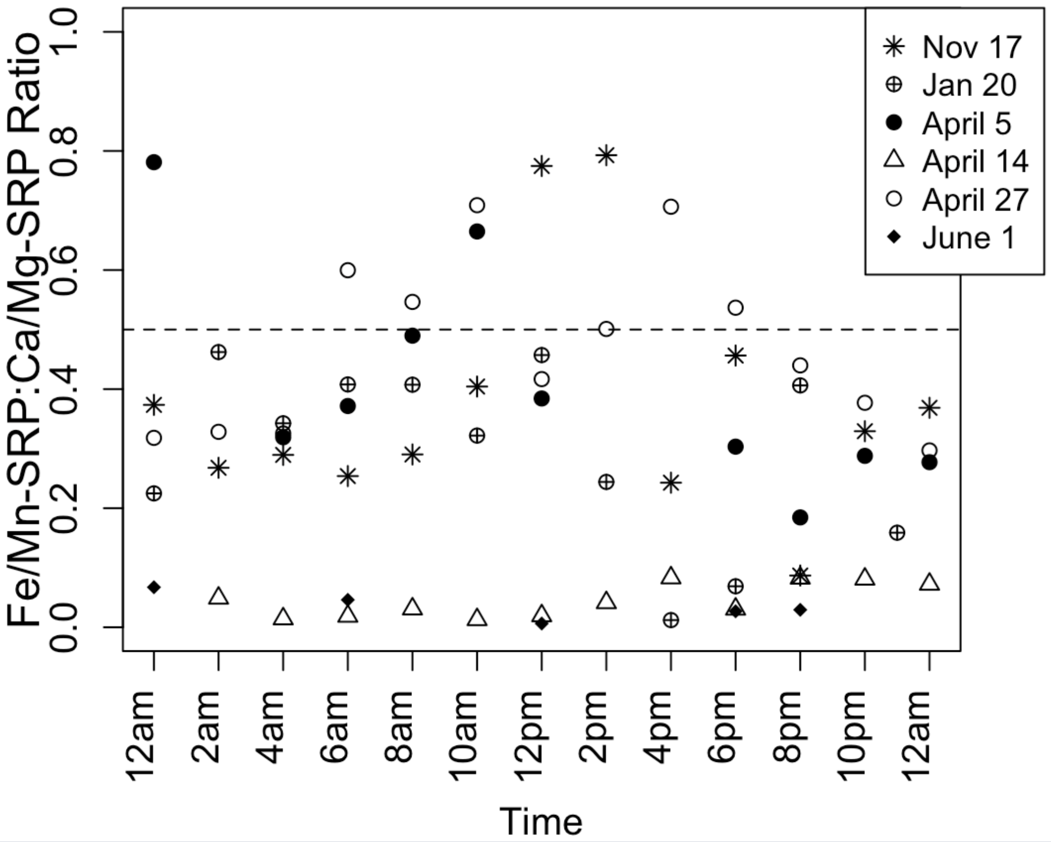

Figure 2.0.14: The Fe/Mn: Ca/Mg-P Ratio for 6 sampling days from November 17th to June 1st at Missouri Flat Creek

Figure 2.0.13 shows the ratio between SRP bound to Fe/Mn and SRP bound to Ca/Mg. In November and January, the ratio was low, meaning there was more Ca in the sediment. In April and June, the ratio increased, meaning there were more equal amounts of both minerals in the sediment.

On average, 50% of the Fe/Mn-P and Ca/Mg-P fraction was extractable. The highest ratio of extractable Ca/Mg-P was in November and the highest ratio of extractable Fe/Mn-P was in June. This supports Figure 2.0.13. The full data for the residual P and total P for each sediment fraction can be found in Appendix E.

Seasonal Trends in Total Phosphorus

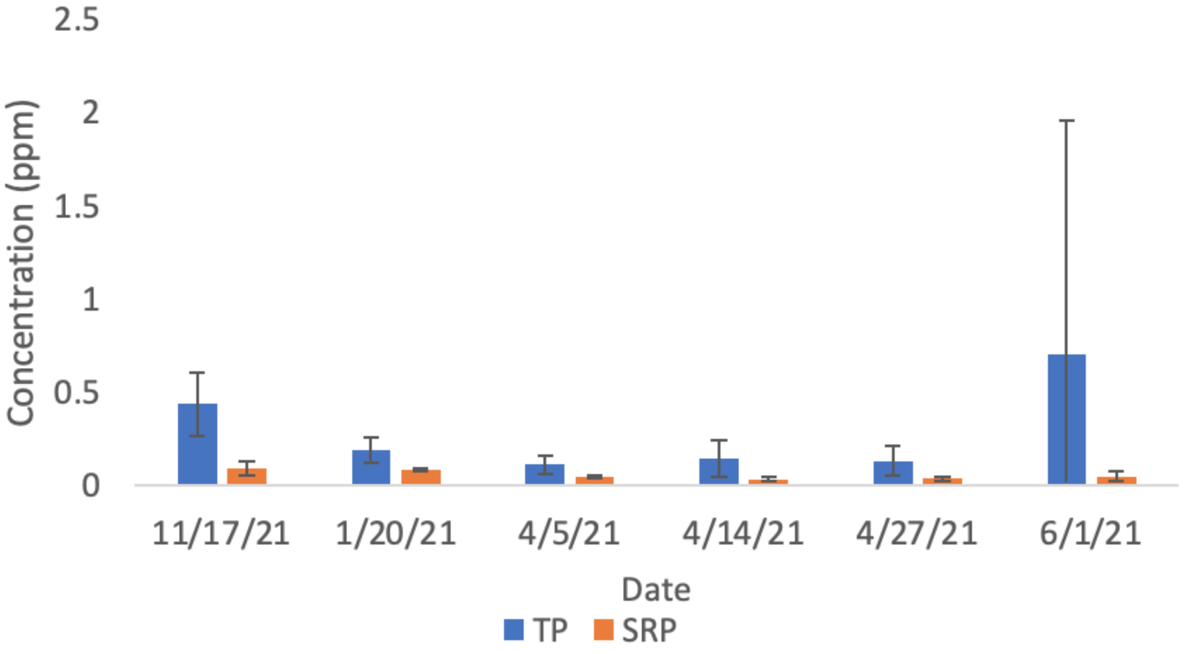

Figure 2.0.15 Daily average total phosphorus (TP) and soluble reactive phosphorus (SRP) over the 2021 water year at Missouri Flat Creek. Error bars represent the standard deviation of the measurements over the sampling day (*n*= *5-9*).

Overall, the majority (approximately 80%) of the P transported in the stream was bound to suspended sediment (i.e., particulate phosphorus) (Figure 2.6). On average, across all sample dates, the SRP fraction was 30% of the TP, with the greatest fractions occurring in January. June had the highest average TP and the greatest variation. Two points were excluded from June 1st data because SRP and TP concentration was over 7 ppm. On these data points, there were noticeable algal blooms where the samples were collected. P loading data is provided in Appendix F.

The highest TP load (2.25 mg/s) occurred during the winter, coinciding with the largest streamflow. The average summer and spring P loading was 0.35 mg/s. Estimates of TP loading can be found in Appendix F. Full concentration data for sediment extractable P concentration (mg/g), stream SRP concentration (ppm), and sediment metal concentration are in Appendix G and H.

Correlation analysis

Overall correlations between metal-P complexes and abiotic factors varied across sampling dates. Figures 2.16-2.24 indicate correlation coefficients, the level of significance based on the Kendall tau and p test, and the linear relationship between extractable SRP and temperature, dissolved oxygen, pH, and sediment metal concentrations. Three asterisks signify high significance (p value< 0.001), two asterisks signify medium significance (p value 0.01), and one asterisk medium-low significance (p value 0.05), and a dot indicates low significance (P value <0.1). Abiotic conditions correlations with metals in stream are in Appendix I and the majority of seasonal abiotic conditions correlations with extractable P graphs are in Appendix J

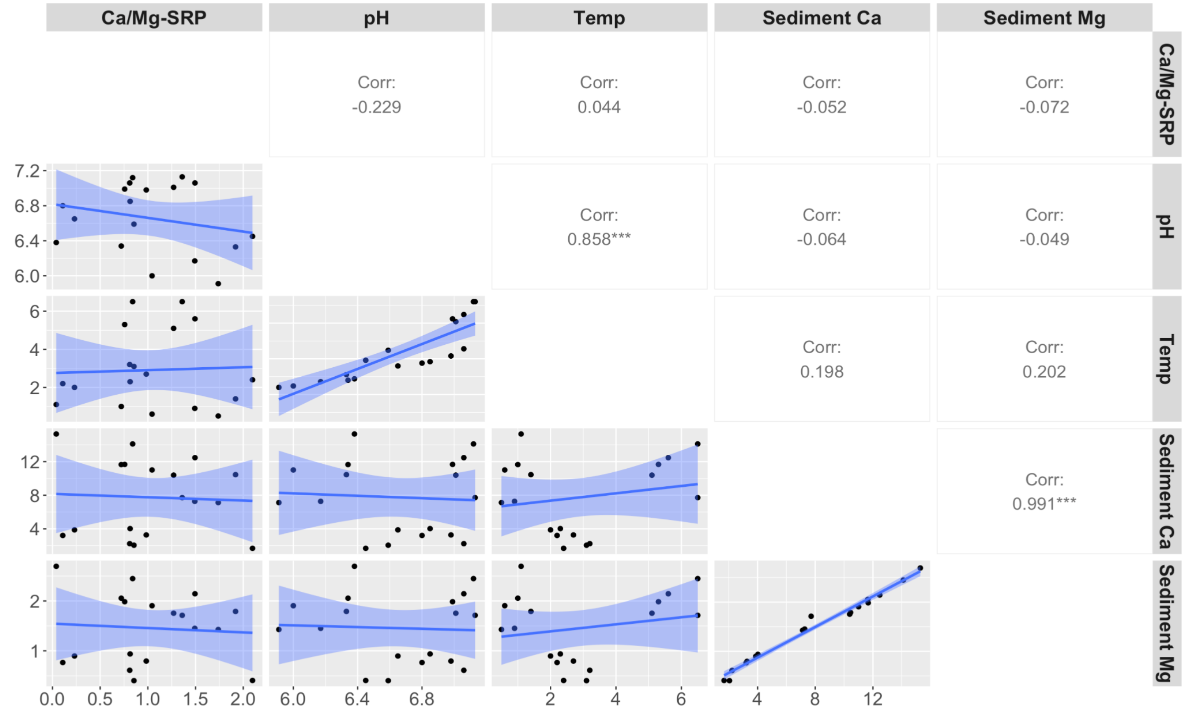

Figure 2.0.16: Correlation matrix between abiotic factors and SRP bound to Ca and Mg during winter sample dates at Missouri Flat Creek.

During the winter sampling period, the only statistically significant correlations were between pH and temperature (0.858; p-value <0.001) and Ca and Mg (0.991; p-value <0.001) (Figure 2.0.15). While the correlation was not significant, there was a negative correlation between pH and Ca-SRP (-0.229; p-value > 0.1). Temperature was not correlated with SRP-Ca/Mg. There was a significant negative correlation between pH and stream Mg (-0.52; p-value <0.05) and pH and stream Ca respectfully (-0.60; P value <0.05) (see Appendix I). There was also a significant negative correlation between water temperature and Ca in the stream water (-0.51; p value<0.05) (See Appendix I)

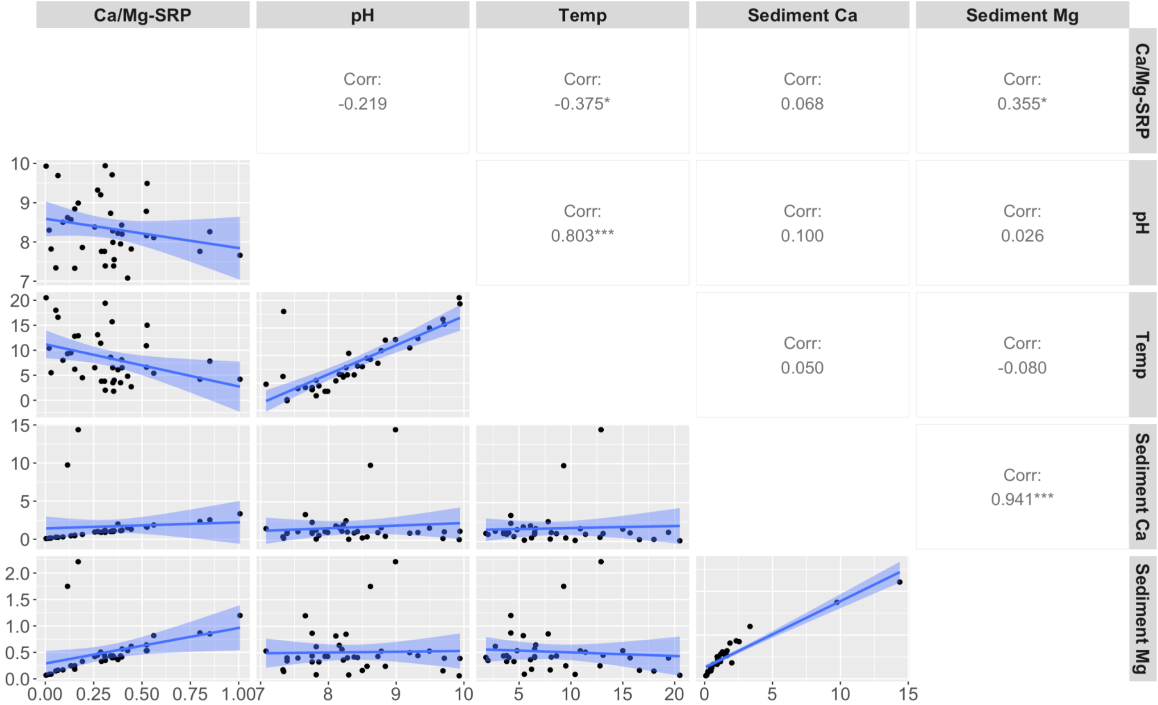

Figure 2.0.17: Correlation matrix between abiotic factors and SRP bound to Ca and Mg during spring sample dates at Missouri Flat Creek.

In contrast to the winter sampling, there was a significant correlation between temperature and SRP-Ca/Mg during the spring sampling months. The higher the temperature the less SRP bound to Ca and Mg in the sediments. Similar to the winter, the correlation between pH and Ca/Mg-SRP was not statistically significant; however, the data suggest a slight trend exists. Ca was more present in the sediment than Mg. There were also two unusually high Ca and Mg values in the sediment from April 5th at 4 and 6pm. Removal of these two points increased the correlation to 0.97 and 0.96 between sediment Ca and Ca/Mg-SRP and sediment Mg and Ca/Mg-SRP, respectively. The p- level increased to 0.001. Removal of these two points also increased the correlation to -0.34 and -0.36 between sediment Ca and temperature and sediment Mg and temperature, respectively (p value <0.05).

Besides correlations between sediment metals and abiotic factors, there were some correlations between stream SRP and measured abiotic factors. There is -0.36 and -0.37 correlation between stream Mg and pH and stream Mg and temperature (p value <0.05) (See Appendix I). There is a -0.46 correlation between stream Mg and stream SRP (p value <0.01). Lastly, there is a -0.27 correlation between stream Ca and pH and a -0.29 correlation between stream Ca and temperature (p value <0.1). The correlations for these metals are in Appendix I.

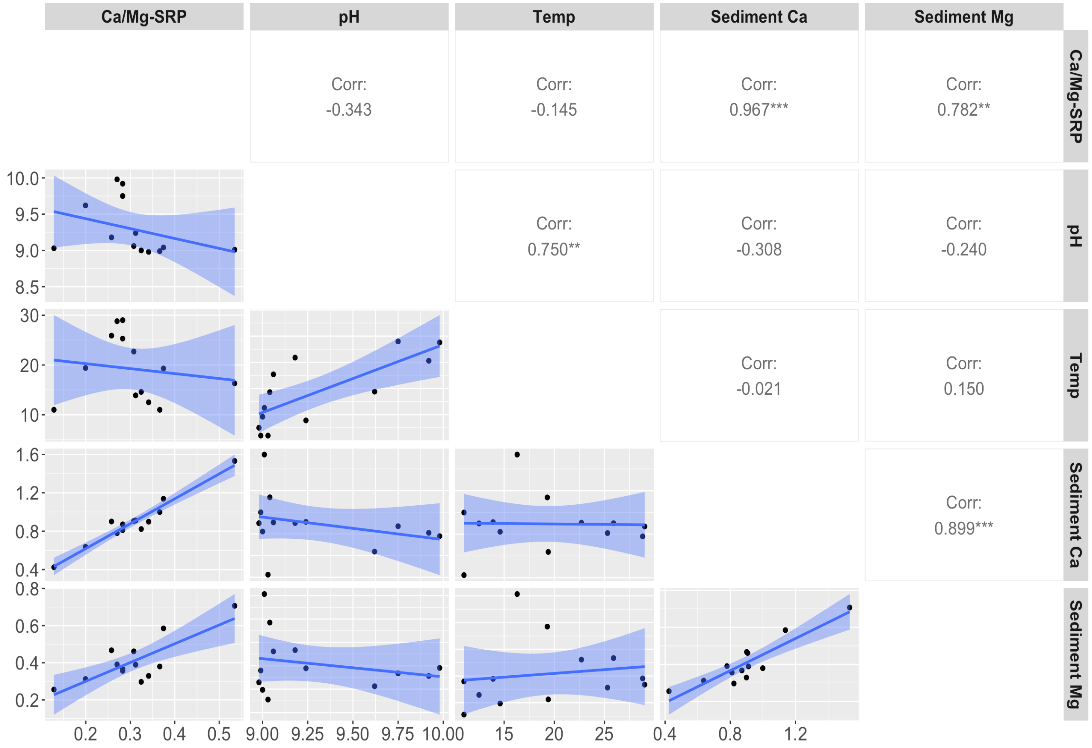

Figure 2.0.18: Correlation matrix between abiotic factors and SRP bound to Ca and Mg during summer sample dates at Missouri Flat Creek.

In contrast to past seasons, there was a non-significant correlation between SRP-Ca/Mg and temperature. There was a weak, but slightly higher correlation between pH and Ca/Mg-SRP. Likewise, the higher the pH in the stream, the less Ca and Mg found in the sediment. Similar to pH, temperature has a weak negative association. If the temperature was higher, then there was less SRP- bound to Ca and Mg in the sediments. There is an average amount of 2times more Ca in the sediment than Mg. There is a -0.66 correlation between stream Ca and stream SRP (p value <0.05), and a -0.77 correlation between stream Mg and stream SRP, and a (p value <0.01). The correlations for these metals are in Appendix I.

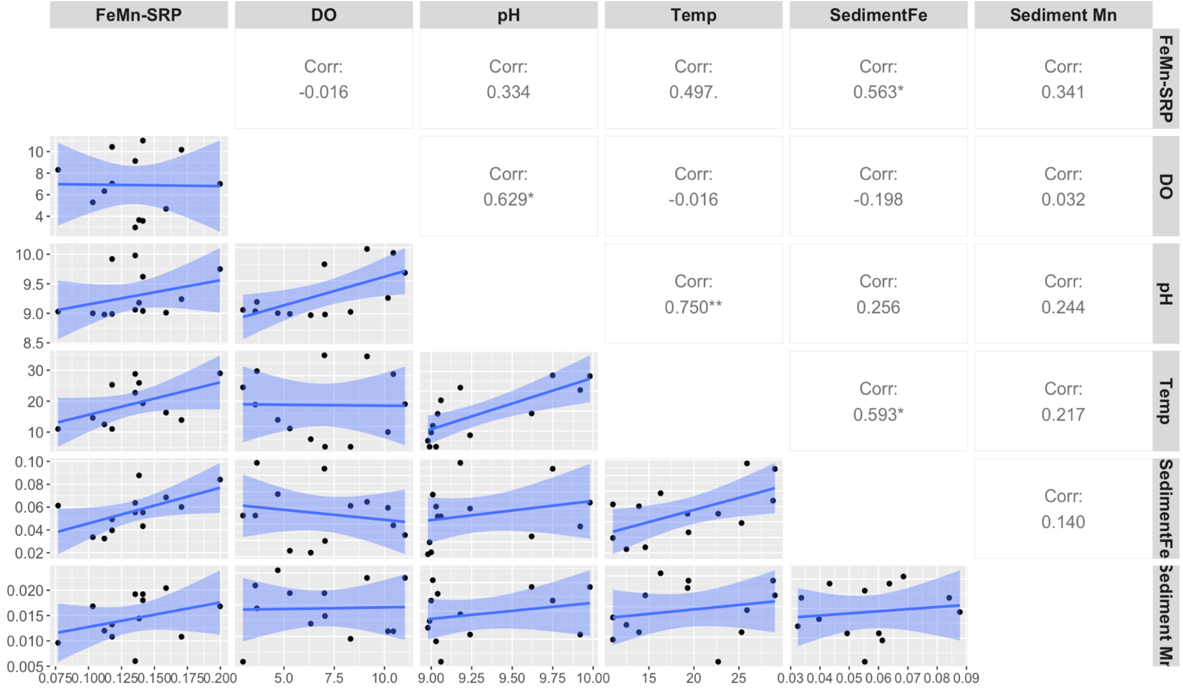

Figure 2.0.19: Correlation matrix between abiotic factors and of SRP bound to Fe and Mn in the summer at Missouri Flat Creek

In contrast to spring, there were non-significant correlations between SRP-Fe/Mn and temperature, and pH. There was no correlation with dissolved oxygen. There was a non-significant correlation between pH and Summer SRP-Fe/Mn. There was a positive correlation with temperature, meaning the higher the temperature the more SRP is bound to Fe and Mn. There is a -0.84 correlation between stream Mn and pH (p value <0.001), and a -0.76 correlation between stream Mn and temperature (P value <0.01). The correlations for these metals are in Appendix I.

Anoxic Incubation

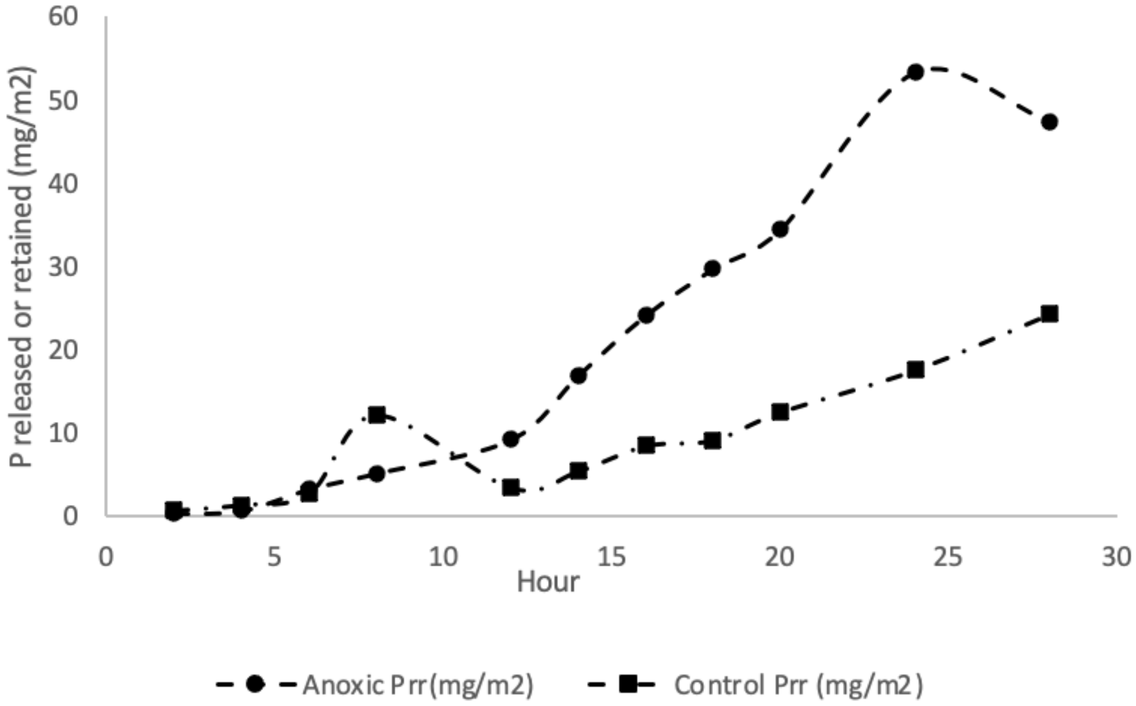

Figure 2.0.20: P release under anoxic and normal conditions with controlled temperature and pH conditions. The control group indicates P release without added oxygen or nitrogen.

Sediments under anoxic conditions had higher P release rates than those measured under non-anoxic conditions. The first few hours demonstrated that there was little difference in P release rates between the two treatments. After 12 h after starting the experiment, P release from the anoxic treatment started to increase at a faster rate than the control treatment. Sediments exposed to anoxic treatments release P at faster rates than non-anoxic treatments. In the last few hours the P released (P_{rr})started to decrease in the anoxic treatment. For the oxic treatment, the water column was bubbled with air for the first 5 hours, however, due to a leak in the regulator there was not enough gas to continue the bubbling for the oxic treatment. The DO was not regulated, but the control sediment was exposed to air from the surrounding environment, ensuring the overlying water would not be non-anoxic

Discussion

Streamflow

Streamflow of the Missouri Flat Creek did not drastically change over the course of 24 hours during the sampling dates, however, it did vary seasonally. During the April and June sampling date, the air temperature warmed, which resulted in increased plant growth. Both the increased plant growth and dry spring resulted in unusually low streamflow in April and June. On November 17th, there were some periods throughout late afternoon and early evening where there was some on and off drizzling. On April 5th there was also some precipitation early in the morning and late evening on Sunday. While these events were not extreme storms, the slight precipitation may have caused an increase in streamflow. While streamflow may not be directly correlated with SRP sorption from sediments, the highest concentrations of sorbed metals-P coincides with the highest streamflow sampling days (see Figure 2.0.4, 2.05). It is also important to note that April was extremely dry with little rain, which may have affected later April and June sampling days.

Patters of water diel SRP variation

There was a presence of SRP diel cycling from April to June. In the winter, the SRP concentrations in the stream and streamflow were higher compared to other seasons (Ortega-Pieck et. al. 2020). While tile drains may have released some P in the stream, high surface runoff likely introduced most of P in the stream (Carpenter et al., 2018; Haque, 2021). April was also unusually dry, which may have decreased the amount of SRP export to the stream.

There are two mechanisms that may have contributed to a decrease in P in the stream in April: 1) There were less upland P loading from agricultural fields due to less storm events, 2) More P was temporarily retained through autotrophic assimilation compared to other seasons due to the higher autotrophic biomass. The higher DO concentration during the day-time in the spring supports P direct assimilation was present. Although SRP concentrations were lower during spring, there was also greater variation in diel SRP concentrations due to the stream being more biologically active. Diel of pH, temperature, and DO were also present from April to June (Fig 2). These greater diel could indicate the stream was more active (i.e. greater metabolism) in the spring than the winter (Demars et al., 2015; Odum, 1956). In June, SRP was substantially higher than April. DO started to approach anoxic conditions (i.e., no oxygen present in the water) in June. The higher SRP concentration could have been due to P being released from anoxic sediments (Lannergård et al., 2020; Penn et al., 2000; Tammeorg et al., 2020; Wu et al., 2012).

Stream Metal Concentrations

Ca and Mg were the most prominent ions in MFC, which agrees with the study by Shaljian (2017)which focused on subsurface drainage chemistry at the CAF. Calcic plagioclase is a common mineral found at CAF and in silicate landscapes that can favor dissolution and may increase soil Ca inputs to streams (Shaljian, 2017; Suzuki, 2006). Although a portion of the stream ion concentrations may be from internal loading, there is not enough information in this study to distinguish this source from other sources of major anions, such as effluent from tile drains and runoff from agricultural fields (Shaljian, 2017). Determining the exact sources of ions and the concentration of ions released from internal loading would require further laboratory experiments focused on tracing and kinetics.

Streamflow and Stream SRP effect on Sediment P

Particulate P concentrations in the stream where higher than SRP concentrations throughout the 2021 water year, which could potentially indicate that the majority of P delivered to the stream was particulate P. The SRP loading was highest from November-April 5th, possibly indicating for more sorption to streambed sediments. The average P in the sediment fraction was around 50% extractable P (Appendix E), meaning that SRP sorption to sediments may be a dominant pathway of sediment P accumulation (McDaniel et al., 2009). If the majority of P bound to the sediment was residual, as opposed to extractable, than the sediment would not play a dominant role in P retention and release.

Streamflow and stream SRP concentrations likely affected P sorption throughout the year. Higher flow and SRP concentrations may help explain diel cycling of Ca/Mg-SRP in the winter. Specifically, both stream TP loadings and SRP concentrations were higher, potentially favoring sorption in sediments (McDaniel et al., 2009; McDowell, 2015). There were also high flows which could have limited P retention from sediments due to the majority of P being flushed upon entering the stream (Withers & Jarvie, 2008). While the majority of the P delivered to MFC during the sampling days was particulate P, further research is needed to understand the relationship between P retention rates and flow rate.

In the spring and summer, lower SRP concentrations were seen concurrently with lower sediment bound P, likely due to increased autotrophic uptake and decreased runoff. In the spring and summer, all sediment bound P appeared to be slightly correlated. This may be due to variation of P equilibrium between the sediment and stream (McDaniel et al., 2009; McDowell, 2015). Consequently, higher stream SRP concentrations observed during the winter months may have favored increased P sorption rates (McDaniel et al., 2009; McDowell, 2015).

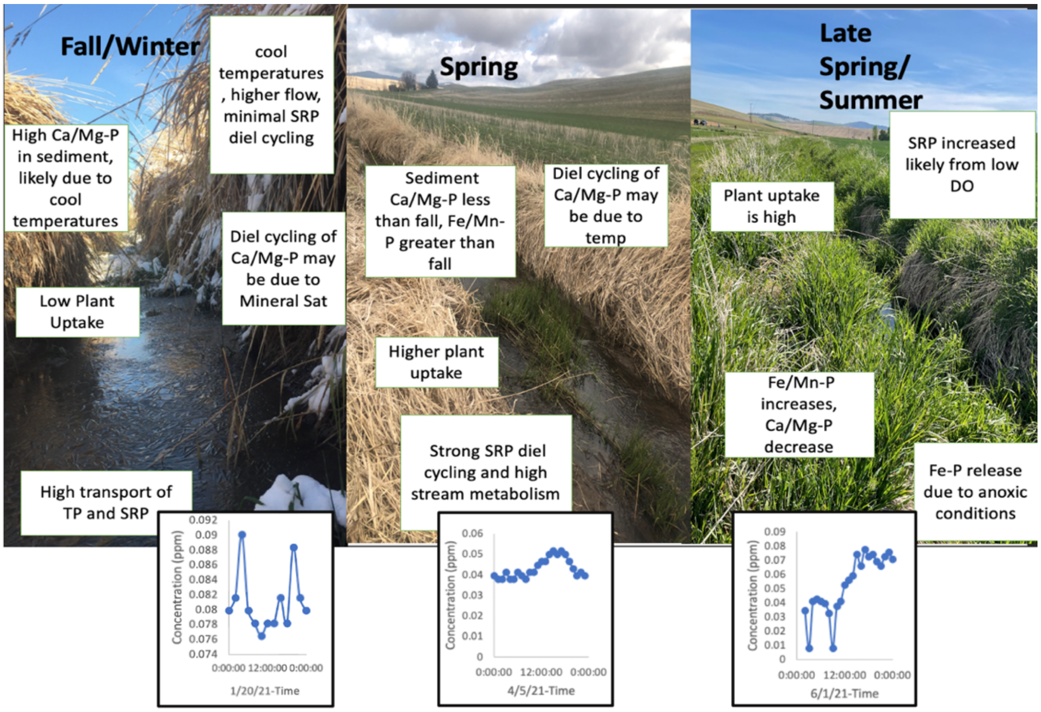

Figure 2.0.21: Seasonal variations of dominant P drivers of P sorption and release mechanisms throughout the year at Missouri Flat Creek.

Based on the data collected in this study, Figure 2.0.20 describes the primary seasonal mechanisms driving P retention and release MFC throughout the 2021 water year. Each mechanism is described below.

Abiotic factors Influence on Bed Sediment throughout the 2021 Water Year

Winter

In the winter season, there is no indication that Ca/Mg-SRP was influenced by temperature and pH. The lack of any correlation between temperature and Ca/Mg-SRP was most likely due to cooler waters and low variance of temperature during the winter season. There was an negative association between pH and Ca/Mg-SRP ($p=0.36$), however, it was the opposite trend based on the known relationships between Ca carbonate and pH (See Figure 1.1) (Morse & Mackenzie, 1990). Past research has shown that pH may have the greatest effect on carbonate minerals at basic (above 8/9) and acidic (below 6) conditions, when calcium is at high concentrations (Diaz et al., 1994; House, 1990; Huang et al., 2005b; Istvánovics, 1988; Wu et al., 2012).

The pH and temperature did not directly affect Ca/Mg-SRP sorption, however, the saturation index may have affected Ca/Mg precipitation (see Figure 2.26). Ca carbonate minerals typically become more saturated during the day (Cohen et al., 2013; de Montety et al., 2011; Simpson et al., 2019). Although there was a weak correlation between pH and Ca/Mg-SRP in the winter, peak pH and peak SRP-Ca/Mg occurred around the same time, suggesting that the stream may be approaching calcite saturation.

In the winter, there was low diel variability of Fe/Mn-SRP, and there were no correlations between Fe/Mn-SRP and abiotic factors. The circumneutral pH, high DO concentration, and limited temperature variability may not have favored Fe/Mn-SRP release (Huang et al., 2005; Jin et al., 2006; Wu et al., 2012). Nevertheless, the limited Fe/Mn-SRP may have been due to differences in saturation states; for example, if the predominant Ca/Mg mineral had a higher saturation index than the predominant Fe/Mn mineral, this could have favored the precipitation of Ca carbonate or magnesium carbonate (Simpson et al., 2019).

Similar to Fe/Mn-SRP, Al-SRP was not as dominant as Ca/Mg-SRP. The concentration of Al-SRP was slightly higher than Fe/Mn-SRP. Consequently, some P released from Fe may have bound to Al as Al oxides-phosphates. Any limited variance in concentration could have been attributed to circumneutral pH (see Figure 1.0.1) (Jan et al., 2015; Kopáček et al., 2005; Reitzel et al., 2013).

Spring

As the stream temperature warmed, autotrophs (i.e. algae, vegetation) increased. Consequently, there was an increase in stream metabolism (GPP and respiration), as evident by diel cycling of DO (see Figure 2.0.7) (Cooper et al., 2020). While Ca/Mg-SRP was still present in the ecosystem, Fe-SRP became more dominant and P uptake through assimilation likely became more dominant during the spring season.

While the Ca/Mg-SRP concentration were lower in the spring, Ca/Mg-SRP still experienced diel variation, likely due to temperature changes (Wu et al., 2012). In the spring there was a significant negative correlation between temperature and Ca/Mg-SRP ($p=0.02$) (i.e., higher temperatures may decrease precipitation). This trend is unusual based on solubility theories (Morse & Mackenzie, 1990). Temperature, however, warmer temperatures may have decreased the sediment sorption capacity and increased decomposition of organic matter, indirectly releasing SRP (Cornelissen et al., 1997; R Gächter & Meyer, 1993; Wu et al., 2012). Similar to temperature, the pH may appear to have an association with Ca/Mg-P (p=0.19), but this trend is unexpected to what is known about carbonate dissolution (see Figure 1.0.1) (Diaz et al., 1994; Morse & Mackenzie, 1990). The pH may not have had substantial influence on Ca/Mg-SRP, however, Ca concentrations are not extremely high (above 100 mg/L) (Diaz et al., 1994; House, 1990). Alternatively, any association with pH and Ca/Mg-SRP could have been due to the interactions between temperature and pH.

In the spring, temperature, DO concentration, and pH did not appear to affect diel Fe/Mn-SRP sorption. The stream was still extremely oxic, indicating Fe-SRP release was not favored. Likewise, the pH did not influence Fe/Mn-SRP. As the pH increases, the Fe/Mn-SRP should decrease (see Figure 1.0.1). Based on the data from April, the trend does not apply, indicating that pH was not a major driver Fe/Mn-SRP release (Huang et al., 2005; Jin et al., 2006; Wu et al., 2012).

Temperature and pH had little effect on Al-SRP in the spring, however, generally, there was less Al-SRP than in the winter. The pH reached levels above 8, meaning that more Al-SRP could have been released in the spring or sorbed to Fe as P had a greater affinity towards Fe than Al (Jan et al., 2015; Kopáček et al., 2005; Pa Ho Hsu, 1976; Reitzel et al., 2013).

Summer

Similar to spring, in-stream vegetation and algae were likely assimilating the majority of the stream P in the summer, as there was a high number of stream biota present during this time (Wang et al., 2018). Diel variation was minimal with all metal complexes, however, temperature may have affected Ca/Mg-SRP. While diel variation was minimal with Fe-SRP, concentrations decreased in the summer from April 27th, likely due to anoxic conditions

(Filippelli, 2008; Ghaisas et al., 2019). The substantial increase in stream SRP, with a decrease in DO, supports that Fe-SRP was being released (Filippelli, 2008; Ghaisas et al., 2019).

During the summer, there was a weak association between pH and Ca/Mg-SRP (p=0.25), however, it is the opposite trend based on known facts of Ca carbonate (Diaz et al., 1994; Morse & Mackenzie, 1990). In the summer, there was very limited diel variation and typically once the pH reaches 8.5/9 the majority of the Ca and Mg would stay in the solid form (Diaz et al., 1994; Huang et al., 2005b; Istvánovics, 1988; Wu et al., 2012). Ultimately, any relationship between pH and Ca/Mg-SRP may be due to the relationship of temperature and pH.

Temperature and Ca/Mg-SRP had a non-significant correlation (p=0.65). Similar to the spring, the increased temperatures likely increased organic matter decomposition and decreased sediment sorption, ultimately leading to more P release (Cornelissen et al., 1997; R Gächter & Meyer, 1993; Wu et al., 2012).

Similar to Ca/Mg-SRP, diel variation of Fe/Mn-SRP was minimal. There was no correlation between DO concentration and Fe-SRP. In the summer, there was a significant correlation between temperature and Fe/Mn-SRP (p=0.084) and a non-significant correlation between pH and Fe/Mn-SRP (p=0.2646). The temperature and Fe/Mn-SRP correlation was unexpected as increased temperatures are supposed to indirectly decrease P bound to Fe/Mn in the sediments (H. Li et al., 2013). Likewise, the trend between pH and Fe/Mn-SRP was unusual. Typically, if the pH is basic, there would be less SRP sorbed to Fe (Huang et al., 2005; Lijklema, 1980; Wu et al., 2012). As Fe/Mn-SRP experienced minimal concentration change, any correlations with pH and temperature could not have been substantial. Fe/Mn-

SRP concentrations, however, decreased from April to June. The warmer temperatures and less saturated DO observed in June likely released Fe-P in the sediment oxic microlayer into the overlying water (Lannergård et al., 2020; Penn et al., 2000; Wu et al., 2012).

Similar to Fe/Mn-SRP and Ca/Mg-SRP, Al-SRP had minimal diel variation in June and no associations with pH. The concentrations of Al-SRP in June and April were similar, except a few hours on April 27th. As the pH was consistently above 8 from April-June, Al-SRP likely favored dissolution in the spring/summer months. Al-SRP had a non-significant association with temperature (p=0.5277), however, based on the little diel variation in June, temperature was not a main driver of P release in Al-SRP.

Fe/Mn-P: Ca/Mg-P Ratio

The seasonal increase in the Fe/Mn-P: Ca/Mg-P ratio indicated that Fe/Mn-P gradually became more dominant as the year progressed into the spring and summer season. The Fe-P: Ca-P ratio indicated that certain stream conditions such as the pH of the water; may promote P release from sediments (Figure 2.0.13). In November and January, the ratio was small, indicating there was a higher amount of Ca-P in the sediment. During these months, P would be more soluble under acidic conditions (Huang et al., 2005). Alternatively, sediments that had higher Fe:Ca ratios released more P under more alkaline conditions (Huang et al., 2005).While the majority of the sediments had a lower Fe:Ca ratio, sediments from April consisted of a higher ratio than sediments from winter. By April 27th, a few sediments had a higher ratio (above 0.5), meaning that P release is highest during alkaline environments, and most likely from Fe. This is further supported by the extractable SRP on the sediments. In April and June, there was less extractable P bound to Ca on the sediments, compared to winter months. These ratios are important to understand the influence abiotic factors have on P release. Based on the ratios, P release from iron is to be expected in the summer months, whereas P release from calcite is to be expected in winter conditions (Huang et al., 2005).

Management

The results of this study indicate that SRP sorption to sediments is an important P sorption pathway and suggests different management practices may enhance P release from sediments.

Increasing riparian vegetation cover to reduce stream temperature might lead to decreased biological activity in the stream (C. Kelley & Krueger, 2007). As temperature greatly affects Ca/Mg-P sorption, adding riparian vegetation is likely to affect P sorption. Based on the results from MFC one might expect to see increased P sorption to Ca and Mg.

Sediment release may also be affected by dredging (Smith & Pappas, 2007). If stream channels are altered, P transport to sediment may decrease and excess P may be released to overlying water and continue to travel downstream (Smith & Pappas, 2007). It is suggested that managers should avoid dredging when P loads are high and during fertilizer season (Smith & Pappas, 2007; Smith et al., 2006).

Soil acidification due to N-fertilizer additions is a continuing issue (Huggins & Shiwakoti, 2020; Tian & Niu, 2015). Excess hydrogen ions from soil may enter stream water, which would decrease pH. A decrease in pH may dissolve calcium carbonate, releasing any SRP bound to Ca. To mitigate this issue, farmers are currently applying lime to soils, which could increase Ca loading to streams and the pH of stream water (Anderson et al., 2013).

Any soil additions (i.e. lime and biochar) that may increase Ca concentrations to the stream may amplify MFC's dependency on pH. Hydrogen ions may also enter groundwater systems, which may decrease groundwater pH (Wersin et al., 1994). However, there are reactions that may buffer the hydrogen ion concentration in the groundwater such as weathering, sulphate sorption, Al equilibria, and redox reactions (Wersin et al., 1994).

Lastly, the observed diel cycling at MFC, could be problematic for assessing yearly trends if samples are collected only once a day, and or at different times of the day. For example, collecting samples at 8 am when SRP has not peaked yet will underestimate the mass of P in the stream and therefore yearly trends would be low as well (Gammons et al., 2011).

Conclusion

Understanding in-stream retention, transport, release, of P is critical for evaluating the impact if diel changes in a stream. High frequency water and bed sediment sampling across seasons during one water year was used in this study to assess the impacts of biotic and abiotic factors on P dynamics. In this study we observed significant diel cycling of stream SRP and bed sediment P which responded to changes in stream metabolism. Ca/Mg-SRP was the predominant metal complex found at MFC, specially during the winter and fall season. During this season, Ca/Mg-SRP peaked during the afternoon, likely due to the saturation state. In the spring and summer, less Ca/Mg-SRP was observed with warmer temperatures. In contrast to Ca/Mg-SRP, Fe/Mn-SRP became more prominent in the spring and summer. Supersaturated oxygen conditions were observed throughout April, prohibiting Fe/Mn-SRP release from sediments. Once anoxic conditions were observed in June, P was likely to be released from Fe/Mn-SRP. This is evident by lower concentrations of Fe/Mn-SRP, increased algal growth, the results from the anoxic lab incubations, and high stream SRP data in June. Furthermore, small agricultural streams, such as Missouri Flat Creek, are enriched with legacy P. Seasonal variation in abiotic factors may greatly affect the length of time legacy P is sorbed to sediment. As geological P sources are limited and usage of P fertilizer is decreasing, P loading from runoff may decrease in the future. Ultimately, more of the extractable P in the sediment may be attributed to legacy P. Likewise, the terrestrial landscape is filled with Ca, which is the dominant metal bound to P. In other ecosystems where Ca may not be as dominant, P binding may be controlled by other abiotic factors. Alternatively, the aquatic ecosystem hydrology (i.e., flooding) can influence redox conditions, and consequently P retention and release. At MFC, however, Ca/Mg and Fe/Mn play a role in P retention and release at different seasons.

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Chapter 3: Stimulating STEM Education in Environmental Chemistry through an Applied Stream Chemistry Experiment

Introduction

In 2012, the average American students' science, technology, engineering, and mathematics (STEM) literacy rating was approximately 10 points below the average score of all developed countries and most students performed at the 10% mark when compared to all developed countries (Schleicher, 2007; Boylan, 2014; National Science Board, 2016; Mihelich et. al. 2017). This test, which was designed to test students' ability to perform a variety of task, consisted of open ended and multiple-choice questions that affect both their personal life and the world. Furthermore, in the early 2000 STEM discoveries have recently increased, Americans have not been contributing to these discoveries (National Academy of Sciences, 2007; Mohr-Schroeder et al., 2019). This led to great fear that America would lose their competitive edge. Consequently, Mohr-Schroeder concluded that the number of individuals prepared to enter STEM workforce must increase (Mohr-Schroeder et. al. 2019). Two key solutions to this problem are to improve STEM curriculums and to prepare more students to enter STEM fields (Mohr-Schroeder et al., 2019). While this seems like an easy fix, the problem runs deeper than encouraging teachers to focus more on STEM subjects. Oftentimes when children, especially girls and other minorities (i.e., African Americans), reach middle school their interest in science steadily declines (Lei et.al., 2019). Numerous studies have shown that young children view scientists as white, upper-class males with genius-level brain function, an image that is difficult for many students to identify with (Lei et.al., 2019). In addition to not being able to identify with science, research has shown that young professionals do not pursue a STEM career out of fear that it would be too difficult

(Kennedy et.al., 2018). Increasing engagement by teachers and encouragement by school officials and parents could mitigate any fears of difficulty and not belonging in the world and aid in the increase of STEM professionals (Hall et. al., 2011; Hansi and Potvin, 2015) Results of research studies suggest that the major factors resulting in the lack of young professionals going into STEM careers include 1) loss of interest in STEM over the course of secondary education most likely due to fear they do not fit in the science stereotype (Lei et.al., 2019), 2) fear science is too difficult to pursue (Kennedy et.al., 2018;), and lack of engagement by teachers (Hansi and Potvin, 2015).

There have been studies indicating the importance of improving our science and math curriculum to strengthen our society (Mandler,2012; National Board for Professional Teaching Standards, 2009). In 2013, the Next Generation Science Standards were created to improve science and math standards across the country (Pruitt,2014). The primary recommended strategy was to provide greater depth of instruction in fewer topics rather than light exposure to many subjects. The purpose behind this is to ensure students can connect different ideas across all subjects (Pruitt, 2014). Specifically with regards to chemistry, there has been increased discussion redirecting the focus away from memorization of facts to more integrative strategies which educate students through more applied problems (Mandler, 2012). In 2017, researchers studied the effect of Idahoan parents' attitude towards science on their children's views on science (Mihelich et. al., 2017). While a child's attitude about science is highly reflective of their parents, this study concludes that offering students an opportunity to learn more meaningful, powerful topics will allow students to develop their own beliefs about science. Mihelich et. al (2017) concluded that to improve science and math in Idaho, the K-12 curriculum should be revamped to include more important social issues, such as climate change (Mihelich et. al., 2017). A study in the Inland Pacific Northwest demonstrated that teachers are hesitant to teach about climate change due to budget and lack of time and curriculum (White et.al., 2014). The researchers suggest developing local lesson plans, which may make it easier for teachers to include climate change in their curriculum (White et.al., 2014). Offering a class that encompasses more local social issues, such as climate change could improve science and math in Idaho (Mihelich et. al., 2017). Likewise, the chemistry curriculum specifically can incorporate topics such as climate change.

In recent years there has been increased discussion on improving the chemistry curriculum for high schools, specifically focusing on applying chemistry to real life situations (Mandler, 2012). Providing students with a critical social-chemistry problem can motivate students to study and learn chemistry, as opposed to only memorizing chemistry concepts. Traditional chemistry curriculum focuses on teaching an a substantial number of facts and equations, which students typically just memorize rather than fully understanding the applications of these topics (Ultay and Calik, 2012; Avargil et.al., 2012; Littlejohn, 2017). While understanding certain reactions and theories is necessary, giving students a real-life problem to apply chemistry theories can promote interest in the topic. Therefore, a specific lesson plan focused on socio-scientific issues/topics can increase scientific and environmental literacy. Socio-scientific lessons specific to chemistry include bringing local social issues into the classroom. These could include a specific climate change issue that affects the students' hometown. Addressing these highly debated issues into the classroom will prepare responsible and caring citizens that use science to improve our world (Dishadewi et al., 2020). Gormally, Brickman, and Lutz (2012), discuss how improved literacy can prepare students for life and revolving around science. Combining these topics can help improve students' interest in chemistry, encourage students to develop their own beliefs about science, and allow students to learn more about climate change (Marks and Eilks, 2009; White et.al., 2014; Mihelich et. al., 2017).

If students decide to pursue a career in environmental chemistry, another common interdisciplinary component is conveying new environmental chemistry data to important social groups (i.e., community members, government workers, farmers). Environmental chemistry is a relatively new and growing field of study within the discipline of chemistry (Zoller, 2004). Currently, our world is facing alarming environmental issues. While society needs young-motivated scientists to explore new research ideas and remediation efforts, it is also important for students to learn how to properly communicate the data and their findings (Spektor-Levy et. al., 2008). Especially in the environmental field, not all social groups will be on board with the same action plan. Ultimately, any future environmental scientist will need to present their research in a way that everyone can understand and listen to feedback from stakeholders. If these young adults decide to pursue a career in Environmental Chemistry, not only will they need a strong background in chemistry, but they will need good communication skills (Spektor -Levy et. al., 2008).

A key component to developing key good communication skills is becoming more literate when it comes to environmental terms. If educators start to teach students about environmental problems, students might become more environmental and chemistry literate (Mandler, 2012; Burmeister et. al, 2012). When entering the workforce, students can use this knowledge to address any future world problems (Mandler, 2012). Exposing young adults to real life environmental problems is one step to improving social and environmental literacy skills, however, it is important for them to comprehend that environmental chemistry is an extremely interdisciplinary field. Environmental chemistry has interconnections with other fields, such as ecology, earth science, and writing (Jardim, 1998; Ali and Khan, 2017). Applying other science and math classes will assist students in comprehending the big picture when analyzing their results. Therefore, students will not just understand their results from a chemistry standpoint, but from the standpoint of other disciplines as well. Lastly, students will need to know how to write a scientific paper so they can present their research to the public (Brownell et.al., 2013). Gathering these important skills from other classes will greatly improve their ability to become a researcher. Environmental chemistry, however, consists of more than just understanding simple chemistry and scientific theories. As Mandler (2012) discusses, some economic and political moves can drive environmental choices. Environmental chemists need to have strong knowledge of general chemistry to understand levels of contamination, how to run experiments, and the chemical processes that occur in a certain ecosystem, however, they also need a background in biological, human health and economic factors to fully understand the scope of environmental problems (Ali and Khan, 2016).

In agricultural settings, elevated P concentrations represent a common water quality issue (Daniel et. al., 1998). Excess phosphorus can lead to problems such as eutrophication, which negatively affects aquatic ecosystems (Daniel et. al., 1998; Mallin and Cahoon; 2020; Kleinman et.al., 2011). A common method to reduce soluble reactive phosphorus (bioavailable P) is treating water systems with alum, as shown in reaction 1.

$$Al_2(SO_4)_3\ 14H_2O + 2H_3PO_4^- \rightarrow 2AlPO_4 + 3H_2SO_4 + 18\ H_2O$$

If students can understand the molar ratio of aluminum (Al) and P, they will have the tools to understand the Al and P adsorption mechanisms in stream sediments.

The goal of this study was to develop and test the effectiveness of a lesson plan aimed at incorporating a real-life environmental issue in the chemistry curriculum, to increase knowledge of phosphorus cycling, and providing students with environmental chemistry lab experience. Specifically for this project, students will be studying phosphorus (P) cycling in streams and different P adsorption/desorption mechanisms.

Objectives:

1. Create a lesson plan to promote the connection between chemistry and real-world environmental problems, increase knowledge of phosphorus cycling, and allow students to gain experience in an environmental chemistry laboratory
2. Evaluate the effectiveness of this lesson plan by analyzing the percent improvement of local honors high school chemistry students

Approach

A lesson plan and lab protocol were developed covering topics mentioned in Next Generation Science Standards (Appendix K). Next Generation standards are topics from different fields that teachers across the US should cover during the school year. The lesson plan covers specific goals, Next Generation Science standards covered, and the approximate time spent on each section of the lab. This lab protocol was designed for high school juniors or seniors with some earth science and chemistry background. A high school teacher with a background in chemistry was recruited to test the laboratory exercise.

Below is an overview of the field and lab methods that are used in the lab protocol:

Field Methods

A) Pre-Field Trip Precipitation

A brief quiz will be given to each student to gauge how much they know about stream ecosystems and stream chemistry before the lab (Appendix L). Before starting any field events, a brief introduction will be given to introduce the field site, briefly explain why monitoring water chemistry is important, and the purpose behind each specific activity.

B) Field work

Each group will be split into groups of 3-4. This may be adjusted based on time constraints or the amount of students. Each group will execute all field and lab portions of the lab together.

1. Grab Samples:

Each group will write their group information (i.e., names/initials) on a polyethylene bottle. One person in the group rinses a 125mL polyethylene bottle three times with the stream water before taking the actual sample. Sample bottles are filled completely. The samples are placed in a cooler before being stored at approximately 4 ºC until analysis. Maintaining the samples in a cool environment is important to preserve any phosphorus in the stream. A designated lab refrigerator or cooler would suffice.

2. Sediment Core:

In the laboratory, one student from each group will take a sediment sample with a small plumbing pipe. Each group allocated part of the sediment in a labeled centrifuge tube to complete the first step in a sequential extraction. 25mL of DI water were added to the centrifuge tube, and students will shake the tube for two minutes. Each student will add the 25mL of water to a new tube labeled “Sediment Extract”. Another 25mL of DI water will be added to the centrifuge tube and students will shake this tube again for another two minutes.

3. Streamflow measurement:

For the safety of the students, there are a few disclaimers for measuring streamflow: Waders or boots (depending on the depth) should be provided to students, long pants and a change of clothes is recommended, and recording flow is not recommended in all situations (i.e. too deep of stream). If the stream is safe to enter, one group member will enter the stream and record the width and water depth at set locations across the stream. At each site velocity will be recorded using a flow meter. The exact method to record flow is in Appendix M If no flow meter is available or the stream is unsafe, the teacher can possibly collect streamflow measurement from a USGS stream gauge site.

Laboratory Methods

A detailed version of the laboratory protocol, with specific concentrations and chemicals is in Appendix M. Within 48 h of sample collection, each student group must analyze their water samples on a spectrometer that has a wavelength of 880nm. Each group will create their own set of standards and use Beer's Law for the standard curve. Using a 10ppm P stock solution made ahead of time, students will create the following concentrations: 0.01 ppm, 0.1ppm, 0.5ppm, 1 ppm. While some of the group members work on the serial diluting the standards, other group members will filter their sample, preferably with a 0.45um membrane filter to remove any particulate P. This filtering is to remove any particulate phosphorus.

The color reagent is created ahead of time (within 8 h) to save time and supplies. Alternatively, students could create their own color reagent if time is not of the essence. 0.4mL of the color reagent is added to each of their samples and standards. Before running any standards on the spectrometer, each group should run a blank sample to calibrate the spectrometer. After measuring the absorbance values of the standards and samples, group members create a standard curve and determine any unknown concentrations.

Lecture

The extent to which students are familiar with stream ecosystems and stream chemistry is unknown. Furthermore, it might be best to teach a brief lesson on the importance of connecting the field work and the lab work. In relation to this lesson plan, important topics to cover include: phosphorus and water cycles, the significance of stream pH and dissolved oxygen in relationship P concentration, the importance of TMDL and alum reduction (equation above) of P, the reaction between the color reagent and phosphorus and the theory behind Beer's law. These topics can be adjusted based on what was covered in the class previously. Core standards that are satisfied by this lab report are in Appendix K. After each group completed their lab, a quiz or lab report can be used to assess how much they learned. A quiz (Appendix L) can be used if the teacher does not have a lot of time for grading or if students are short on time. A lab report with an introduction, method, result, and discussion section can be completed by students if time permits. A suggested grading rubric for this lab report is in Appendix K.

Case Study (Satisfies Objective 2)

A trial run of this lab protocol was completed with two high school honors chemistry classes at a local high school in May 2021 at Paradise Creek. Paradise Creek was chosen because it is local to Moscow, Idaho and the students are familiar with the creek. The first class had approximately 15 students attending both the lab and field sections of this activity.

The second class had approximately 18 students attending both the lab and field sections. Both classes had a mix of females and males, however, most of the students were of Caucasian descent. On the morning of May 25th, 2021, the first class visited Joseph field to collect streamflow and samples. Approximately half the class collected streamflow at Paradise Creek, while the other half collected stream and sediment samples. Due to time restrictions, each student was only able to complete either the sample collection or streamflow measurements. The second class visited Joseph Field in the afternoon. Similar to the first class, they were split into two groups, one measuring streamflow and one collecting sediments. Additionally, the field method became more efficient allowing for every student to complete both the streamflow and sample collection sections of the field methods. All the students' samples were stored at 4 degrees C for 48 hours.

On Thursday May 27th, 2021, every student from both classes analyzed their collected samples. The students who were not able to collect their own samples were paired with other students who were able to collect samples. The color reagent was made ahead of time to save materials and time. Due to budget issues at the high school, filter housings, and 0.45um membrane filters were not provided. Furthermore, each group had to vacuum filter their sample using a less expensive filter. While one member filtered their sample, the other group members created known standards using serial dilution. Next, each group added approximately 0.4mL of the pre-prepared color reagent to their standards and samples. As Moscow High School has two LabQuest Spectrometers, every group was able to run the Soluble Reactive Phosphorus. The following day, a brief lecture (10 min) was given on the importance of the reaction between alum and phosphate, the different metals that bind to phosphorus, certain water conditions that affect phosphate release, and the harmful effects of eutrophication.

Results

The trial run of this lab protocol had some challenges. The original plan was for each group of students to add alum to the collected sediment core before taking a water sample to demonstrate how alum binds to P. Due to time constraints, however, this portion was omitted. While the students were able to understand the chemical reaction between alum and phosphate, it may have been easier to comprehend if this was included in the lab. Secondly, students could only filter their samples using a glass fiber filter instead of a 0.45um PES filter typically used for soluble reactive phosphorus. The PES filter is used to remove all particulate phosphorus. A few of the samples had a decent number of particulates in the water, and based on the color of the filtered sample, not all the particulates were removed. Changing to the less accurate filter will alter any results. Lastly not every student was able to complete all the exercises. In order to get an accurate representation of water quality, students need to complete both field and lab sections, as well as both activities (stream and sediment sampling) in the field.

While the lab protocol may not have been without flaws, overall, the students did gain knowledge in stream chemistry. The students' quiz grades and the soluble reactive phosphorus results from the spectrometer are in Appendix N. The average on the first quiz for the first class was 12.96%, and the average for the second quiz was 92.11%. The second class had an average of 23.09% on the first quiz and an average of 90.03% on the second exam. Based on these results, both honors chemistry classes gained an understanding of phosphorus cycling, stream chemistry, and how ecology and chemistry are interrelated and apply to real world issues. This also demonstrated that combining a short lecture with field and lab work can improve understanding and interest in environmental chemistry.

On the final quiz, students were asked to indicate any interesting fact they learned during the water chemistry unit. For class 1, common responses related to the P cycle, phosphorus's effect on living organisms, and phosphorus levels in streams. One student commented that "science disciplines are highly interconnected such as chemistry and earth science". For class 2, common responses included how Al binds to phosphorus and what the word eutrophication meant. Before the lab, some students had a very basic understanding of why streams are important; however, most did not understand the meaning of eutrophication or any negative consequences of algal blooms. Overall, both groups appeared to learn more about water chemistry.

While there could be future improvements with the lab protocol, the high school honors chemistry teacher Jen Pollard was interested in continuing this in the future. Nowadays, high school experiments for measuring nutrient concentrations are typically quick and easy but not as accurate. Utilizing a more extensive lab component that challenged the students was a major plus to this lab protocol. While the field component will continue, hopefully other lab analysis will be added (i.e., nitrate concentration).

Discussion

Balancing a lesson plan with both environmental chemistry and earth science was difficult, as most "environmental chemistry" lesson plans are more earth science focused. A big component to the chemistry part of this lesson plan was a challenging lab experience.

Furthermore, one of the biggest lessons I learned was it takes students more time to complete certain lab tasks than one might think. I naturally assumed they would have a baseline knowledge of environmental chemistry, however, as most of the students did not understand the topics, all the lab protocols took a little longer to explain. The students are extremely intelligent, but I wanted them to fully understand the chemical reactions and the purpose behind these experiments. As the experiment was a little rushed, some of the results were not extremely accurate. Fortunately, there are a few simple solutions to improve the results and smoothness of the lesson plan. Future students utilizing the lesson plan may allocate two class periods or two hours for lab work. This extra time is necessary for students to fully comprehend all the lab procedures. I was able to spend one-on-one time with a few groups, going over the chemical reaction with the color reagent and phosphorus and how to create a standard curve. These groups seemingly grasped the chemical procedures a lot quicker than did other groups. Secondly, having a few more months to prepare would improve the smoothness and efficiency of the lab, which goes hand in hand with the second improvement I would make for future lesson plans.

Due to the need for social distancing and other COVID restrictions, implementing the lesson plan took more time than usual. Unfortunately, when I was able to complete a trial run of the lesson plan there was no budget available from the high school chemistry department. Furthermore, we could not provide the 0.45um membrane filters and filter casings. Instead, we used glass fiber filters, which is not preferable for measuring soluble reactive phosphorus. Additionally, there was only one vacuum filter, meaning only one group could filter at a time. During this time, groups could work on creating the standards; however, there was still down time. If Moscow High School could buy the filters and syringes ahead of time, then each group could filter their samples and create their standards at the same time. Ultimately, this will improve the efficiency of the lab protocol.

Applying these few changes will improve the efficiency and accuracy of the lab, allowing for a denser water chemistry unit. Jen Pollard, the Moscow High School chemistry teacher, was eager to add more lab experiments in the future. Additional experiments could include adding a nitrate component to teach students about another important nutrient involved with water quality and stream chemistry, having students add alum to stream water themselves, adding a soil desorption/ adsorption isotherm experiment, and having students recording stream pH, dissolved oxygen, and specific conductivity to receive a more complete picture of stream chemistry.

Conclusion

When students reach middle school, their interest in science, such as chemistry and earth science steadily decreases. While there have been improvements to science standards through the Next Generation Science Standards, further improvements to chemistry curriculums can be made. Students typically memorize theories, equations, and facts but fail to grasp their importance. This lesson plan was created to demonstrate to students how chemistry can be applied to real life problems and how uses of chemistry extends to much more than creating organic substances. Hopefully, the lesson plan can continue to be developed to incorporate more water chemistry subjects and to improve the efficiency of the lab methods specifically. However, as a trial run, high school students demonstrated they understood and learned more about phosphorus chemistry and stream ecology.

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Chapter 4: Conclusion

Missouri Flat Creek Analysis

In a small seasonal agricultural stream, soluble reactive phosphorous (SRP) is known to enter a water body through fertilizer runoff, soil erosion, tile drains, or chemical weathering. P may also enter a waterbody through internal sources such as extractable P from bed sediments and stream biota. While stream P dynamics have been studied on a seasonal scale, there have been few studies identifying major P retention and release mechanism on a diel scale.

Particulate P is the dominant form of P entering the stream from external sources throughout the sampling days. Soluble reactive P (SRP) concentrations were higher during the late fall winter, along with higher streamflow. In the spring and summer, SRP concentrations and streamflow were lower than the winter season. However, diel cycling is more present during the warmer months, indicative of diel cycling. Similar to SRP concentrations, temperature, dissolved oxygen (DO), and pH exhibited diel cycling in the spring and summer. Temperature and pH increased throughout the sampling days, however, DO increased during the spring sampling days and eventually decreased during the summer. Extractable P (P bound in sediments) bound to calcium (Ca) and magnesium (Mg) were dominant in November and January. Temperature was a main diel Ca/Mg-SRP driver throughout the year; however, pH would become important as long as there were high Ca concentrations throughout the day. Extractable P bound to iron (Fe) and (Mn) became more prominent in the spring season, possible due to a build of an oxic microlayer, preventing the release of Fe/Mn extractable P. In the summer the low DO conditions could have contributed to the decrease in extractable P-Fe/Mn and high stream SRP sample. Anoxic conditions typically favor P release from Fe and Mg. Extractable P bound to Al was also found in sediments, however, these complexes were not as prominent as Ca, Mg, Fe and Mn. Loosely sorbed P was present in the sediment, however, the concentration was low compared to the extractable metals- P complexes and exhibited minimal seasonal and daily changes. Besides metal-P complexes, stream biota played a role in stream retention and release. In the spring and summer there were algae and grass present in the stream, which would play a role in P diel cycling in a stream.

There are a multitude of studies that could branch of the findings presented during this research. For instance, understanding the amount of P released every hour due to different metal-P complexes, could ultimately answer questions about the percent of P being released. This research will require more of an in depth- kinetic analysis evaluating different reactions, equilibrium constants, and mineral surface areas for possible minerals. Therefore, it will be useful to know what minerals (i.e., goethite(FeOOH), calcite (CaCO3), magnetite (Fe_2O_4 etc.) exist in this ecosystem and saturation states of all possible Ca, Mg, Fe, and Mn minerals P may bind too. This information will be useful for understanding what mineral is more favored to precipitate. Expanding into saturation states and kinetics could completed a detailed picture of the geochemistry at Cook Agronomy Farm. Future research could include in depth analysis of any Ca and Mg carbonate cycling in the stream (i.e., pCO_2, carbonate species). or Fe cycling with nitrate (NO_3), oxygen in streams, and sulfur (S). It would be necessary to observe the redox potential of the stream if analyzing Fe-P. This study indicated Extractable P-Fe and stream SRP were influenced when the DO levels were anoxic in the summer. It would be beneficial to collect samples a few more times in June before the stream dries up. These extra sampling days, the redox potential, and Fe cycling with NO_3, and S would be beneficial for a complete picture of Fe cycling.

Educational Outreach

The final chapter of this thesis included an educational outreach program. Honors chemistry students were able to learn more about environmental chemistry, however, there could be future improvements to the lesson plan to implement a more efficient curriculum. First is to ensure there are enough volunteers to help with the students during any field work. Secondly, is to prepare before any budget is due. Allowing a high school to provide any materials will improve not only the quality of the results, but the time commitment as well. If each group had syringe filters as opposed to one vacuum filter for the whole class, a decent amount of time could have been saved. Ultimately, this time could have been spent on other water quality analysis, such as nitrate or isotherms.

Appendix A: Soluble Reactive Phosphorous (SRP) Laboratory Protocol

Protocols for DRP analyzed on the Spectrophotometer

University of Idaho - Soil and Water Systems

Developed by Alex Crump

Written by: Katrina Slabaugh and Aline Ortega

Dissolved Reactive Phosphorus:

1. Prep materials

a. Prep syringe filters

i. .45 um filter paper, o-rings, filters and caps.

b. In notebook and workbook assign and record each sample ID a randomized Analytical ID. *Note: this Analytical ID will be used for both DRP and TP

c. Label sample containers (Isco bottles) with analytical ID

d. Label 2 15 mL plastic vials with each Sample ID and Analytical ID. Note: Do not label vials for standards or QC samples

e. Label 1 cuvette per sample with analytical ID. Note: Only label sides that will NOT interfere with the light path.

2. Prep and filter samples

1. Samples must be analyzed fresh from the field
2. Filter approximately 30mL of sample into vials (15 mL per vial)
3. Filter 15 mL Standard

        4. Filter 15 mL QC

3. Make Color Reagent

a. To make 10 mL of the combined reagent (for approx. 20 samples)

- i. 5mL – 2.5 M H2SO4
- ii. 1.5 mL – Ammonium Molybdate solution
- iii. 3.0 mL – 0.1 Ascorbic Acid solution
- iv. 0.5 mL – Potassium Antimonyl Tartrate solution

NOTE: Color reagent must be made in this order. Otherwise, the solution will not work. This reagent must be made fresh daily as it is only stable for 8 hours.

4. Cover reagent and set aside
5. Turn Spectrophotometer on.
6. Aliquot 2.5 mL filtered sample into cuvettes
7. Aliquot 2.5 mL filtered standards and QC check into cuvettes
8. Aliquot 2.5 mL blank (DDi water) into cuvette

9. 13 minute countdown.
    a. Add .4 mL Reagent into each cuvette except blank

11. Read and record the results from the spectrophotometer in a lab notebook (880 nm wavelength)

12. Put the 15 mL tubes into the freezer. (Loosen caps for expansion)
13. Record data into workbook

14. Rinse and wash filters

Calibration curve for DRP:

1. 0.01 ppm
2. 0.05 ppm
3. 0.1 ppm
4. 0.5 ppm
5. 1.0 ppm

Appendix B: Sequential P Extraction Developed by L.E.Kinsman-Costello Kent State University

This is the original protocol. Standard concentrations maybe adjusted depending on samples and instruments.

Overview

This protocol for sequential chemical extraction of phosphorus (P) in sediments is adapted from (Paludan and Jensen 1995), with a few modifications per a personal communication from Jensen (e-mail to LE Kinsman Aug 23, 2007). See Figure 1 in Paludan and Jensen (1995) for a flow-chart schematic.

Many sequential extraction procedures have been used to extract individual P binding fractions in soils and sediments, although all provide operationally defined results that are useful indicators, but not pure samples, of chemical forms of P (Pettersson et al. 1988).

In this procedure, the first step uses de-oxygenated de-ionized water to extract loosely bound P (H_2O~P). Next, bicarbonate-buffered dithionite (0.11 M) extracts PO_4^{3-} bound to redox-sensitive oxidized iron minerals (BD~P) and some non-reactive (mostly organic) P (BD~DNRP) (Reitzel et al. 2006). This step also may extract some apatite-bound P in calcareous sediment (Reitzel 2005). The third step uses sodium hydroxide (0.1 M NaOH) to extract PO_4^{3-} bound to redox-insensitive aluminum and iron oxides that undergo anionic exchange with hydroxide (NaOH~SRP) and non-reactive organic and inorganic P (pyro- and polyphosphates). Non-reactive P extracted by NaOH is acidified to separate out precipitating humic-acid associated P (HA~P) from other non-reactive P molecules (NaOH~DNRP). After NaOH extraction, HCl (0.5 M) extracts acid-soluble P, mostly bound to apatite and other calcareous minerals (HCl~P). Residual P in the sediment pellet following the preceding chemical treatments is presumed to be bound in highly recalcitrant organic matter or crystalline mineral substances, and is extracted with nitric acid in a Hot Block (Res~P). Reactive P in each operationally defined fraction was detected using standard colorimetric methods, and non-reactive P is measured as the difference between reactive P and P detected using ICP-OES (total P).

Table 1 List of Operationally-defined P fractions measured using this protocol

Extractant	**P Fraction**	**Expected P forms**
Deoxygenated water	H_2O~P	Loosely sorbed phosphorus
0.11 M sodium bicarbonate and sodium dithionite	BD~SRP	Phosphate associated with redox-sensitive iron minerals
	BD~DNRP	Non-reactive (mostly organic) phosphorus extracted by BD solution
0.1 M sodium hydroxide	NaOH~SRP	Phosphate associated with aluminum oxides and non-redox sensitive iron minerals

	NaOH~DNRP	Non-reactive phosphorus including organic P and pyro- and poly- phosphates
0.1 M sodium hydroxide + 1 M sulfuric acid [EXCLUDED]	HA~P	Phosphorus associated with humic acids that precipitate from acidified NaOH extract
0.5 M hydrochloric acid	HCl~P	Phosphate associated with pH-sensitive apatite and calcareous minerals
Hot Block Extraction with Nitric Acid [EXCLUDED]	Res~P	Refractory organic and inorganic phosphorus

Notes

A) Sample Handling and Storage

If sediment samples are taken from a presumably anoxic environment (the majority of flooded, organic soils/sediments), efforts should be made to maintain anoxic conditions in the sediments as exposure to oxygen will change many chemical forms of phosphorus. Highly organic sediments can be assumed to have a high oxygen demand, so within 24 hours storage under refrigerated conditions in a tightly sealed bag with all the air removed should be sufficient. Storing in an oxygen-free atmosphere (e.g., in a N_2-filled glove bag or box), will ensure that anoxic conditions are maintained. In addition, freezing and thawing sediments causes lysis of microbial biomass, so sediment samples should be stored under refrigerated, not frozen, conditions.

B) Detecting Phosphorus in Extractants

Measure reactive P in H_2O~P, BD~P, NaOH~P, and HCl~P water samples using the Soluble Reactive Phosphorus (SRP) colorimetric procedure

Measure total dissolved P (TDP) in all water samples (H_2O~P, BD~P, NaOH~P, HCl~P, as well as Res~P and HA~P digestates) using inductively coupled plasma optical emission spectroscopy (ICP-OES).

Subtract reactive P from total P values to obtain nonreactive P concentrations where applicable

C) Materials & Equipment

Equipment
Centrifuge capable of holding 50 mL falcon tubes
Hot Block (for digestion of HA~P precipitate and residual sediment pellet)
Aquarium bubbler(s) and manifold for aerating multiple samples
Shaker table
Supplies
Erlenmeyer flasks (for aerating BD samples)
Glove bag or glove box (Disposable glove bags Fisher NC0534692)
Consumables
Tank of Nitrogen gas (for de-oxygenating reagents and glove bag atmosphere)
50 mL falcon tubes (5 per sample: One tube to hold sediment being extracted, one tube each for H2O~P, BD~P, NaOH~P, HCl~P water samples; Fisher #05-539-8)
Aluminum weighing tin (for parallel dry weight to wet weight ratio analysis)

Syringe 0.45 µm filters (to filter H_2O~P supernatant, Sterilitech, Cat# CAG04530200)
Hot Block digestion vials (Environmental Express, Cat #SC475)
Watch glass for Hot Block digestions (Environmental Express, Cat # SC505)
47 mm Pall A/E filters (for HA-P fraction; Fisher #NC052157)
Chemical Reagents
Sodium Bicarbonate ($NaHCO_3$), CAS #144-55-8
Sodium Dithionite ($Na_2S_2O_4$), CAS # 775-14-6
Sulfuric Acid (H_2SO_4)
Sodium Hydroxide (NaOH)
Solutions

a) Bicarbonate-buffered Dithionite for BD~P Extraction Step ("BD reagent")

1. ***Use de-aerated water***
2. *Use as fresh as possible, and mix matrix standards* ***within 24 hours*** *of mixing this solution* (see "Standard Matrix solutions for SRP and TDP Analysis")
3. Sodium dithionite ($Na_2S_2O_4$) will oxidize with exposure to oxygen. Minimize exposure of reagent to oxygen to maintain reagent
4. To dissolve dry reagents, mix using a magnetic stir bar on a stir plate while bubbling the solution with N_2 gas to prevent oxidation of the reagent.

i. 0.11 M Sodium Bicarbonate ($NaHCO_3$) and 0.11 M Sodium Dithionite ($Na_2S_2O_4$).		
ii. Desired volume (mL)	iii. $NaHCO_3$ (g)	iv. $Na_2S_2O_4$ (g)
v. 100	vi. 0.924	vii. 1.915
viii. 200	ix. 1.848	x. 3.831
xi. 250	xii. 2.310	xiii. 4.788
xiv. 500	xv. 4.62	xvi. 9.58
xvii. 1000	xviii. 9.24	xix. 19.15
xx. 1500	xxi. 13.86	xxii. 28.73
xxiii. 2000	xxiv. 18.48	xxv. 38.30

Sulfuric Acid (1 molar) for acidifying H_2O~P, BD~P, and NaOH~P extractions: "1 M H_2SO_4"

Add 56 ml concentrated H_2SO_4 to 500ml reagent-grade water and dilute to 1L

Sodium Hydroxide (0.1 molar) for NaOH~P extraction step: "0.1 M NaOH"

xxvi. Desired volume (mL)	xxvii. NaOH (g)
xxviii. 300	xxix. 1.200

xxx. 500	xxxi. 2.000
xxxii. 1000	xxxiii. 4.000
xxxiv. 2000	xxxv. 8.000

Hydrochloric Acid (0.5 molar) for HCl~P extraction step: “0.5 M HCl”

xxxvi. Desired volume (mL)	xxxvii. Vol. Concentrated HCl (12.1N)
xxxviii. 1000	xxxix. 41. mL
xl. 2000	xli. 82 mL

A) Standard Matrix Solutions for SRP and TDP Analyses

Note: 1 mL of 10 mg/L P stock solution contains 10 ug P

a) H_2O~P

Use standards prepared for routine lab use for SRP analysis, but add 0.6 mL 1 M H_2SO_4 to each prior to adding SRP colorimetric reagent. H_2O~P sample concentrations are typically in the range that does not need to be diluted, but be sure to include the 100 ug P/L standard, which is often omitted from SRP analysis of environmental samples.

BD~P

Important: *Mix BD~P standards* ***within 24 hours*** *of mixing the BD solution being used in the standards. Otherwise, SRP reagent will cause precipitate formation.*

5. Use de-aerated water
6. Undiluted BD~P samples are 2/3, or 66%, BD solution. Standard solutions should match the chemical matrix of the sample being analyzed, accounting for if the sample is diluted. BD~SRP samples are usually high and need be diluted prior to SRP analysis.
7. BD~SRP sample concentrations can vary considerably, from 50-100 ug P/L in sediments samples lacking iron, to as high as 30,000 ug P/L in high iron, high phosphorus samples. Use prior knowledge of the sediments being sample to judge how much you will need to dilute samples to achieve a concentration lower than 500ugP/L in each sample. Above 500 ug P/L, the colorimetric SRP reaction saturates.

b) Instructions for mixing BD~SRP standards (for colorimetric detection)

Materials:

- De-aerated reagent grade water
- Clean 200 mL volumetric flask
- Labeling tape and sharpies
- 10 mg/L P stock *at room temperature*
- Fresh BD reagent
- 1 M H_2SO_4

Procedure:

1. Add the appropriate amount of fresh BD reagent to match the matrix of your samples based on their dilution (see
2.
3.
4.
5. Table 2) to the clean 200 mL volumetric flask
6. Add the appropriate amount of room temperature 10 mg/L P stock solution (Table) to the 200 mL volumetric flask using an accurate pipette
7. Add enough de-aerated water to the 200 mL volumetric flask to dilute it up to the 200 mL line
8. Cover the top of the volumetric flask with a lid or parafilm and invert ten times to mix
9. Pour the solution into a labeled clean Erlenmeyer flask and set it aside
10. Repeat steps 1-5 for the remaining standard solutions
11. Aerate the standard solutions in the Erlenmeyer flasks for at least one hour
12. Finally, add the appropriate amount of 1 M H_2SO_4 (see
13.
14.
15.
16. Table 2) to each aerated standard solution
17. Store standard solutions in labeled 250 mL bottles.
    a. The label on each standard should include:
        i. the known concentration of P in the standard (e.g., “50 µgP/L”)
        ii. the label “BD~P standard”
        iii. the matrix dilution concentration (e.g., “For 10x diluted samples”)
        iv. the initials of the person who mixed the standards
        v. the date that the standards were mixed with the name of the month spelled out
        vi. information about the amount of hazardous substances (in this case, “Contains <1% Sulfuric Acid and ~5% Sodium bicarbonate and sodium dithionite solution”
18. NOTE: When analyzing samples fir SRP, pour the entire 30 mL of the standard that is mixed following these directions. DO NOT DILUTE THE STANDARD. The standards are mixed to contain the appropriate amount of chemical reagent to match the dilution factor of the samples.
19.

Table 2 Volume of BD reagent and H_2SO_4 to add to SRP standards to match the matrix of undiluted samples, and samples diluted 6x, 10x, and 30x.

xlii. Sample Dilution	xliii. Proportion BD	xliv. Volume of BD	xlvi. Volume of 1 M H_2SO_4 (mL) to

	reagent (%)	Reagent (mL) xlv. to add to 200 mL Standards	add after aerating standards
xlvii. Undiluted	xlviii. 66	xlix. 132	l. 12.5
li. 2x (15 mL Sample->30 mL total)	lii. 33	liii. 66	liv. 6.25
lv. 6x (5 mL Sample→ 30 mL total)	lvi. 11	lvii. 22	lviii. 2
lix. 10x (3 mL Sample→ 30 mL total)	lx. 6	lxi. 12	lxii. 1.2
lxiii. 30x (1 mL Sample→ 30 mL total)	lxiv. 2.2	lxv. 4.4	lxvi. 0.4
lxvii. 150x (0.2 mL Sample→ 30 mL total)	lxviii. 0.44	lxix. 0.8	lxx. 0.08

Table 3 Volume of room temperature 10 mg/L P stock solution to add when mixing 200 mL of each standard solution listed below (for SRP colorimetric detection)

lxxi. Standard Number	lxxii. Volume of 10 mg/L P stock (mL)	lxxiii. Final P conc (µg P/L)
lxxiv. Blank	lxxv. 0	lxxvi. 0
lxxvii. 1	lxxviii. 0.2	lxxix. 10

lxxx. 2	lxxxi. 0.4	lxxxii. 20
lxxxiii. 3	lxxxiv. 1	lxxxv. 50
lxxxvi. 4	lxxxvii. 2	lxxxviii. 100
lxxxix. 5	xc. 10	xci. 500

c) *Instructions for mixing BD~NRP standards (for detection by ICP)*

8. Materials:
    - Reagent-grade water
    - Clean 200 mL volumetric flask
    - Labeling tape and sharpies
    - 1,000 mg/L P stock solution at room temperature
    - 10,000 mg/L Fe stock solution at room temperature
    - One Erlenmeyer flask per standard
    - BD reagent
    - 1 M H_2SO_4

Procedure:

1. Add the appropriate amount of BD reagent to match the matrix of your samples based on their dilution (see
2.
3.
4.
5. Table 2) to the clean 200 mL volumetric flask
6. Add the appropriate amount of room temperature 1000 mg/L P stock solution (Table) to the 200 mL volumetric flask using an accurate pipette
7. Add the appropriate amount of room temperature 10000 mg/L Fe stock solution (Table) to the 200 mL volumetric flask using an accurate pipette
8. Add enough ultra-pure water to the 200 mL volumetric flask to dilute it up to the 200 mL line
9. Cover the top of the volumetric flask with a lid or parafilm and invert ten times to mix
10. Pour the solution into a labeled clean Erlenmeyer flask and set it aside
11. Repeat steps 1-5 for the remaining standard solutions
12. Finally, add the appropriate amount of 1 M H_2SO_4 based on the dilution factor of your samples (see
13.
14.
15.
16. Table 2) to each standard solution
17. Store standard solutions in labeled 250 mL bottles.
    a. The label on each standard should include:

i. the known concentration of P and Fe in the standard (e.g., “50 µgP/L”)
ii. the label “BD~P ICP standard” with the number of the standard
iii. the matrix dilution concentration (e.g., “For 10x diluted samples”)
iv. the initials of the person who mixed the standards
v. the date that the standards were mixed with the name of the month spelled out
vi. information about the amount of hazardous substances (in this case, “Contains <1% Sulfuric Acid and ~5% Sodium bicarbonate and sodium dithionite solution”

Table 4 Volume of room temperature stock solutions to add when mixing 200 mL of each standard solution listed below (for ICP-OES detection)

xcii. Standard Number	xciii. Volume of 1000 mg/L P stock (mL)	xciv. Volume of 10,000 mg/L Fe stock (mL)	xcv. Final P conc (mg P/L)	xcvi. Final Fe conc (mg/L)
xcvii. Blank	xcviii. 0	xcix. 0	c. 0	ci. 0
cii. 1	ciii. 0.02	civ. 0.01	cv. 0.1	cvi. 0.5
cvii. 2	cviii. 0.1	cix. 0.02	cx. 0.5	cxi. 1
cxii. 3	cxiii. 0.2	cxiv. 0.1	cxv. 1	cxvi. 5
cxvii. 4	cxviii. 1	cxix. 0.2	cxx. 5	cxxi. 10
cxxii. 5	cxxiii. 2	cxxiv. 1	cxxv. 10	cxxvi. 50

NaOH~P

In high iron sediments, NaOH~SRP was measured as high as 1600 ug/L and NaOH~TP as high as 5300 ug/L in extractant solution (see August 2008 P fractionation experiment using sediments from the Fort Custer Area 2 Wetland). In a diverse set of sediments (Sed x Hydro experiment), NaOH~SRP concentrations ranged from 57-4497 ug P/L. If concentrations are unknown, diluting samples 6x and mixing standards to match this matrix concentration is a good place to start.

d) Instructions for mixing NaOH~SRP standards

Materials:

- Reagent-grade water
- Squirt bottle
- Clean 200 mL volumetric flask
- Labeling tape and sharpies
- 10 mg/L P stock *at room temperature*
- 0.1 M NaOH reagent used for NaOH extraction
- 1 M H_2SO_4
- Accurate pipettes

Procedure:

20. Add the appropriate amount of 0.1 M NaOH reagent to match the matrix of your samples based on their dilution (see Table 5) to the clean 200 mL volumetric flask
21. Add the appropriate amount of room temperature 10 mg/L P stock solution (Table) to the 200 mL volumetric flask using an accurate pipette
22. Add enough reagent grade water to the 200 mL volumetric flask to dilute it up to the 200 mL line. Use squirt bottle.
23. Cover the top of the volumetric flask with a lid or parafilm and invert ten times to mix
24. Pour the solution into a labeled clean 250 mL bottle
25. Repeat steps 1-5 for the remaining standard solutions
26. Finally, add the appropriate amount of 1 M H_2SO_4 (see Table 5) to each standard solution
27. Store standard solutions in labeled 250 mL bottles.
    a. The label on each standard should include:
        i. the known concentration of P in the standard (e.g., "50 µgP/L")
        ii. the label "NaOH~P standard"
        iii. the matrix dilution concentration (e.g., "For 6x diluted samples")
        iv. the initials of the person who mixed the standards
        v. the date that the standards were mixed with the name of the month spelled out
        vi. information about the amount of hazardous substances (in this case, "Contains <1% Sulfuric Acid and ~5% Sodium bicarbonate and sodium dithionite solution"
28. NOTE: When analyzing samples for SRP, pour the entire 30 mL of the standard that is mixed following these directions. DO NOT DILUTE THE STANDARD. The standards are mixed to contain the appropriate amount of chemical reagent to match the dilution factor of the samples.

Table 5 Volume of 0.1 M NaOH reagent and 1 M H_2SO_4 to add to SRP standards to match the matrix of undiluted samples, and samples diluted 6x, 10x, and 30x.

cxxvii.	Sample Dilution	cxxviii.	Proportion 0.1 M	cxxix.	Volume of 0.1 M	cxxxi.	Volume of 1 M H_2SO_4

			NaOH (%)	cxxx.	NaOH (mL) to add to 200 mL Standards		(mL) to add after mixing standards
cxxxii.	Undiluted	cxxxiii.	66	cxxxiv.	132	cxxxv.	8
cxxxvi.	6x (5 mL Sample→ 30 mL total)	cxxxvii.	11	cxxxviii.	22	cxxxix.	1.3
cxl.	10x (3 mL Sample→ 30 mL total)	cxli.	6	cxlii.	12	cxliii.	0.8
cxliv.	30x (1 mL Sample→ 30 mL total)	cxlv.	2.2	cxlvi.	4.4	cxlvii.	0.26
cxlviii.	150x (0.2 mL Sample→ 30 mL total)	cxlix.	0.44	cl.	0.8	cli.	0.053

HCl-P

For each standard, add 100 mL of 0.5M HCl solution to a 200 mL volumetric flask. Add the appropriate amount of P stock solution and fill with DI water to 200 mL. In high iron sediments, HCl~SRP was measured as high as 1400 ug/L and HCl~TP as high as 2500 ug/L in extractant solution (see August 2008 P fractionation experiment using sediments from the Fort Custer Area 2 Wetland).

clii.	cliii. Volume of 10 mg/L P stock (mL)	cliv. Final P conc (µg P/L)
clv. HCl blank	clvi. 0	clvii. 0
clviii. HCl std 1	clix. 0.4	clx. 20

clxi. HCl std 2	clxii. 1	clxiii. 50
clxiv. HCl std 3	clxv. 2	clxvi. 100
clxvii. HCl std 4	clxviii. 10	clxix. 500
clxx. HCl std 5	clxxi. 20	clxxii. 1000
clxxiii. HCl std 6	clxxiv. 60	clxxv. 3000

B) P Fractionation Sequential Extraction Procedure

Sediment Sample Preparation

In an oxygen-free glove bag (e.g., N_2 gas), homogenize each sediment sample by squeezing the plastic bag that the sediment is held in.

Aliquot approximately 1 gram dry weight (~ 5 mL) sediments into numbered, pre-weighed plastic centrifuge tubes (one for each P fractionation analytical replicate). Tightly secure the cap on the tube in the glove bag to minimize oxygen exposure when samples are removed from the glove bag. *Aliquot at least one empty “sample” tube for a method blank.*

For each sample, also aliquot a similar amount as aliquoted for P fractionation into a pre-weighed Al tin for analysis of dry weight to wet weight ratio (dw/ww)

Record the weight of the P fractionation tubes and Al tins now containing the wet sediment samples (in notebook, title the values “Tube + Cap + Wet Sediment (g)” and “Tin + Wet Sediment (g)”, respectively)

Store aliquoted sediment samples in P fractionation tubes at 4degC (in fridge) in a sealed glove bag filled with N_2 to prevent microbial activity and exposure to oxygen

Place Al tins containing wet sediments aliquoted for dw/ww ratio in a drying oven set to 105°C .

H_2O-P

In glove bag: Add 25 mL of de-oxygenated reagent grade water to wet sediment sample previously aliquoted into numbered 50 mL centrifuge tubes for P fractionation. Tightly seal caps on tubes prior to removing them from the glove bag before the next step.

Shake samples for 1 hr at 250 rpm (H_2O Extraction)

Centrifuge P fractionation samples at 4,400 rpm for 10 min.

In glove bag: Pour supernatant and filter into sample analysis tube (labeled with sample number, name, and “H_2O~P”) using 0.45 µm syringe filters. Use a new filter for each sample. Use one 30 mL syringe, rinsing well with reagent grade water in between samples.

In glove bag: Add 25 mL de-oxygenated reagent grade water to each P fractionation tube to rinse the pellet. Tightly cap each sample tube before removing them from the glove bag. (H_2O rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 20 min.

In glove bag: Pour supernatant and filter into labeled sample tube, adding to the 25 mL from the previous step, using 0.45 µm syringe filters.

- 8.1. Use a new filter for each sample.
- 8.2. Use one 30 mL syringe, rinsing well with reagent grade water in between samples.

Add 1 mL 1M H_2SO_4 to each H_2O~P extractant sample to prevent precipitation of Fe. Each H_2O~P sample should contain 51 mL (25 mL H_2O extraction + 25 mL H_2O rinse + 1 mL H_2SO_4)

Store H_2O~P extractant samples in a refrigerator and analyze for reactive phosphorus (colorimetric SRP) within two weeks and total phosphorus (ICP-OES) at any time in the future.

- 8.3. Use 30 mL of the H_2O~P sample (undiluted) to measure reactive phosphorus using the colorimetric SRP method
- 8.4. Use 10 mL of the remaining 20 mL of the H_2O~P sample (undiltued) to measure total P using ICP-OES.

Store the sediment pellet remaining in the P fractionation tubes at 4degC (in fridge) in a sealed glove bag filled with N_2 to prevent microbial activity and exposure to oxygen

BD-P

1. *In glove bag*: Add 25 mL de-oxygenated BD reagent to each sediment sample remaining after the H_2O~P extraction step. Tightly seal caps on tubes prior to removing them from the glove bag before the next step.

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Shake samples for 1 hr at 250 rpm (BD extraction).

Centrifuge P fractionation samples at 4,400 rpm for 20 min.

In glove bag: Pour supernatant into numbered clean 125 mL plastic bottles.

In glove bag: Add 25 mL de-oxygenated BD reagent to each P fractionation tube to rinse the pellet. Tightly cap each sample tube before removing them from the glove bag. (BD-rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 10 min.

In glove bag: Pour supernatant into numbered 125 mL plastic bottles, adding to the 25 mL from the previous step.

In glove bag: Add 25 mL de-oxygenated reagent grade water to each tube. Tightly cap each sample tube before removing them from the glove bag. (BD H_2O rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 10 min.

In glove bag: Pour supernatant and into 125 mL plastic bottles, adding to the 25 mL from the previous step.

Filter samples through A/E filters using filter tower housings outside of glove bag.

1.1. Start with a clean (3x rinsed with reagent grade water) filter housing

1.2. Sample rinse the filter and filter housing by pouring a small amount (~3-5 mL) of unfiltered BD extract into filter housing and filter. Discard filtrate into a labeled hazardous waste container.

1.3. Filter the remainder of the sample. To minimize sample oxidation by mixing with the atmosphere, pour unfiltered sample down wall of filter funnel carefully.

1.4. To sample rinse an Erlenmeyer flask, pour a small amount (~3-5 mL) of the filtered sample into a clean, numbered Erlenmeyer flask. Discard into a hazardous waste container

1.5. Pour the remaining filtered sample into the Erlenmeyer flask

Aerate the filtered BD~P samples for at least 1 hr!

1.6. Aerate samples using aquarium bubblers in 250 mL Erlenmeyer flasks

After at least one hour of aeration, add 4.7 mL of 1 M H_2SO_4 to each BD~P water sample

1.7. ***If a precipitate forms when acid is added (which is unlikely, but may happen),* this is likely HA~P. Filter this precipitate out onto A/E filters and save filters for future analysis. Record the volume of liquid filtered.

Pour aerated, acidified BD~P samples into numbered, labeled 50 mL centrifuge tubes. Save 50 mL of each sample and discard remaining volume in an appropriate hazardous waste container.

Store BD~P extractant samples in a refrigerator and analyze for reactive phosphorus (colorimetric SRP) within two weeks and total phosphorus (ICP-OES) at any time in the future.

1.8. For analysis of reactive P in BD~P samples using the colorimetric SRP method, dilute samples 10x, or 3 mL of BD~P sample diluted to a total of 30 mL using 27 mL of reagent grade water. Undiluted samples are very high in P and typically exceed saturation of the colorimetric chemical reaction in the SRP method.

1.9. Use 1 mL of the remaining BD~P sample, diluting up to a total of 10 mL (again, a 10 x dilution) to measure total P using ICP-OES.

Store the sediment pellet remaining in the P fractionation tubes at 4degC (in fridge) to prevent microbial activity

NaOH-P and Humic Acid-P (notes: samples no longer need to be handled in glove bag; doing 8 samples at a time is optimal because of extra time for filtering and HA~P precipitating.)

Add 25 mL 0.1 M NaOH to each sediment sample remaining after the BD~P extraction step.

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Shake samples for 16 hr at 250 rpm (NaOH extraction)

1.10. If samples start shaking at 4:00 PM, they can be left overnight and the extraction will be completed 16 hr later at 8:00 AM the following day

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 20 min.

Pour supernatant into numbered 125 mL plastic bottles

Add 25 mL 0.1 M NaOH to each sample (NaOH rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 10 min.

Pour supernatant into numbered 125 mL plastic bottles, adding to the 25 mL from the previous step

Add 25 mL reagent grade water to each sample (NaOH H_2O rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge P fractionation samples at 4,400 rpm for 10 min.

Pour supernatant into numbered 125 mL plastic bottles, adding to the 50 mL from the previous steps

Filter supernatant through A/E filter to remove particles that did not centrifuge out

1.11. Start with a clean (3x rinsed with reagent grade water) filter housing with as much water shaken out as possible

1.12. DO NOT SAMPLE RINSE

1.13. Filter all of 75 of NaOH~P sample (25 mL NaOH Extract + 25 mL NaOH rinse + 25 mL NaOH H_2O rinse) through the A/E filter

1.14. Pour the filtrate into a clean, numbered Erlenmeyer flask

Add 3.0 mL 1 M H_2SO_4 to filtrate in Erlenmeyer flask.

Remove precipitate (HA~P) from solution by filtration through Pall A/E filter. *Note: samples are very difficult to filter, use vacuum pump and leave plenty of time. Each sample takes up to one hour to completely filter.*

1.15. Place filter in labeled weigh tin and dry in oven.

1.16. After drying, store dried filter in labeled hot block vial.

1.17. Pour filtrate solution into labeled sample analysis tube. Save 50 mL, discard remainder in an appropriate labeled hazardous waste container.

1.18. multiple filters can be used if needed, but be sure all are labeled well as to which sample they are associated with and record the volume filtered through each filter

****After this step, analyses are no longer time-sensitive****

Store NaOH~P extractant solution samples in a refrigerator and analyze for soluble reactive phosphorus (colorimetric SRP) within two weeks and total phosphorus (ICP-OES) at any time in the future

Dry filter with precipitate at 105 deg C, then combust at 520 deg C.

1.19. After combustion, place combusted filter and material in a Hot Block digestion vial and digest with 7 mL concentrated trace metal grade nitric acid to extract all phosphorus into solution . Dilute the digestate up to 50 mL using ultra-pure reagent grade water

1.20. Detect P in extracted HA~P sample using ICP-OES and standards with a 10% HNO3 matrix

HCl-P

Add 25 mL of 0.5 M HCl to each sediment sample remaining after the NaOH~P extraction step.

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Shake samples for 1 hr at 250 rpm (HCl extraction)

Centrifuge P fractionation samples at 4,400 rpm for 20 min

Pour supernatant into labeled, numbered 50 mL centrifuge tubes

Add 25 mL reagent grade water to each sample (HCl H_2O rinse)

Agitate each sample using a vortex to resuspend pelleted sediments into solution

Centrifuge samples at 4,400 rpm for 20 min

Pour supernatant into labeled 50 mL centrifuge tubes, adding to the 25 mL solution from the previous step.

Store HCl~P extractant samples in a refrigerator and analyze for reactive phosphorus (colorimetric SRP) within two weeks and total phosphorus (ICP-OES) at any time in the future.

Residual P (Res~P)

Dry pellet from #19 in 105 deg C, then transfer dried material to a crucible and combust at 520 deg C

1.21. After combustion, place combusted material in a Hot Block digestion vial and digest with 7 mL concentrated trace metal grade nitric acid to extract all phosphorus into solution. Dilute the digestate up to 50 mL using ultra-pure reagent grade water

1.22. Detect P in extracted Res~P sample using ICP-OES and standards with a 10% HNO3 matrix

C) Notes on SRP and TDP Analyses

BD~P Fraction

2. SRP color-forming reaction occurs more slowly in samples with BD extractant solution (Figure 1). After adding SRP reagent, allow color to develop for 1 hour prior to reading absorbances.
3. In BD~P samples: If aeration does not remove all dithionite, then a white precipitate (elemental sulfur) will form either when H2SO4 or SRP mixed reagent is added. If precipitate forms prior to addition of mixed reagent, allow precipitate to settle and sample supernatant. If it forms after addition of mixed reagent, read samples both at 885 (color reflects P concentration) and 420 nm (to measure turbidity). 420 nm is the wavelength at which the lowest amt of SRP color is detected (Figure 8).

NaOH~P Fraction

4. Allow about 30 minutes for SRP color development in samples with NaOH extractant solution (Figure 2)—This may not always be an issue. Did not notice this slow reaction during 5/13/2010 SRP run on NaOH~P samples
5. Color develops in as little as 10 minutes for NaOH samples that have been digesting with persulfate oxidizer during TDP run (Figure 3).
6. If NaOH~P samples are very yellow, read the absorbance of the sample with no reagent added. If the absorbance w/o reagent is .005 or higher, it can mean a difference of ~8-12 ugP/g dw in the final calculation.

Appendix C: Stream Metal Concentrations over 24 hours for 6 different sampling months

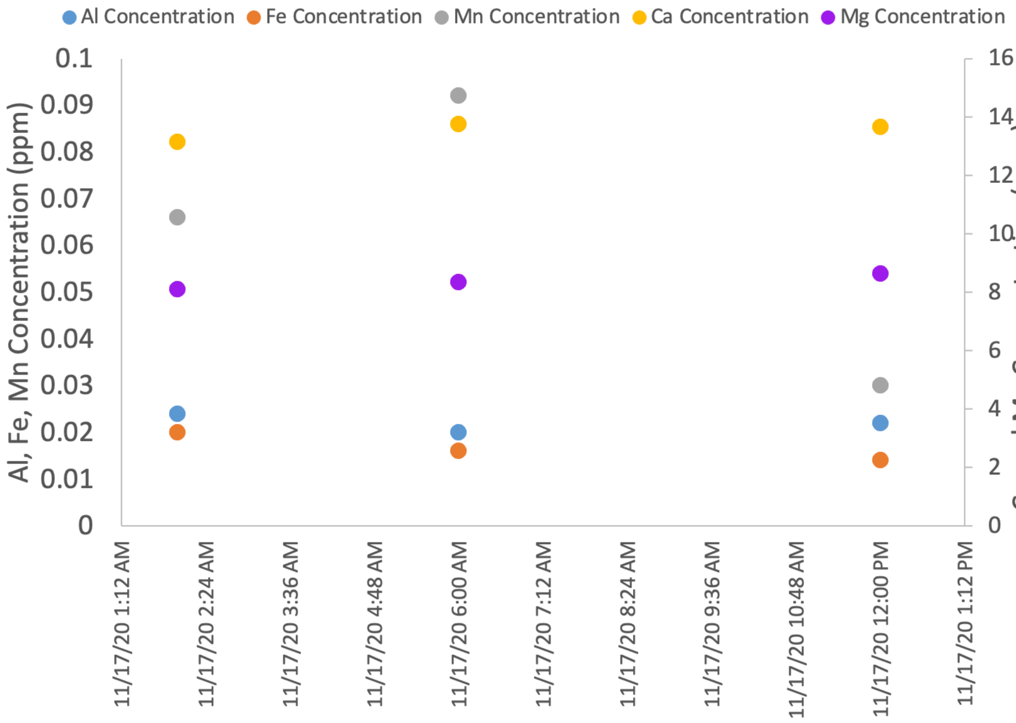


Figure C.0.1:Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of November 17, 2020. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.1: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of November 17, 2020

Time	Date	Location	Element	Concentration ppm	Dilution ppm	SRP ID
12am	11/17/2020	CF1	Al	0.015	0.015	1
12am	11/17/2020	CF4	Al	0.012	0.024	4
6am	11/17/2020	CF1	Al	0.011	0.022	13
6am	11/17/2020	CF4	Al	0.01	0.02	16
12pm	11/17/2020	CF1	Al	0.012	0.024	25
12pm	11/17/2020	CF4	Al	0.011	0.022	28

Time	Date	Location	Element Label	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	11/17/2020	CF1	Fe	0.025	0.025	1

12am	11/17/2020	CF4	Fe	0.01	0.02	4
6am	11/17/2020	CF1	Fe	0.006	0.012	13
6am	11/17/2020	CF4	Fe	0.008	0.016	16
12pm	11/17/2020	CF1	Fe	0.009	0.018	25
12pm	11/17/2020	CF4	Fe	0.007	0.014	28

Time	Date	Location	Element Label	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	11/17/2020	CF1	Mn	0.529	0.529	1
12am	11/17/2020	CF4	Mn	0.033	0.066	4
6am	11/17/2020	CF1	Mn	0.264	0.528	13
6am	11/17/2020	CF4	Mn	0.046	0.092	16
12pm	11/17/2020	CF1	Mn	0.162	0.324	25
12pm	11/17/2020	CF4	Mn	0.015	0.03	28

Time	Date	Location	Element Label	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	11/17/2020	CF1	Ca	26.21	26.21	1
12am	11/17/2020	CF4	Ca	13.148	26.296	4
6am	11/17/2020	CF1	Ca	12.629	25.258	13
6am	11/17/2020	CF4	Ca	13.744	27.488	16
12pm	11/17/2020	CF1	Ca	12.835	25.67	25
12pm	11/17/2020	CF4	Ca	13.67	27.34	28

Time	Date	Location	Element Label	Concentration (ppm)	Dilution ppm	SRP ID
12am	11/17/2020	CF1	Mg	8.092	8.092	1
12am	11/17/2020	CF4	Mg	4.053	8.106	4
6am	11/17/2020	CF1	Mg	4.003	8.006	13
6am	11/17/2020	CF4	Mg	4.171	8.342	16
12pm	11/17/2020	CF1	Mg	4.295	8.59	25
12pm	11/17/2020	CF4	Mg	4.316	8.632	28

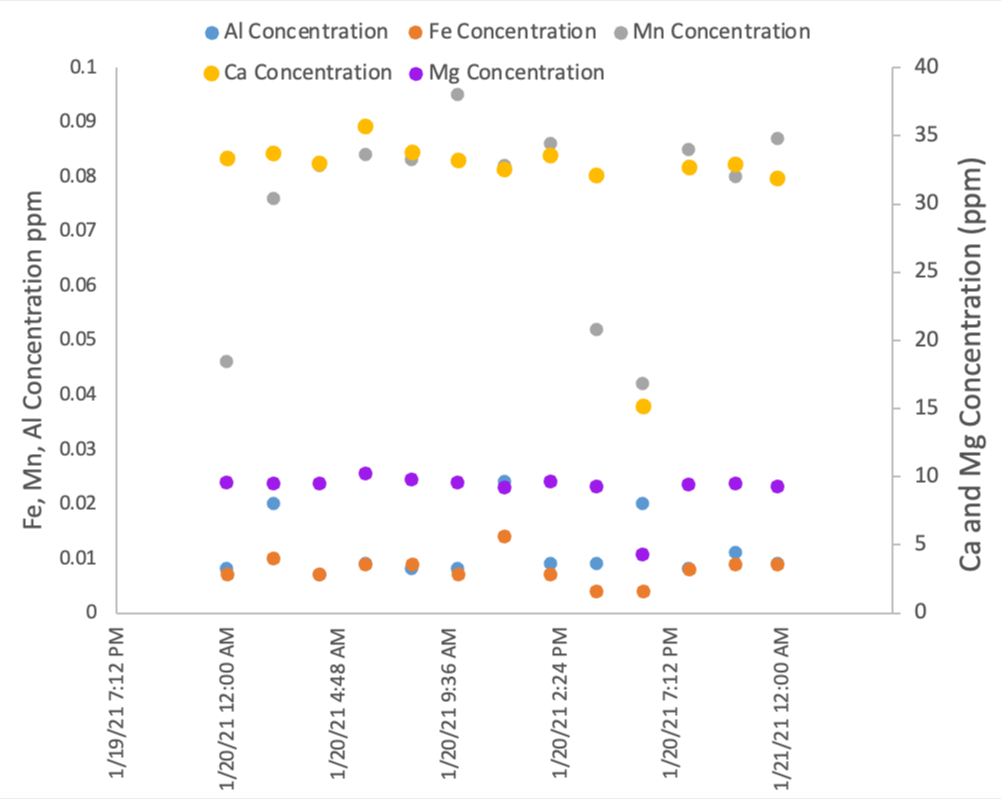


Figure C.0.2: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of January 20, 2021. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.2: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of January 20, 2021

Time	Date	Location	Element	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	1/20/2021	CF4	Al	0.008	0.008	53
2am	1/20/2021	CF4	Al	0.01	0.02	54
4am	1/20/2021	CF4	Al	0.007	0.007	55
6am	1/20/2021	CF4	Al	0.009	0.009	56
8am	1/20/2021	CF4	Al	0.008	0.008	57
10am	1/20/2021	CF4	Al	0.008	0.008	58
12pm	1/20/2021	CF4	Al	0.012	0.024	59
2pm	1/20/2021	CF4	Al	0.009	0.009	60
4pm	1/20/2021	CF4	Al	0.009	0.009	61
6pm	1/20/2021	CF4	Al	0.01	0.02	62
8pm	1/20/2021	CF4	Al	0.008	0.008	63
10pm	1/20/2021	CF4	Al	0.011	0.011	64
12am	1/20/2021	CF4	Al	0.009	0.009	65
12am	1/20/2021	CF4	Fe	0.007	0.007	53
2am	1/20/2021	CF4	Fe	0.005	0.01	54
4am	1/20/2021	CF4	Fe	0.007	0.007	55
6am	1/20/2021	CF4	Fe	0.009	0.009	56
8am	1/20/2021	CF4	Fe	0.009	0.009	57
10am	1/20/2021	CF4	Fe	0.007	0.007	58
12pm	1/20/2021	CF4	Fe	0.007	0.014	59
2pm	1/20/2021	CF4	Fe	0.007	0.007	60
4pm	1/20/2021	CF4	Fe	0.004	0.004	61
6pm	1/20/2021	CF4	Fe	0.002	0.004	62
8pm	1/20/2021	CF4	Fe	0.008	0.008	63
10pm	1/20/2021	CF4	Fe	0.009	0.009	64
12am	1/20/2021	CF4	Fe	0.009	0.009	65
12am	1/20/2021	CF4	Fe	0.007	0.007	53
12am	1/20/2021	CF4	Mn	0.046	0.046	53
2am	1/20/2021	CF4	Mn	0.038	0.076	54
4am	1/20/2021	CF4	Mn	0.082	0.082	55
6am	1/20/2021	CF4	Mn	0.084	0.084	56
8am	1/20/2021	CF4	Mn	0.083	0.083	57
10am	1/20/2021	CF4	Mn	0.095	0.095	58

12pm	1/20/2021	CF4	Mn	0.041	0.082	59
2pm	1/20/2021	CF4	Mn	0.086	0.086	60
4pm	1/20/2021	CF4	Mn	0.052	0.052	61
6pm	1/20/2021	CF4	Mn	0.021	0.042	62
8pm	1/20/2021	CF4	Mn	0.085	0.085	63
10pm	1/20/2021	CF4	Mn	0.08	0.08	64
12am	1/20/2021	CF4	Mn	0.087	0.087	65
12am	1/20/2021	CF4	Ca	33.344	33.344	53
2am	1/20/2021	CF4	Ca	16.85	33.7	54
4am	1/20/2021	CF4	Ca	32.952	32.952	55
6am	1/20/2021	CF4	Ca	35.665	35.665	56
8am	1/20/2021	CF4	Ca	33.802	33.802	57
10am	1/20/2021	CF4	Ca	33.231	33.231	58
12pm	1/20/2021	CF4	Ca	16.279	32.558	59
2pm	1/20/2021	CF4	Ca	33.562	33.562	60
4pm	1/20/2021	CF4	Ca	32.103	32.103	61
6pm	1/20/2021	CF4	Ca	7.578	15.156	62
8pm	1/20/2021	CF4	Ca	32.675	32.675	63
10pm	1/20/2021	CF4	Ca	32.929	32.929	64
12am	1/20/2021	CF4	Ca	31.851	31.851	65
12am	1/20/2021	CF4	Mg	9.549	9.549	53
2am	1/20/2021	CF4	Mg	4.747	9.494	54
4am	1/20/2021	CF4	Mg	9.48	9.48	55
6am	1/20/2021	CF4	Mg	10.237	10.237	56
8am	1/20/2021	CF4	Mg	9.766	9.766	57
10am	1/20/2021	CF4	Mg	9.562	9.562	58
12pm	1/20/2021	CF4	Mg	4.586	9.172	59
2pm	1/20/2021	CF4	Mg	9.622	9.622	60
4pm	1/20/2021	CF4	Mg	9.236	9.236	61
6pm	1/20/2021	CF4	Mg	2.128	4.256	62
8pm	1/20/2021	CF4	Mg	9.419	9.419	63
10pm	1/20/2021	CF4	Mg	9.479	9.479	64
12am	1/20/2021	CF4	Mg	9.274	9.274	65

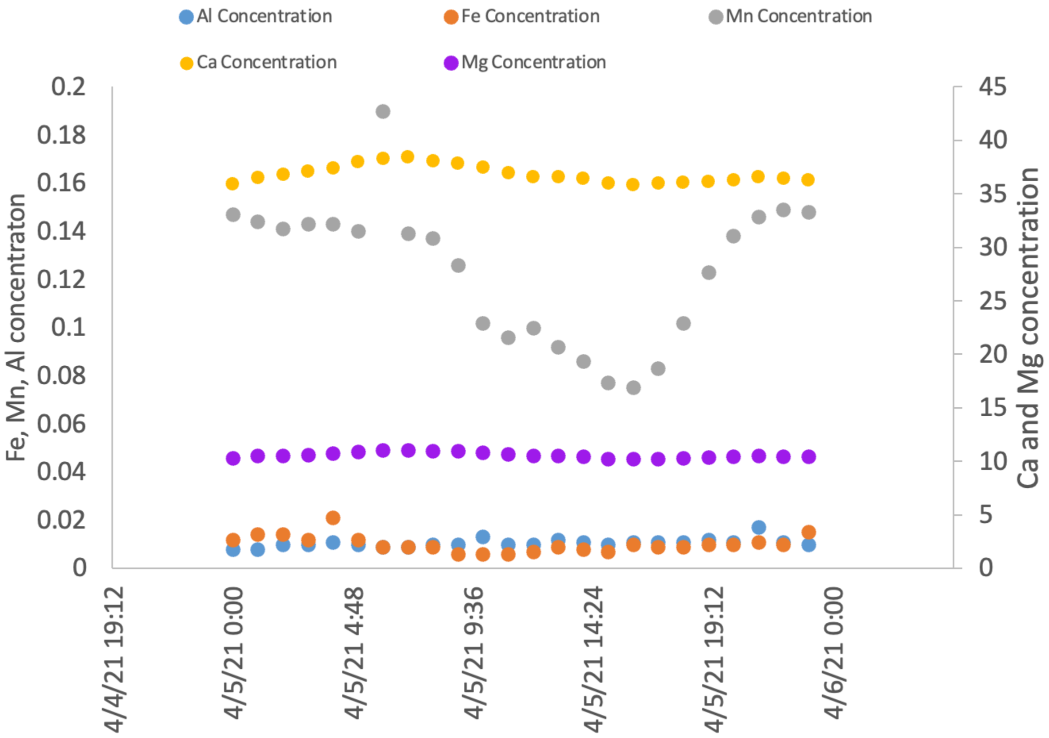


Figure C.0.3: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 5, 2021. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.3: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 5, 2021

Time	Date	Location	Element	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	4/5/2021	CF4	Al	0.008	0.008	66
1am	4/5/2021	CF4	Al	0.008	0.008	67
2am	4/5/2021	CF4	Al	0.01	0.01	68
3am	4/5/2021	CF4	Al	0.01	0.01	69
4am	4/5/2021	CF4	Al	0.011	0.011	70
5am	4/5/2021	CF4	Al	0.01	0.01	71
6am	4/5/2021	CF4	Al	0.009	0.009	72
7am	4/5/2021	CF4	Al	0.009	0.009	73
8am	4/5/2021	CF4	Al	0.01	0.01	74
9am	4/5/2021	CF4	Al	0.01	0.01	75
10am	4/5/2021	CF4	Al	0.013	0.013	76
11am	4/5/2021	CF4	Al	0.01	0.01	77
12pm	4/5/2021	CF4	Al	0.01	0.01	78
1pm	4/5/2021	CF4	Al	0.012	0.012	79
2pm	4/5/2021	CF4	Al	0.011	0.011	80
3pm	4/5/2021	CF4	Al	0.01	0.01	81
4pm	4/5/2021	CF4	Al	0.011	0.011	82
5pm	4/5/2021	CF4	Al	0.011	0.011	83
6pm	4/5/2021	CF4	Al	0.011	0.011	84
7pm	4/5/2021	CF4	Al	0.012	0.012	85
8pm	4/5/2021	CF4	Al	0.011	0.011	86
9pm	4/5/2021	CF4	Al	0.017	0.017	87
10pm	4/5/2021	CF4	Al	0.011	0.011	88
11pm	4/5/2021	CF4	Al	0.01	0.01	89
12am	4/5/2021	CF4	Fe	0.012	0.012	66
1am	4/5/2021	CF4	Fe	0.014	0.014	67
2am	4/5/2021	CF4	Fe	0.014	0.014	68
3am	4/5/2021	CF4	Fe	0.012	0.012	69
4am	4/5/2021	CF4	Fe	0.021	0.021	70
5am	4/5/2021	CF4	Fe	0.012	0.012	71
6am	4/5/2021	CF4	Fe	0.009	0.009	72
7am	4/5/2021	CF4	Fe	0.009	0.009	73
8am	4/5/2021	CF4	Fe	0.009	0.009	74

9am	4/5/2021	CF4	Fe	0.006	0.006	75
10am	4/5/2021	CF4	Fe	0.006	0.006	76
11am	4/5/2021	CF4	Fe	0.006	0.006	77
12pm	4/5/2021	CF4	Fe	0.007	0.007	78
1pm	4/5/2021	CF4	Fe	0.009	0.009	79
2pm	4/5/2021	CF4	Fe	0.008	0.008	80
3pm	4/5/2021	CF4	Fe	0.007	0.007	81
4pm	4/5/2021	CF4	Fe	0.01	0.01	82
5pm	4/5/2021	CF4	Fe	0.009	0.009	83
6pm	4/5/2021	CF4	Fe	0.009	0.009	84
7pm	4/5/2021	CF4	Fe	0.01	0.01	85
8pm	4/5/2021	CF4	Fe	0.01	0.01	86
9pm	4/5/2021	CF4	Fe	0.011	0.011	87
10pm	4/5/2021	CF4	Fe	0.01	0.01	88
11pm	4/5/2021	CF4	Fe	0.015	0.015	89
12am	4/5/2021	CF4	Mn	0.147	0.147	66
1am	4/5/2021	CF4	Mn	0.144	0.144	67
2am	4/5/2021	CF4	Mn	0.141	0.141	68
3am	4/5/2021	CF4	Mn	0.143	0.143	69
4am	4/5/2021	CF4	Mn	0.143	0.143	70
5am	4/5/2021	CF4	Mn	0.14	0.14	71
6am	4/5/2021	CF4	Mn	0.19	0.19	72
7am	4/5/2021	CF4	Mn	0.139	0.139	73
8am	4/5/2021	CF4	Mn	0.137	0.137	74
9am	4/5/2021	CF4	Mn	0.126	0.126	75
10am	4/5/2021	CF4	Mn	0.102	0.102	76
11am	4/5/2021	CF4	Mn	0.096	0.096	77
12pm	4/5/2021	CF4	Mn	0.1	0.1	78
1pm	4/5/2021	CF4	Mn	0.092	0.092	79
2pm	4/5/2021	CF4	Mn	0.086	0.086	80
3pm	4/5/2021	CF4	Mn	0.077	0.077	81
4pm	4/5/2021	CF4	Mn	0.075	0.075	82
5pm	4/5/2021	CF4	Mn	0.083	0.083	83
6pm	4/5/2021	CF4	Mn	0.102	0.102	84
7pm	4/5/2021	CF4	Mn	0.123	0.123	85
8pm	4/5/2021	CF4	Mn	0.138	0.138	86
9pm	4/5/2021	CF4	Mn	0.146	0.146	87
10pm	4/5/2021	CF4	Mn	0.149	0.149	88

11pm	4/5/2021	CF4	Mn	0.148	0.148	89
12am	4/5/2021	CF4	Ca	35.931	35.931	66
1am	4/5/2021	CF4	Ca	36.565	36.565	67
2am	4/5/2021	CF4	Ca	36.817	36.817	68
3am	4/5/2021	CF4	Ca	37.125	37.125	69
4am	4/5/2021	CF4	Ca	37.392	37.392	70
5am	4/5/2021	CF4	Ca	37.996	37.996	71
6am	4/5/2021	CF4	Ca	38.332	38.332	72
7am	4/5/2021	CF4	Ca	38.473	38.473	73
8am	4/5/2021	CF4	Ca	38.093	38.093	74
9am	4/5/2021	CF4	Ca	37.887	37.887	75
10am	4/5/2021	CF4	Ca	37.493	37.493	76
11am	4/5/2021	CF4	Ca	37.014	37.014	77
12pm	4/5/2021	CF4	Ca	36.574	36.574	78
1pm	4/5/2021	CF4	Ca	36.588	36.588	79
2pm	4/5/2021	CF4	Ca	36.463	36.463	80
3pm	4/5/2021	CF4	Ca	36.01	36.01	81
4pm	4/5/2021	CF4	Ca	35.871	35.871	82
5pm	4/5/2021	CF4	Ca	36.023	36.023	83
6pm	4/5/2021	CF4	Ca	36.109	36.109	84
7pm	4/5/2021	CF4	Ca	36.125	36.125	85
8pm	4/5/2021	CF4	Ca	36.33	36.33	86
9pm	4/5/2021	CF4	Ca	36.593	36.593	87
10pm	4/5/2021	CF4	Ca	36.47	36.47	88
11pm	4/5/2021	CF4	Ca	36.333	36.333	89
12am	4/5/2021	CF4	Mg	10.291	10.291	66
1am	4/5/2021	CF4	Mg	10.501	10.501	67
2am	4/5/2021	CF4	Mg	10.556	10.556	68
3am	4/5/2021	CF4	Mg	10.612	10.612	69
4am	4/5/2021	CF4	Mg	10.739	10.739	70
5am	4/5/2021	CF4	Mg	10.902	10.902	71
6am	4/5/2021	CF4	Mg	11.022	11.022	72
7am	4/5/2021	CF4	Mg	11.056	11.056	73
8am	4/5/2021	CF4	Mg	11.004	11.004	74
9am	4/5/2021	CF4	Mg	10.943	10.943	75
10am	4/5/2021	CF4	Mg	10.821	10.821	76
11am	4/5/2021	CF4	Mg	10.667	10.667	77
12pm	4/5/2021	CF4	Mg	10.531	10.531	78

1pm	4/5/2021	CF4	Mg	10.517	10.517	79
2pm	4/5/2021	CF4	Mg	10.456	10.456	80
3pm	4/5/2021	CF4	Mg	10.243	10.243	81
4pm	4/5/2021	CF4	Mg	10.246	10.246	82
5pm	4/5/2021	CF4	Mg	10.253	10.253	83
6pm	4/5/2021	CF4	Mg	10.282	10.282	84
7pm	4/5/2021	CF4	Mg	10.353	10.353	85
8pm	4/5/2021	CF4	Mg	10.427	10.427	86
9pm	4/5/2021	CF4	Mg	10.494	10.494	87
10pm	4/5/2021	CF4	Mg	10.479	10.479	88
11pm	4/5/2021	CF4	Mg	10.459	10.459	89

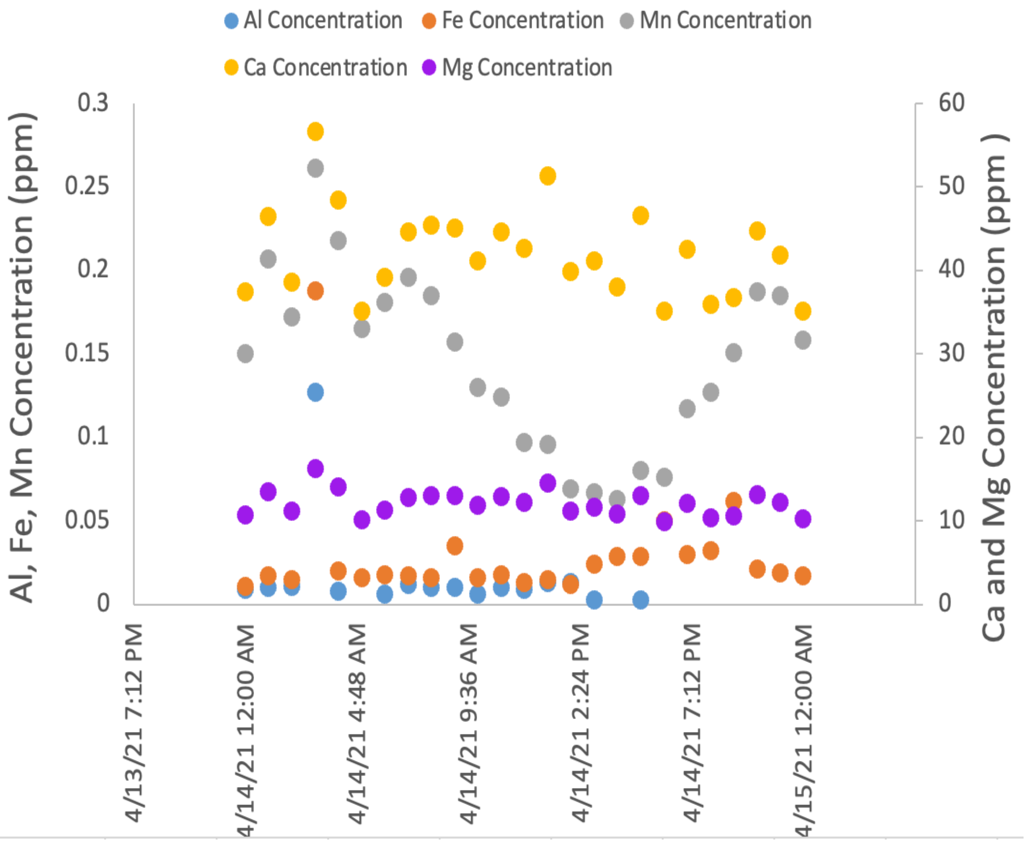


Figure C.0.4: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 14, 2021. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.4: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 14, 2021

Time	Date	Location	Element	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	4/14/2021	CF4	Al	0.009	0.009	91
1am	4/14/2021	CF4	Al	0.01	0.01	92
2am	4/14/2021	CF4	Al	0.011	0.011	93
3am	4/14/2021	CF4	Al	0.127	0.127	94
4am	4/14/2021	CF4	Al	0.008	0.008	95
5am	4/14/2021	CF4	Al	0.003		96
6am	4/14/2021	CF4	Al	0.006	0.006	97
7am	4/14/2021	CF4	Al	0.012	0.012	98
8am	4/14/2021	CF4	Al	0.01	0.01	99

9am	4/14/2021	CF4	Al	0.01	0.01	100
10am	4/14/2021	CF4	Al	0.006	0.006	101
11am	4/14/2021	CF4	Al	0.01	0.01	102
12pm	4/14/2021	CF4	Al	0.009	0.009	103
1pm	4/14/2021	CF4	Al	0.013	0.013	104
2pm	4/14/2021	CF4	Al	0.013	0.013	105
3pm	4/14/2021	CF4	Al	0.003	0.003	106
4pm	4/14/2021	CF4	Al	-0.004	BDL	107
5pm	4/14/2021	CF4	Al	0.003	0.003	108
6pm	4/14/2021	CF4	Al	0	BDL	109
7pm	4/14/2021	CF4	Al	0.002	BDL	110
8pm	4/14/2021	CF4	Al	-0.008	BDL	111
9pm	4/14/2021	CF4	Al	-0.007	BDL	112
10pm	4/14/2021	CF4	Al	-0.002	BDL	113
11pm	4/14/2021	CF4	Al	0	BDL	114
12am	4/14/2021	CF4	Al	-0.006	BDL	115
12am	4/14/2021	CF4	Fe	0.011	0.011	91
1am	4/14/2021	CF4	Fe	0.017	0.017	92
2am	4/14/2021	CF4	Fe	0.015	0.015	93
3am	4/14/2021	CF4	Fe	0.188	0.188	94
4am	4/14/2021	CF4	Fe	0.02	0.02	95
5am	4/14/2021	CF4	Fe	0.016	0.016	96
6am	4/14/2021	CF4	Fe	0.018	0.018	97
7am	4/14/2021	CF4	Fe	0.017	0.017	98
8am	4/14/2021	CF4	Fe	0.016	0.016	99
9am	4/14/2021	CF4	Fe	0.035	0.035	100
10am	4/14/2021	CF4	Fe	0.016	0.016	101
11am	4/14/2021	CF4	Fe	0.018	0.018	102
12pm	4/14/2021	CF4	Fe	0.013	0.013	103
1pm	4/14/2021	CF4	Fe	0.015	0.015	104
2pm	4/14/2021	CF4	Fe	0.012	0.012	105
3pm	4/14/2021	CF4	Fe	0.024	0.024	106
4pm	4/14/2021	CF4	Fe	0.029	0.029	107
5pm	4/14/2021	CF4	Fe	0.029	0.029	108
6pm	4/14/2021	CF4	Fe	0.05	0.05	109
7pm	4/14/2021	CF4	Fe	0.03	0.03	110
8pm	4/14/2021	CF4	Fe	0.032	0.032	111
9pm	4/14/2021	CF4	Fe	0.062	0.062	112

10pm	4/14/2021	CF4	Fe	0.021	0.021	113
11pm	4/14/2021	CF4	Fe	0.019	0.019	114
12am	4/14/2021	CF4	Fe	0.017	0.017	115
12am	4/14/2021	CF4	Mn	0.15	0.15	91
1am	4/14/2021	CF4	Mn	0.207	0.207	92
2am	4/14/2021	CF4	Mn	0.172	0.172	93
3am	4/14/2021	CF4	Mn	0.261	0.261	94
4am	4/14/2021	CF4	Mn	0.218	0.218	95
5am	4/14/2021	CF4	Mn	0.165	0.165	96
6am	4/14/2021	CF4	Mn	0.181	0.181	97
7am	4/14/2021	CF4	Mn	0.196	0.196	98
8am	4/14/2021	CF4	Mn	0.185	0.185	99
9am	4/14/2021	CF4	Mn	0.157	0.157	100
10am	4/14/2021	CF4	Mn	0.13	0.13	101
11am	4/14/2021	CF4	Mn	0.124	0.124	102
12pm	4/14/2021	CF4	Mn	0.097	0.097	103
1pm	4/14/2021	CF4	Mn	0.096	0.096	104
2pm	4/14/2021	CF4	Mn	0.069	0.069	105
3pm	4/14/2021	CF4	Mn	0.067	0.067	106
4pm	4/14/2021	CF4	Mn	0.063	0.063	107
5pm	4/14/2021	CF4	Mn	0.08	0.08	108
6pm	4/14/2021	CF4	Mn	0.076	0.076	109
7pm	4/14/2021	CF4	Mn	0.117	0.117	110
8pm	4/14/2021	CF4	Mn	0.127	0.127	111
9pm	4/14/2021	CF4	Mn	0.151	0.151	112
10pm	4/14/2021	CF4	Mn	0.187	0.187	113
11pm	4/14/2021	CF4	Mn	0.185	0.185	114
12am	4/14/2021	CF4	Mn	0.158	0.158	115
12am	4/14/2021	CF4	Ca	37.484	37.484	91
1am	4/14/2021	CF4	Ca	46.504	46.504	92
2am	4/14/2021	CF4	Ca	38.606	38.606	93
3am	4/14/2021	CF4	Ca	56.599	56.599	94
4am	4/14/2021	CF4	Ca	48.452	48.452	95
5am	4/14/2021	CF4	Ca	35.17	35.17	96
6am	4/14/2021	CF4	Ca	39.122	39.122	97
7am	4/14/2021	CF4	Ca	44.658	44.658	98
8am	4/14/2021	CF4	Ca	45.427	45.427	99
9am	4/14/2021	CF4	Ca	45.042	45.042	100

10am	4/14/2021	CF4	Ca	41.15	41.15	101
11am	4/14/2021	CF4	Ca	44.563	44.563	102
12pm	4/14/2021	CF4	Ca	42.694	42.694	103
1pm	4/14/2021	CF4	Ca	51.344	51.344	104
2pm	4/14/2021	CF4	Ca	39.912	39.912	105
3pm	4/14/2021	CF4	Ca	41.106	41.106	106
4pm	4/14/2021	CF4	Ca	38.02	38.02	107
5pm	4/14/2021	CF4	Ca	46.571	46.571	108
6pm	4/14/2021	CF4	Ca	35.107	35.107	109
7pm	4/14/2021	CF4	Ca	42.479	42.479	110
8pm	4/14/2021	CF4	Ca	35.941	35.941	111
9pm	4/14/2021	CF4	Ca	36.766	36.766	112
10pm	4/14/2021	CF4	Ca	44.772	44.772	113
11pm	4/14/2021	CF4	Ca	41.845	41.845	114
12am	4/14/2021	CF4	Ca	35.128	35.128	115
12am	4/14/2021	CF4	Mg	10.715	10.715	91
1am	4/14/2021	CF4	Mg	13.458	13.458	92
2am	4/14/2021	CF4	Mg	11.168	11.168	93
3am	4/14/2021	CF4	Mg	16.314	16.314	94
4am	4/14/2021	CF4	Mg	14.025	14.025	95
5am	4/14/2021	CF4	Mg	10.19	10.19	96
6am	4/14/2021	CF4	Mg	11.343	11.343	97
7am	4/14/2021	CF4	Mg	12.845	12.845	98
8am	4/14/2021	CF4	Mg	13.015	13.015	99
9am	4/14/2021	CF4	Mg	12.993	12.993	100
10am	4/14/2021	CF4	Mg	11.877	11.877	101
11am	4/14/2021	CF4	Mg	12.872	12.872	102
12pm	4/14/2021	CF4	Mg	12.25	12.25	103
1pm	4/14/2021	CF4	Mg	14.49	14.49	104
2pm	4/14/2021	CF4	Mg	11.144	11.144	105
3pm	4/14/2021	CF4	Mg	11.679	11.679	106
4pm	4/14/2021	CF4	Mg	10.835	10.835	107
5pm	4/14/2021	CF4	Mg	13.077	13.077	108
6pm	4/14/2021	CF4	Mg	9.942	9.942	109
7pm	4/14/2021	CF4	Mg	12.071	12.071	110
8pm	4/14/2021	CF4	Mg	10.371	10.371	111
9pm	4/14/2021	CF4	Mg	10.626	10.626	112
10pm	4/14/2021	CF4	Mg	13.101	13.101	113

11pm	4/14/2021	CF4	Mg	12.223	12.223	114
12am	4/14/2021	CF4	Mg	10.265	10.265	115

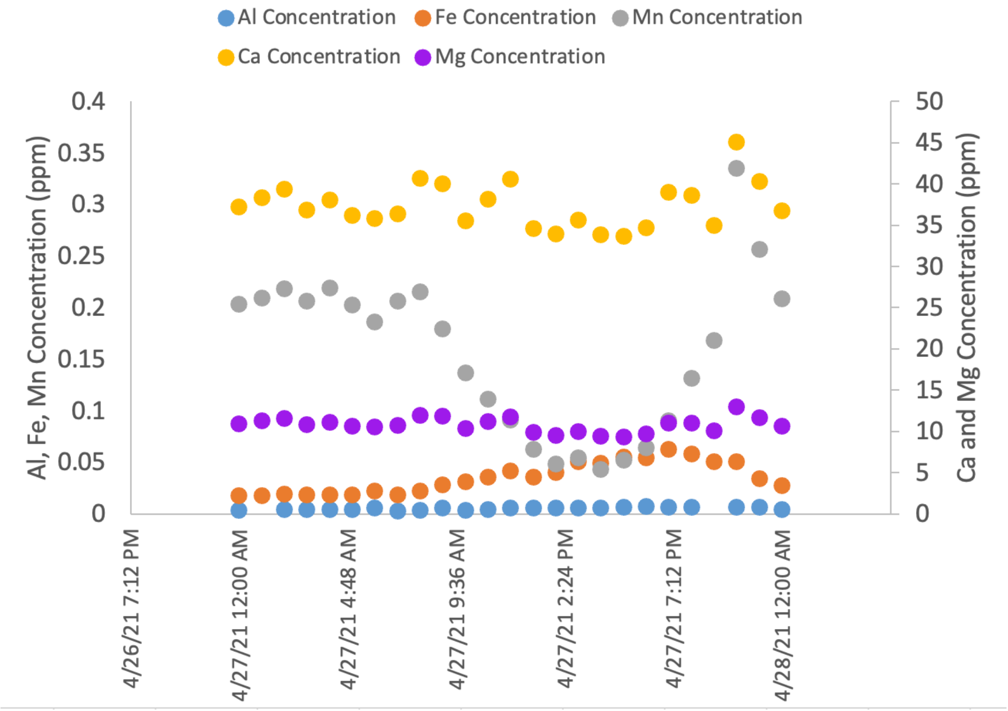


Figure C.0.5: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 27, 2021. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.5: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of April 27, 2021

Time	Date	Location	Element	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	4/27/2021	CF4	Al	0.003	0.003	116
1am	4/27/2021	CF4	Al	0.002	BDL	117
2am	4/27/2021	CF4	Al	0.004	0.004	118
3am	4/27/2021	CF4	Al	0.004	0.004	119

4am	4/27/2021	CF4	Al	0.004	0.004	120
5am	4/27/2021	CF4	Al	0.004	0.004	121
6am	4/27/2021	CF4	Al	0.005	0.005	122
7am	4/27/2021	CF4	Al	0.002	0.002	123
8am	4/27/2021	CF4	Al	0.003	0.003	124
9am	4/27/2021	CF4	Al	0.005	0.005	125
10am	4/27/2021	CF4	Al	0.003	0.003	126
11am	4/27/2021	CF4	Al	0.004	0.004	127
12pm	4/27/2021	CF4	Al	0.005	0.005	128
1pm	4/27/2021	CF4	Al	0.005	0.005	129
2pm	4/27/2021	CF4	Al	0.005	0.005	130
3pm	4/27/2021	CF4	Al	0.005	0.005	131
4pm	4/27/2021	CF4	Al	0.005	0.005	132
5pm	4/27/2021	CF4	Al	0.006	0.006	133
6pm	4/27/2021	CF4	Al	0.007	0.007	134
7pm	4/27/2021	CF4	Al	0.006	0.006	135
8pm	4/27/2021	CF4	Al	0.006	0.006	136
9pm	4/27/2021	CF4	Al	0.002	BDL	137
10pm	4/27/2021	CF4	Al	0.006	0.006	138
11pm	4/27/2021	CF4	Al	0.006	0.006	139
12am	4/27/2021	CF4	Al	0.004	0.004	140
12am	4/27/2021	CF4	Fe	0.017	0.017	116
1am	4/27/2021	CF4	Fe	0.017	0.017	117
2am	4/27/2021	CF4	Fe	0.019	0.019	118
3am	4/27/2021	CF4	Fe	0.018	0.018	119
4am	4/27/2021	CF4	Fe	0.018	0.018	120
5am	4/27/2021	CF4	Fe	0.018	0.018	121
6am	4/27/2021	CF4	Fe	0.022	0.022	122
7am	4/27/2021	CF4	Fe	0.018	0.018	123
8am	4/27/2021	CF4	Fe	0.022	0.022	124
9am	4/27/2021	CF4	Fe	0.028	0.028	125
10am	4/27/2021	CF4	Fe	0.031	0.031	126
11am	4/27/2021	CF4	Fe	0.035	0.035	127
12pm	4/27/2021	CF4	Fe	0.041	0.041	128
1pm	4/27/2021	CF4	Fe	0.035	0.035	129
2pm	4/27/2021	CF4	Fe	0.04	0.04	130
3pm	4/27/2021	CF4	Fe	0.05	0.05	131
4pm	4/27/2021	CF4	Fe	0.049	0.049	132

5pm	4/27/2021	CF4	Fe	0.055	0.055	133
6pm	4/27/2021	CF4	Fe	0.054	0.054	134
7pm	4/27/2021	CF4	Fe	0.062	0.062	135
8pm	4/27/2021	CF4	Fe	0.058	0.058	136
9pm	4/27/2021	CF4	Fe	0.05	0.05	137
10pm	4/27/2021	CF4	Fe	0.05	0.05	138
11pm	4/27/2021	CF4	Fe	0.034	0.034	139
12am	4/27/2021	CF4	Fe	0.027	0.027	140
12am	4/27/2021	CF4	Mn	0.203	0.203	116
1am	4/27/2021	CF4	Mn	0.209	0.209	117
2am	4/27/2021	CF4	Mn	0.218	0.218	118
3am	4/27/2021	CF4	Mn	0.206	0.206	119
4am	4/27/2021	CF4	Mn	0.219	0.219	120
5am	4/27/2021	CF4	Mn	0.202	0.202	121
6am	4/27/2021	CF4	Mn	0.186	0.186	122
7am	4/27/2021	CF4	Mn	0.206	0.206	123
8am	4/27/2021	CF4	Mn	0.215	0.215	124
9am	4/27/2021	CF4	Mn	0.179	0.179	125
10am	4/27/2021	CF4	Mn	0.136	0.136	126
11am	4/27/2021	CF4	Mn	0.111	0.111	127
12pm	4/27/2021	CF4	Mn	0.091	0.091	128
1pm	4/27/2021	CF4	Mn	0.062	0.062	129
2pm	4/27/2021	CF4	Mn	0.048	0.048	130
3pm	4/27/2021	CF4	Mn	0.054	0.054	131
4pm	4/27/2021	CF4	Mn	0.043	0.043	132
5pm	4/27/2021	CF4	Mn	0.052	0.052	133
6pm	4/27/2021	CF4	Mn	0.064	0.064	134
7pm	4/27/2021	CF4	Mn	0.09	0.09	135
8pm	4/27/2021	CF4	Mn	0.131	0.131	136
9pm	4/27/2021	CF4	Mn	0.168	0.168	137
10pm	4/27/2021	CF4	Mn	0.335	0.335	138
11pm	4/27/2021	CF4	Mn	0.256	0.256	139
12am	4/27/2021	CF4	Mn	0.208	0.208	140
12am	4/27/2021	CF4	Ca	37.184	37.184	116
1am	4/27/2021	CF4	Ca	38.28	38.28	117
2am	4/27/2021	CF4	Ca	39.349	39.349	118
3am	4/27/2021	CF4	Ca	36.78	36.78	119
4am	4/27/2021	CF4	Ca	38.013	38.013	120

5am	4/27/2021	CF4	Ca	36.106	36.106	121
6am	4/27/2021	CF4	Ca	35.717	35.717	122
7am	4/27/2021	CF4	Ca	36.32	36.32	123
8am	4/27/2021	CF4	Ca	40.601	40.601	124
9am	4/27/2021	CF4	Ca	39.951	39.951	125
10am	4/27/2021	CF4	Ca	35.505	35.505	126
11am	4/27/2021	CF4	Ca	38.115	38.115	127
12pm	4/27/2021	CF4	Ca	40.566	40.566	128
1pm	4/27/2021	CF4	Ca	34.502	34.502	129
2pm	4/27/2021	CF4	Ca	33.853	33.853	130
3pm	4/27/2021	CF4	Ca	35.552	35.552	131
4pm	4/27/2021	CF4	Ca	33.829	33.829	132
5pm	4/27/2021	CF4	Ca	33.644	33.644	133
6pm	4/27/2021	CF4	Ca	34.62	34.62	134
7pm	4/27/2021	CF4	Ca	38.951	38.951	135
8pm	4/27/2021	CF4	Ca	38.563	38.563	136
9pm	4/27/2021	CF4	Ca	34.937	34.937	137
10pm	4/27/2021	CF4	Ca	44.974	44.974	138
11pm	4/27/2021	CF4	Ca	40.249	40.249	139
12am	4/27/2021	CF4	Ca	36.701	36.701	140
12am	4/27/2021	CF4	Mg	10.833	10.833	116
1am	4/27/2021	CF4	Mg	11.196	11.196	117
2am	4/27/2021	CF4	Mg	11.513	11.513	118
3am	4/27/2021	CF4	Mg	10.75	10.75	119
4am	4/27/2021	CF4	Mg	11.073	11.073	120
5am	4/27/2021	CF4	Mg	10.6	10.6	121
6am	4/27/2021	CF4	Mg	10.484	10.484	122
7am	4/27/2021	CF4	Mg	10.64	10.64	123
8am	4/27/2021	CF4	Mg	11.889	11.889	124
9am	4/27/2021	CF4	Mg	11.764	11.764	125
10am	4/27/2021	CF4	Mg	10.339	10.339	126
11am	4/27/2021	CF4	Mg	11.146	11.146	127
12pm	4/27/2021	CF4	Mg	11.667	11.667	128
1pm	4/27/2021	CF4	Mg	9.856	9.856	129
2pm	4/27/2021	CF4	Mg	9.5	9.5	130
3pm	4/27/2021	CF4	Mg	9.916	9.916	131
4pm	4/27/2021	CF4	Mg	9.341	9.341	132
5pm	4/27/2021	CF4	Mg	9.301	9.301	133

6pm	4/27/2021	CF4	Mg	9.654	9.654	134
7pm	4/27/2021	CF4	Mg	10.965	10.965	135
8pm	4/27/2021	CF4	Mg	10.929	10.929	136
9pm	4/27/2021	CF4	Mg	9.985	9.985	137
10pm	4/27/2021	CF4	Mg	12.94	12.94	138
11pm	4/27/2021	CF4	Mg	11.608	11.608	139
12am	4/27/2021	CF4	Mg	10.606	10.606	140

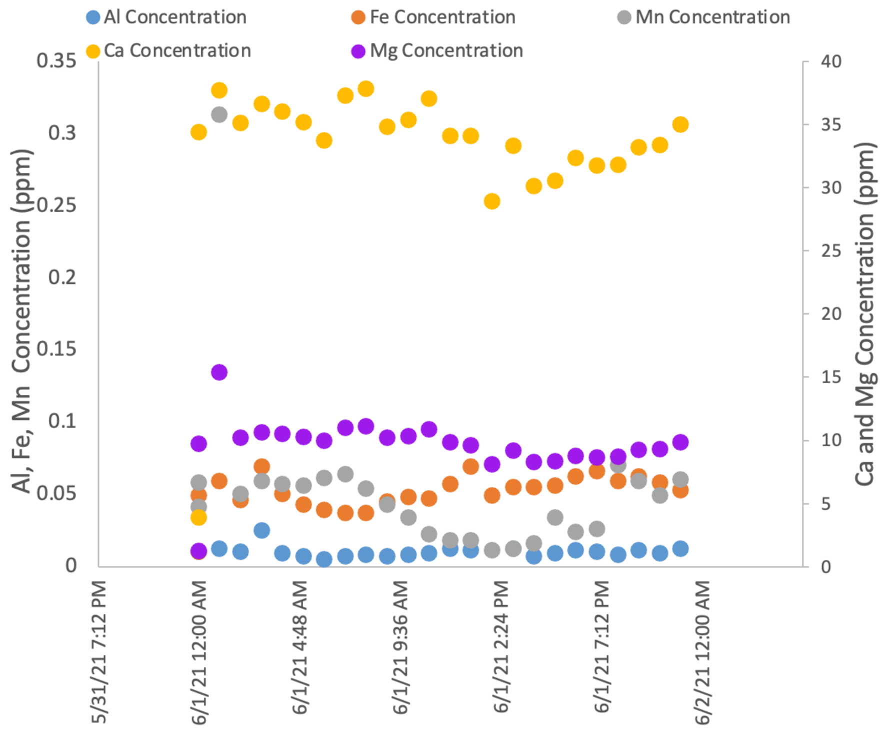


Figure C.0.6: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of June 1, 2021. Ca and Mg are on the right y axis and Al, Fe, Mn are on the left y axis.

Table C.0.6: Al, Fe, Mn, Ca, and Mg Concentrations (ppm) in stream samples for the morning of June 1, 2021

Time	Date	Location	Element	Concentration (ppm)	Dilution (ppm)	SRP ID
12am	6/1/2021	CF4	Al	0.001	BDL	141
1am	6/1/2021	CF4	Al	0.012	0.012	142
2am	6/1/2021	CF4	Al	0.01	0.01	143
3am	6/1/2021	CF4	Al	0.025	0.025	144
4am	6/1/2021	CF4	Al	0.009	0.009	145
5am	6/1/2021	CF4	Al	0.007	0.007	146
6am	6/1/2021	CF4	Al	0.005	0.005	147
7am	6/1/2021	CF4	Al	0.007	0.007	148
8am	6/1/2021	CF4	Al	0.008	0.008	149
9am	6/1/2021	CF4	Al	0.007	0.007	150
10am	6/1/2021	CF4	Al	0.008	0.008	151
11am	6/1/2021	CF4	Al	0.009	0.009	152
12pm	6/1/2021	CF4	Al	0.012	0.012	153
1pm	6/1/2021	CF4	Al	0.011	0.011	154
2pm	6/1/2021	CF4	Al	-0.001	BDL	155
3pm	6/1/2021	CF4	Al	0.012	0.012	156
4pm	6/1/2021	CF4	Al	0.007	0.007	157
5pm	6/1/2021	CF4	Al	0.009	0.009	158
6pm	6/1/2021	CF4	Al	0.011	0.011	159
7pm	6/1/2021	CF4	Al	0.01	0.01	160
8pm	6/1/2021	CF4	Al	0.008	0.008	161
9pm	6/1/2021	CF4	Al	0.011	0.011	162
10pm	6/1/2021	CF4	Al	0.009	0.009	163
11pm	6/1/2021	CF4	Al	0.012	0.012	164
12am	6/1/2021	CF4	Al	0.01	0.01	165
12am	6/1/2021	CF4	Fe	0.01	0.01	141
1am	6/1/2021	CF4	Fe	0.059	0.059	142
2am	6/1/2021	CF4	Fe	0.046	0.046	143
3am	6/1/2021	CF4	Fe	0.069	0.069	144
4am	6/1/2021	CF4	Fe	0.05	0.05	145
5am	6/1/2021	CF4	Fe	0.043	0.043	146
6am	6/1/2021	CF4	Fe	0.039	0.039	147
7am	6/1/2021	CF4	Fe	0.037	0.037	148

8am	6/1/2021	CF4	Fe	0.037	0.037	149
9am	6/1/2021	CF4	Fe	0.045	0.045	150
10am	6/1/2021	CF4	Fe	0.048	0.048	151
11am	6/1/2021	CF4	Fe	0.047	0.047	152
12pm	6/1/2021	CF4	Fe	0.057	0.057	153
1pm	6/1/2021	CF4	Fe	0.069	0.069	154
2pm	6/1/2021	CF4	Fe	0.049	0.049	155
3pm	6/1/2021	CF4	Fe	0.055	0.055	156
4pm	6/1/2021	CF4	Fe	0.055	0.055	157
5pm	6/1/2021	CF4	Fe	0.056	0.056	158
6pm	6/1/2021	CF4	Fe	0.062	0.062	159
7pm	6/1/2021	CF4	Fe	0.066	0.066	160
8pm	6/1/2021	CF4	Fe	0.059	0.059	161
9pm	6/1/2021	CF4	Fe	0.062	0.062	162
10pm	6/1/2021	CF4	Fe	0.058	0.058	163
11pm	6/1/2021	CF4	Fe	0.053	0.053	164
12am	6/1/2021	CF4	Fe	0.049	0.049	165
12am	6/1/2021	CF4	Mn	0.041	0.041	141
1am	6/1/2021	CF4	Mn	0.313	0.313	142
2am	6/1/2021	CF4	Mn	0.05	0.05	143
3am	6/1/2021	CF4	Mn	0.059	0.059	144
4am	6/1/2021	CF4	Mn	0.057	0.057	145
5am	6/1/2021	CF4	Mn	0.056	0.056	146
6am	6/1/2021	CF4	Mn	0.061	0.061	147
7am	6/1/2021	CF4	Mn	0.064	0.064	148
8am	6/1/2021	CF4	Mn	0.054	0.054	149
9am	6/1/2021	CF4	Mn	0.043	0.043	150
10am	6/1/2021	CF4	Mn	0.034	0.034	151
11am	6/1/2021	CF4	Mn	0.022	0.022	152
12pm	6/1/2021	CF4	Mn	0.018	0.018	153
1pm	6/1/2021	CF4	Mn	0.018	0.018	154
2pm	6/1/2021	CF4	Mn	0.011	0.011	155
3pm	6/1/2021	CF4	Mn	0.012	0.012	156
4pm	6/1/2021	CF4	Mn	0.016	0.016	157
5pm	6/1/2021	CF4	Mn	0.034	0.034	158
6pm	6/1/2021	CF4	Mn	0.024	0.024	159
7pm	6/1/2021	CF4	Mn	0.026	0.026	160
8pm	6/1/2021	CF4	Mn	0.07	0.07	161

9pm	6/1/2021	CF4	Mn	0.059	0.059	162
10pm	6/1/2021	CF4	Mn	0.049	0.049	163
11pm	6/1/2021	CF4	Mn	0.06	0.06	164
12am	6/1/2021	CF4	Mn	0.058	0.058	165
12am	6/1/2021	CF4	Ca	3.882	3.882	141
1am	6/1/2021	CF4	Ca	37.69	37.69	142
2am	6/1/2021	CF4	Ca	35.078	35.078	143
3am	6/1/2021	CF4	Ca	36.61	36.61	144
4am	6/1/2021	CF4	Ca	36.007	36.007	145
5am	6/1/2021	CF4	Ca	35.151	35.151	146
6am	6/1/2021	CF4	Ca	33.732	33.732	147
7am	6/1/2021	CF4	Ca	37.273	37.273	148
8am	6/1/2021	CF4	Ca	37.827	37.827	149
9am	6/1/2021	CF4	Ca	34.798	34.798	150
10am	6/1/2021	CF4	Ca	35.326	35.326	151
11am	6/1/2021	CF4	Ca	37	37	152
12pm	6/1/2021	CF4	Ca	34.081	34.081	153
1pm	6/1/2021	CF4	Ca	34.066	34.066	154
2pm	6/1/2021	CF4	Ca	28.927	28.927	155
3pm	6/1/2021	CF4	Ca	33.299	33.299	156
4pm	6/1/2021	CF4	Ca	30.132	30.132	157
5pm	6/1/2021	CF4	Ca	30.527	30.527	158
6pm	6/1/2021	CF4	Ca	32.329	32.329	159
7pm	6/1/2021	CF4	Ca	31.748	31.748	160
8pm	6/1/2021	CF4	Ca	31.821	31.821	161
9pm	6/1/2021	CF4	Ca	33.205	33.205	162
10pm	6/1/2021	CF4	Ca	33.375	33.375	163
11pm	6/1/2021	CF4	Ca	34.976	34.976	164
12am	6/1/2021	CF4	Ca	34.394	34.394	165
12am	6/1/2021	CF4	Mg	1.238	1.238	141
1am	6/1/2021	CF4	Mg	15.354	15.354	142
2am	6/1/2021	CF4	Mg	10.173	10.173	143
3am	6/1/2021	CF4	Mg	10.601	10.601	144
4am	6/1/2021	CF4	Mg	10.468	10.468	145
5am	6/1/2021	CF4	Mg	10.246	10.246	146
6am	6/1/2021	CF4	Mg	9.931	9.931	147
7am	6/1/2021	CF4	Mg	10.936	10.936	148
8am	6/1/2021	CF4	Mg	11.084	11.084	149

9am	6/1/2021	CF4	Mg	10.189	10.189	150
10am	6/1/2021	CF4	Mg	10.308	10.308	151
11am	6/1/2021	CF4	Mg	10.815	10.815	152
12pm	6/1/2021	CF4	Mg	9.806	9.806	153
1pm	6/1/2021	CF4	Mg	9.602	9.602	154
2pm	6/1/2021	CF4	Mg	8.062	8.062	155
3pm	6/1/2021	CF4	Mg	9.143	9.143	156
4pm	6/1/2021	CF4	Mg	8.23	8.23	157
5pm	6/1/2021	CF4	Mg	8.288	8.288	158
6pm	6/1/2021	CF4	Mg	8.747	8.747	159
7pm	6/1/2021	CF4	Mg	8.635	8.635	160
8pm	6/1/2021	CF4	Mg	8.701	8.701	161
9pm	6/1/2021	CF4	Mg	9.227	9.227	162
10pm	6/1/2021	CF4	Mg	9.276	9.276	163
11pm	6/1/2021	CF4	Mg	9.81	9.81	164
12am	6/1/2021	CF4	Mg	9.726	9.726	165

Appendix D: Loosely Sorbed Phosphorus Concentrations for Each Sampling Day

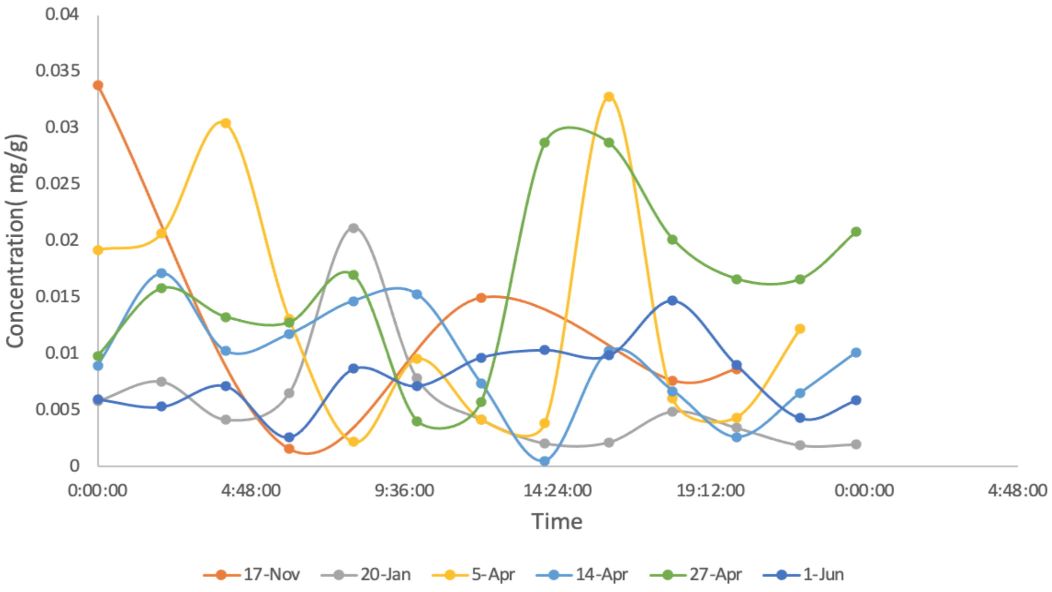


Figure D.0.7: Loosely Sorbed-P concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table D.0.7: Concentrations for Loosely Sorbed P in sediment for each of the 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

11/17/2020- Time	Location	mg/g	SRP ID
8:00:00 PM	CF4	0.008623539784	52
8:00:00 PM	CF1	0.000002755124532	49
6:00:00 PM	CF4	0.007639960326	48
6:00:00 PM	CF1* below detection limit	-0.0002093894644	45
12:00:00 PM	CF4	0.01496377011	28
12:00:00 PM	CF1	0.001044192197	25
6:00:00 AM	CF4	0.001564910734	16
6:00:00 AM	CF1	0.001005620454	13
12:00:00 AM	CF4	0.03383017412	4
12:00:00 AM	CF1 * below detection limit	-0.001000110205	1
1/21/20-Time	Location		
12:00:00 AM	CF4	0.00581836631	53

2:00:00 AM	CF4	0.007545693808	54
4:00:00 AM	CF4	0.004182288121	55
6:00:00 AM	CF4	0.006545999435	56
8:00:00 AM	CF4	0.02118248985	57
10:00:00 AM	CF4	0.007818429729	58
12:00:00 PM	CF4	0.004182288121	59
14:00:00 PM	CF4	0.002090975393	60
16:00:00 PM	CF4	0.002181887366	61
18:00:00 PM	CF4	0.00490958391	62
20:00:00 PM	CF4	0.003454992332	63
22:00:00 PM	CF4	0.001909151446	64
24:00:00 AM	CF4	0.002000400755	65
April 5,14-Time	Location		
4/5/21 12:00:00 AM	CF4	0.01922002963	66a
4/5/21 2:00:00 AM	CF4	0.02064621801	68
4/5/21 4:00:00 AM	CF4	0.0304617498	70
4/5/21 6:00:00 AM	CF4	0.01309580893	72
4/5/21 8:00:00 AM	CF4	0.002189662495	74
4/5/21 10:00:00 AM	CF4	0.0095722847	76
4/5/21 12:00:00 PM	CF4	0.004203104915	78
4/5/21 2:00:00 PM	CF4	0.003867531178	80
4/5/21 4:00:00 PM	CF4	0.03281076596	82
4/5/21 6:00:00 PM	CF4	0.006048760466	84
4/5/21 8:00:00 PM	CF4	0.004370891783	86
4/5/21 11:00:00 PM	CF4	0.01225687459	89
4/14/21 12:00:00 AM	CF4	0.008985030661	91
4/14/2021 2:00:00 AM	CF4	0.01712269377	93
4/14/2021 4:00:00 AM	CF4	0.01024343217	95
4/14/2021 6:00:00 AM	CF4	0.01175351399	97
4/14/2021 8:00:00 AM	CF4	0.01468978418	99
4/14/2021 10:00:00 AM	CF4	0.01527703822	101
4/14/2021 12:00:00 PM	CF4	0.007391055412	103

4/14/2021 2:00:00 PM	CF4	0.0005117938123	105
4/14/2021 4:00:00 PM	CF4	0.01024343217	107
4/14/2021 6:00:00 PM	CF4	0.006719907939	109
4/14/2021 8:00:00 PM	CF4	0.002609129666	111
4/14/2021 10:00:00 PM	CF4	0.006552121071	113
4/14/2021 12:00:00 AM	CF4	0.01015953874	115
4/27/21-Time	Location		
12:00:00 AM	CF4	0.00980626672	116
2:00:00 AM	CF4	0.01207237652	118
4:00:00 AM	CF4	0.009554476742	120
6:00:00 AM	CF4	0.009050896786	122
8:00:00 AM	CF4	0.01324739642	124
10:00:00 AM	CF4	0.0003221775476	126
12:00:00 PM	CF4	0.002000777401	128
2:00:00 PM	CF4	0.02499759539	130
4:00:00 PM	CF4	0.02499759539	132
6:00:00 PM	CF4	0.01643673614	134
8:00:00 PM	CF4	0.01291167645	136
10:00:00 PM	CF4	0.01291167645	138
12:00:00 AM	CF4	0.01710817608	140
6/1/21-Time	Location		
0:00	CF4	0.005992600746	141
2:00	CF4	0.005320535491	143
4:00	CF4	0.007168714941	145
6:00	CF4	0.002632274473	147
8:00	CF4	0.008680861764	149
10:00	CF4	0.007168714941	151
12:00	CF4	0.009688959646	153
14:00	CF4	0.0103610249	155
16:00	CF4	0.00985697596	157
18:00	CF4	0.01472944906	159
20:00	CF4	0.009016894391	161

22:00	CF4	0.004312437609	163
12:00:00 AM	CF4	0.005908592589	165

Appendix E: Residual Phosphorous, Extractable Phosphorous (SRP), and Total Phosphorous (TP) on the Sediments

Table E.0.1: Residual and Extractable P Data for Each Sampling Day

Date, Time	TP (Total Phosphorous) ID	Extractable P-Ca	TP	Percent of Extractable phosphorous
1/20/21-12am	14	0.03995799	1.02793876	3.88719583
1/20/21-2am	15	0.72144485	1.60045126	45.0775897
1/20/21-4am	16	1.73792718	3.53199769	49.2052184
1/20/21-6am	17	1.04413766	2.00688837	52.0276897
1/20/21-8am	18	1.49187392	3.27953418	45.4904215
1/20/21-10am	19	1.91944188	3.88418547	49.4168442
1/20/21-12pm	20	2.09692292	3.28362164	63.8600653
1/20/21-2pm	21	0.85455563	1.71988515	49.686785
1/20/21-4pm	22	0.81018537	1.52653153	53.073609
1/20/21-6pm	23	0.98363276	1.92202817	51.1768126

1/20/21-8pm	24	0.81421903	1.69643057	47.9960128
1/20/21-10pm	25	0.10832853	0.26807065	40.4104403
1/20(21)/21-12pm	26	0.23135516	0.48851848	47.3585275
11/17/20-12am	64	0.75734451	0.86479437	87.5750975
11/17/20-6am	66	1.2704695	1.44597093	87.8627275
11/17/20-12pm	68	1.49389267	1.6980474	87.977089
11/17/20-6pm	70	1.36026637	1.55009445	87.7537733
11/17/20-8pm	72	0.84072732	0.95462417	88.0689331
4/5/21-12am	105	0.152078554	0.3307644514	45.9779016
4/5/21-2am	106	0.029732294	0.07861049913	37.82229388
4/5/21-4am	107	0.805249718	1.658615103	48.54952284
4/5/21-6am	108	0.305998043	0.6561582994	46.6347897
4/5/21-8am	109	0.19154509	0.4167053464	45.96655446
4/5/21-10am	110	0.850636234	1.758488798	48.37313919

4/5/21-12pm	111	0.132345286	0.2893965681	45.73146354
4/5/21-2pm	112	0.152078554	0.3299631694	46.08955426
4/5/21-4pm	113	0.169970887	2.975259349	5.712809106
4/5/21-6pm	114	0.114717737	2.254140814	5.08920012
4/5/21-8pm	115	0.523063989	1.103192194	47.41367749
4/5/21-11pm	116	1.006529049	2.048195716	49.14222998
4/14/21-12am	166	0.388877768	0.8199675116	47.42599707
4/14/21-2am	167	0.444130917	0.9377206606	47.36281663
4/14/21-4am	168	0.309944696	0.6721241832	46.11420088
4/14/21-6am	169	0.353357886	0.7556014757	46.76511327
4/14/21-8am	170	0.349411232	0.7428407192	47.03716732
4/14/21-10am	171	0.337571271	0.712571271	47.37368524
4/14/21-12pm	172	0.270478161	0.5709589302	47.3726124
4/14/21-2pm	173	0.065252176	0.1453803811	44.88375632

4/14/21-4pm	174	0.345464578	0.7308812447	47.26685498
4/14/21-6pm	175	0.286264775	0.6027711853	47.49144982
4/14/21-8pm	176	0.090905424	0.2054887573	44.2386363
4/14/21-10pm	177	0.396771075	0.8126364596	48.82516288
4/14(15)/21-12am	178	0.5605572	1.171134123	47.86447504
4/27/21-12am	230	0.377238601	0.8243539856	45.76172465
4/27/21-2am	231	0.425570107	0.9055380557	46.99638014
4/27/21-4am	232	0.355972738	0.7662291483	46.45773902
4/27/21-6am	233	0.29024189	0.6299854797	46.07120312
4/27/21-8am	234	0.255443206	0.5511162829	46.35014677
4/27/21-10am	235	0.019585457	0.05804699546	33.74069036
4/27/21-12pm	236	0.056317402	0.1404520174	40.09725389
4/27/21-2pm	237	0.004119375	0.02495270833	16.50872901

4/27/21-4pm	238	0.309574493	0.668548852	46.30544082
4/27/21-6pm	239	0.526099639	1.115843229	47.1481679
4/27/21-8pm	240	0.522233119	1.091143375	47.86109056
4/27/21-10pm	241	0.394637943	0.8353430712	47.24261882
4/27 (28)/21-12am	242	0.357905999	0.7625534349	46.93520252
6/1/21-12am	294	0.32456352	0.653089161	49.69666309
6/1/21-2am	295	0.341267	0.6802093077	50.17088066
6/1/21-4am	296	0.3621463513	0.7387489154	49.02157468
6/1/21-6am	297	0.12829763	0.2725283992	47.07679286
6/1/21-8am	298	0.31203591	0.639760269	48.77388064
6/1/21-10am	299	0.19928742	0.4100245995	48.60377164
6/1/21-12am	300	0.28280482	0.5704650764	49.57443176
6/1/21-2pm	301	0.27027721	0.5250849023	51.47304918
6/1/21-4pm	302	0.28280482	0.5768753328	49.02355915

6/1/21-6pm	303	0.2577496	0.5285829333	48.76237649
6/1/21-8pm	304	0.30786004	0.6275715785	49.0557652
6/1/21-10pm	305	0.3746739611	0.7600906278	49.29332733
6/1/21-12pm	306	0.53474898	1.062793852	50.31540022
			Average	48.09966835

Date, Time	TP ID	NaOH-Extractable P	Total P	Extractable P
1/20/21-12am	2	0.11790229	0.13616877	86.5854145
1/20/21-2am	1	0.11237324	0.288591	38.9385796
1/20/21-4am	3	0.10131513	0.24099994	42.0394828
1/20/21-6am	4	0.07919892	0.18987227	41.7116813
1/20/21-8am	5	0.10131513	0.24529794	41.3028869
1/20/21-10am	6	0.09025702	0.23316533	38.7094521
1/20/21-12pm	7	0.09578608	0.18067146	53.0167159

1/20/21-2pm	8	0.09025702	0.21704785	41.5839277
1/20/21-4pm	9	0.09025702	0.31805072	28.3781854
1/20/21-6pm	10	0.07919892	0.19954275	39.6901984
1/20/21-8pm	11	0.10684418	0.26157198	40.8469534
1/20/21-10pm	12	0.07366986	0.16607674	44.3589285
1/20(21)/21-12pm	13	0.06814081	0.15410069	44.2183656
11/17/20-12am	54	0.12788618	0.27939047	45.7732771
11/17/20-6am	56	0.07833376	0.19115611	40.9789468
11/17/20-12pm	58	0.10001294	0.25151724	39.7638516
11/17/20-6pm	60	0.0829793	0.22803661	36.3885873
11/17/20-8pm	62	0.10156146	0.26918323	37.729488
4/5/21-12am	93	0.0070367	0.02626746923	26.78864849
4/5/21-2am	94	0.0010801	0.01550317692	6.966959129

4/5/21-4am	95	0.0844728	0.2022612615	41.76420109
4/5/21-6am	96	0.0129933	0.06467599231	20.08983478
4/5/21-8am	97	0.0249066	0.06457006154	38.57298477
4/5/21-10am	98	0.0725596	0.1975596	36.7279545
4/5/21-12pm	99	0.0129933	0.03823368462	33.98390746
4/5/21-2pm	100	0.01895	0.05140192308	36.86632497
4/5/21-4pm	101	0.0129933	0.7173202231	1.811366748
4/5/21-6pm	102	0.0308632	1.131824738	2.72685328
4/5/21-8pm	103	0.0606463	0.1375693769	44.08415692
4/5/21-11pm	104	0.105321	0.3060421538	34.41388667
4/14/21-12am	153	0.0427765	0.1100841923	38.85798597
4/14/21-2am	154	0.01895	0.07784423077	24.34348675
4/14/21-4am	155	0.01895	0.06342115385	29.87962036
4/14/21-6am	156	0.0368198	0.08970441538	41.04569417

4/14/21-8am	157	0.0427765	0.09085342308	47.08298108
4/14/21-10am	158	0.0397981	0.1179231	33.74919757
4/14/21-12pm	159	0.0308632	0.1222093538	25.25436804
4/14/21-2pm	160	0.01895	0.05260384615	36.02398187
4/14/21-4pm	161	0.0308632	0.08254589231	37.38914092
4/14/21-6pm	162	0.0427765	0.1076803462	39.72544808
4/14/21-8pm	163	0.0129933	0.04183945385	31.05513769
4/14/21-10pm	164	0.0487331	0.1148388692	42.43606745
4/14(15)/21-12am	165	0.0487331	0.1520984846	32.04049016
4/27/21-12am	217	0.153456235	0.3205235427	47.87674369
4/27/21-2am	218	0.214971026	0.4577594875	46.96156647
4/27/21-4am	219	0.036285206	0.1035928983	35.02673117
4/27/21-6am	220	0.033355931	0.08383670023	39.78678897

4/27/21-8am	221	0.045073033	0.1268038022	35.54549012
4/27/21-10am	222	0.009921725	0.05920057115	16.75950891
4/27/21-12pm	223	0.004063173	0.02569778838	15.81137232
4/27/21-2pm	224	0.045073033	0.1027653407	43.86015041
4/27/21-4pm	225	0.197395371	0.3993184479	49.43307078
4/27/21-6pm	226	0.056790136	0.1313093668	43.24911269
4/27/21-8pm	227	0.027497379	0.07196853285	38.20750252
4/27/21-10pm	228	0.027497379	0.06836276362	40.22274341
4/27(28)/21-12am	229	0.045073033	0.09675572531	46.58435752
6/1/21-12am	281	0.05866069774	0.2257280054	25.98733712
6/1/21-2am	282	0.04148784561	0.09557438407	43.40895943
6/1/21-4am	283	0.04759273251	0.1088908094	43.7068406
6/1/21-6am	284	0.01349751514	0.04114174591	32.80734652

6/1/21-8am	285	0.03999042053	0.1012884974	39.48169983
6/1/21-10am	286	0.02893251219	0.07340366604	39.41562289
6/1/21-12am	287	0.02755027365	0.06240604288	44.14680435
6/1/21-2pm	288	0.03100587001	0.06946740847	44.63369325
6/1/21-4pm	289	0.03077549692	0.07164088153	42.95800981
6/1/21-6pm	290	0.008429307158	0.03607353793	23.36700984
6/1/21-8pm	291	0.02501616966	0.05867001581	42.63876413
6/1/21-10pm	292	0.02893251219	0.08181712758	35.362415
6/1/21-12pm	293	0.034231093	0.09432724685	36.28971919
			Average	37.09021685
	TP ID	BD-Extractable P	Total P	percent Extractable P
1/20/21-12am	27	0.04332773	0.10564865	41.0111539

1/20/21-2am	28	0.03535193	0.09767285	36.1942278
1/20/21-4am	29	0.02471754	0.07629347	32.3979767
1/20/21-6am	30	0.01940035	0.08064676	24.0559501
1/20/21-8am	31	0.04598633	0.11905223	38.6270186
1/20/21-10am	32	0.02471754	0.07306998	33.8272195
1/20/21-12pm	33	0.04066913	0.10191555	39.9047358
1/20/21-2pm	34	0.03535193	0.08800236	40.1715733
1/20/21-4pm	35	0.06725511	0.1521405	44.2059232
1/20/21-6pm	36	0.03003474	0.08483416	35.4040591
1/20/21-8pm	37	0.06725511	0.151066	44.52035
1/20/21-10pm	38	0.00876595	0.04100091	21.3798978
1/20(21)/21-12pm	39	0.01674175	0.06401968	26.1509367
11/17/20-12am	74	0.05089432	0.13470521	37.7819989

11/17/20-6am	76	0.05851096	0.15951382	36.6808066
11/17/20-12pm	78	0.00942597	0.03736293	25.2281302
11/17/20-6pm	80	0.03650734	0.10849875	33.6477084
11/17/20-8pm	82	0.02465924	0.08160767	30.2168197
4/5/21-12am	117	0.034199534	0.09309376477	36.73665372
4/5/21-2am	118	0.0137421	0.04138633077	33.20444153
4/5/21-4am	119	0.2738437	0.5851417769	46.79954684
4/5/21-6am	120	0.1247967	0.2870563154	43.4746401
4/5/21-8am	121	0.0780369	0.1886138231	41.37390289
4/5/21-10am	122	0.2738437	0.5851417769	46.79954684
4/5/21-12pm	123	0.0605019	0.1542519	39.22279077
4/5/21-2pm	124	0.037122	0.1020258462	36.38489794
4/5/21-4pm	125	0.0020521	0.6871482538	0.2986400662
4/5/21-6pm	126	0.0078971	0.9213586385	0.8571146642
4/5/21-8pm	127	0.2124714	0.4528560154	46.91809157

4/5/21-11pm	128	0.1598666	0.3533762154	45.23977366
4/14/21-12am	179	0.1452542	0.3195330462	45.45827161
4/14/21-2am	180	0.1189517	0.2691920846	44.18840924
4/14/21-4am	181	0.0897268	0.2135248769	42.02170787
4/14/21-6am	182	0.0897268	0.2171306462	41.32387647
4/14/21-8am	183	0.1014168	0.2312244923	43.86075151
4/14/21-10am	184	0.1364867	0.3143713154	43.41576134
4/14/21-12pm	185	0.2095489	0.4667604385	44.89431467
4/14/21-2pm	186	0.0517345	0.1274556538	40.59019623
4/14/21-4pm	187	0.0838819	0.2076799769	40.38997945
4/14/21-6pm	188	0.1306417	0.2868917	45.53693955
4/14/21-8pm	189	0.0078971	0.04515671538	17.48820731
4/14/21-10pm	190	0.1306417	0.3049205462	42.84450545

4/14(15)/21-12am	191	0.2066264	0.4578283231	45.13185174
4/27/21-12am	243	0.294657489	0.6348017198	46.41724807
4/27/21-2am	244	0.515944535	1.097675304	47.0033837
4/27/21-4am	245	0.113604452	0.2686525289	42.28676069
4/27/21-6am	246	0.107856736	0.2556932745	42.18207781
4/27/21-8am	247	0.125099883	0.2897633445	43.17312226
4/27/21-10am	248	0.013019431	0.03825981562	34.02899567
4/27/21-12pm	249	0.021641004	0.07452561938	29.03834169
4/27/21-2pm	250	0.222811046	0.4908398922	45.39383403
4/27/21-4pm	251	0.426854945	0.9292587912	45.93499131
4/27/21-6pm	252	0.159586176	0.3651150222	43.70846619
4/27/21-8pm	253	0.096361305	0.2189574588	44.00914475
4/27/21-10pm	254	0.113604452	0.2241813751	50.67524096

4/27 (28)/21-12am	255	0.099235163	0.2290428553	43.32602424
6/1/21-12am	307	0.1032513774	0.1152706082	89.57303084
6/1/21-2am	308	0.11202382	0.1204372815	93.01423826
6/1/21-4am	309	0.1178721084	0.1250836469	94.23462727
6/1/21-6am	310	0.07693406	0.08174175231	94.11843743
6/1/21-8am	311	0.17050674	0.1789202015	95.29764584
6/1/21-10am	312	0.14126528	0.1532845108	92.15887456
6/1/21-12am	313	0.11787211	0.1214778792	97.03174829
6/1/21-2pm	314	0.13541699	0.1462342977	92.60275608
6/1/21-4pm	315	0.1997482019	0.2093635865	95.40732714
6/1/21-6pm	316	0.1383411318	0.1467545933	94.26698589
6/1/21-8pm	317	0.13541699	0.1414266054	95.75071793
6/1/21-10pm	318	0.14126528	0.1472748954	95.91945703
6/1/21-12pm	319	0.15881016	0.1684255446	94.29101765
			Average	48.64791007

Appendix F: Total Phosphorus Concentration and Phosphorous Loading in Stream (mg/L/h)

Table F.0.2: Total Phosphorous and Phosphorous Loading for Certain Sampling days

Name	Date, Time	TP Results (mg/L)	SRP (mg/L)	SRP/TP Ratio	Particulate P	TP Loading (mg/L)
CF4_11/17/20_1	17-Nov,12am	0.418	0.05654673	0.13527925	0.36145327	2.6752
CF4_11/17/20_7	17-Nov,6am	0.239	0.0615409	0.25749331	0.1774591	1.2667
CF4_11/17/20_13	17-Nov, 12pm	0.41	0.0615409	0.15009976	0.3484591	1.763
CF4_11/17/20_6	17-Nov, 6pm	0.713	0.13137775	0.18426053	0.58162225	2.4242
CF4_11/17/20_8	17-Nov, 8pm	0.391	0.13468412	0.34446067	0.25631588	1.3294
CF4_1/20/21_000	20-Jan, 12am	0.153	0.07988728	0.52213906	0.07311272	2.22615
CF4_1/20/21_400	20-Jan, 4am	0.296	0.09009092	0.30436123	0.20590908	3.19088

CF4_1/20/21_1000	20-Jan, 10am	0.157	0.07648606	0.48717236	0.08051394	1.97349
CF4_1/20/21_1600	20-Jan,4pm	0.124	0.08158788	0.65796681	0.04241212	2.36468
CF4_1/20/21_2000	20-Jan, 8pm	0.196	0.08839032	0.450971	0.10760968	3.27516
CF4_1/20/21_2100	20-Jan	0.253	N/A	N/A	0.253	0
CF4_4/5/21_000	4/5/21, 12am	0.123	0.03961118	0.32204213	0.08338882	0.79089
CF4_4/5/21_400	4/5/21,4am	0.0713	0.03788436	0.53133751	0.03341564	0.376464
CF4_4/5/21_800	4/5/21, 8am	0.0675	0.03788436	0.56124984	0.02961564	0.3564
CF4_4/5/21_1400	4/5/21, 2pm	0.102	0.04997209	0.48992244	0.05202791	0.53856
CF4_4/5/21_1700	4/5/21, 5pm	0.096	0.05169891	0.53853027	0.04430109	0.41088

CF4_4/5/21_2000	4/5/21, 8pm	0.214	0.04306482	0.20123747	0.17093518	0.91592
CF4_4/5/21_2300	4/5/21, 11pm	0.103	0.03961118	0.38457458	0.06338882	0.44084
CF4_4/14/21_000	4/14/21, 12am	0.357	0.02157629	0.06043778	0.33542371	0.72471
CF4_4/14/21_500	4/14/21, 5am	0.0871	0.02331828	0.26771853	0.06378172	0.176813
CF4_4/14/21_800	4/14/21, 8am	0.0546	0.02854427	0.52278887	0.02605573	0.110838
CF4_4/14/21_1100	4/14/21, 11am	0.116	0.03725425	0.32115735	0.07874575	0.30856
CF4_4/14/21_1400	4/14/21, 2pm	0.197	0.05641621	0.2863767	0.14058379	0.39991
CF4_4/14/21_1800	4/14/21, 6pm	0.0741	0.03551226	0.47924773	0.03858774	0.150423
CF4_4/14/21_2100	4/14/21, 9pm	0.0842	0.02331828	0.27693924	0.06088172	0.170926

CF4_4/14/21_2400	4/14/21, 12am	0.174	0.02157629	0.12400165	0.15242371	0.35322
CF4_4/27/21_000	4/27/21, 12am	0.0555	0.02303129	0.41497816	0.03246871	0.05994
CF4_4/27/21_500	4/27/21, 5am	0.0998	0.03186907	0.31932931	0.06793093	0.107784
CF4_4/27/21_800	4/27/21, 8am	0.0744	0.02479884	0.33331779	0.04960116	0.080352
CF4_4/27/21_1300	4/27/21, 1pm	0.104	0.03717173	0.3574205	0.06682827	0.11232
CF4_4/27/21_1700	4/27/21, 5pm	0.151	0.06191751	0.41004974	0.08908249	0.16308
CF4_4/27/21_1800	4/27/21, 10pm	0.117	0.03893929	0.33281443	0.07806071	0.12636
CF4_4/27/21_2200	4/27/21, 10pm	0.315	0.02479884	0.07872649	0.29020116	0.3402
CF4_4/27/21_2400	4/27/21, 12am	0.117	0.01949618	0.16663399	0.09750382	0.12636

CF4_6/1/21_0:00	1-Jun, 12am	7.16	7.43730565	1.03872984	-0.2773056	0.5012
CF4_6/1/21_1:00	1-Jun, 1am	15.6	0	0	15.6	2.34
CF4_6/1/21_3:00	1-Jun, 3am	3.53	0.00807283	0.00228692	3.52192717	0.5295
CF4_6/1/21_5:00	1-Jun, 5am	0.132	0.0428079	0.32430225	0.0891921	0.0198
CF4_6/1/21_9:00	1-Jun, 9am	0.443	0.00807283	0.0182231	0.43492717	0.06645
CF4_6/1/21_13:00	1-Jun, 1pm	0.177	0.0560403	0.31661188	0.1209597	0.01239
CF4_6/1/21_17:00	1-Jun, 5pm	0.232	0.07754296	0.33423691	0.15445704	0.01624
CF4_6/1/21_21:00	1-Jun, 9pm	0.289	0.06596461	0.22825124	0.22303539	0.02023
CF4_6/1/21_24:00	1-Jun, 12am	0.135	0.07092676	0.5253834	0.06407324	0.00945

Appendix G: Full Concentration Data for Extractable P concentration (mg/g) and Soluble Reactive Phosphorous (SRP) stream Concentration (ppm)

Extractable P Data

Table G.0.3: Concentration (mg/g) of Extractable P bound to different metals throughout 6 sampling days in the 2021 Water Year

DATE_TIME	Location	Extractable-P-Ca (mg/g)	Extractable-P-Fe (mg/g)	Extractable-P-Al (mg/g)
11/17/20 0:00	CF4	0.7573445	0.050894321	0.127886176
11/17/20 6:00	CF4	1.2704695	0.058510957	0.078333761
11/17/20 12:00	CF4	1.4938927	0.009425969	0.100012942
11/17/20 18:00	CF4	1.3602664	0.036507341	0.0829793
11/17/20 20:00	CF4	0.8407273	0.024659241	0.101561455
1/20/21 0:00	CF4	0.03995799	0.043327729	0.117902291
1/20/21 2:00	CF4	0.72144485	0.035351934	0.112373237
1/20/21 4:00	CF4	1.73792718	0.024717542	0.10131513
1/20/21 6:00	CF4	1.04413766	0.019400345	0.079198915
1/20/21 8:00	CF4	1.49187392	0.045986327	0.10131513
1/20/21 10:00	CF4	1.91944188	0.024717542	0.090257023
1/20/21 12:00	CF4	2.09692292	0.040669131	0.095786076
1/20/21 14:00	CF4	0.85455563	0.035351934	0.090257023
1/20/21 16:00	CF4	0.81018537	0.067255112	0.090257023
1/20/21 18:00	CF4	0.98363276	0.030034738	0.079198915
1/20/21 20:00	CF4	0.81421903	0.067255112	0.106844184
1/20/21 22:00	CF4	0.10832853	0.008765953	0.073669862
1/21/21 0:00	CF4	0.23135516	0.016741747	0.068140808
4/5/21 0:00	CF4	0.034199534	0.152078554	0.0070367
4/5/21 2:00	CF4	0.0137421	0.029732294	0.0010801
4/5/21 4:00	CF4	0.2738437	0.805249718	0.0844728
4/5/21 6:00	CF4	0.1247967	0.305998043	0.0129933
4/5/21 8:00	CF4	0.0780369	0.19154509	0.0249066
4/5/21 10:00	CF4	0.2738437	0.850636234	0.0725596
4/5/21 12:00	CF4	0.0605019	0.132345286	0.0129933

4/5/21 14:00	CF4	0.037122	0.152078554	0.01895
4/5/21 16:00	CF4	0.0020521	0.169970887	0.0129933
4/5/21 18:00	CF4	0.0078971	0.114717737	0.0308632
4/5/21 20:00	CF4	0.2124714	0.523063989	0.0606463
4/5/21 23:00	CF4	0.1598666	1.006529049	0.105321
4/14/21 0:00	CF4	0.1452542	0.388877768	0.0427765
4/14/21 2:00	CF4	0.1189517	0.444130917	0.01895
4/14/21 4:00	CF4	0.0897268	0.309944696	0.01895
4/14/21 6:00	CF4	0.0897268	0.353357886	0.0368198
4/14/21 8:00	CF4	0.1014168	0.349411232	0.0427765
4/14/21 10:00	CF4	0.1364867	0.337571271	0.0397981
4/14/21 12:00	CF4	0.2095489	0.270478161	0.0308632
4/14/21 14:00	CF4	0.0517345	0.065252176	0.01895
4/14/21 16:00	CF4	0.0838819	0.345464578	0.0308632
4/14/21 18:00	CF4	0.1306417	0.286264775	0.0427765
4/14/21 20:00	CF4	0.0078971	0.090905424	0.0129933
4/14/21 22:00	CF4	0.1306417	0.396771075	0.0487331
4/15/21 0:00	CF4	0.2066264	0.5605572	0.0487331
4/27/21 0:00	CF4	0.294657489	0.377238601	0.153456235
4/27/21 2:00	CF4	0.515944535	0.425570107	0.214971026
4/27/21 4:00	CF4	0.113604452	0.355972738	0.036285206
4/27/21 6:00	CF4	0.107856736	0.29024189	0.033355931
4/27/21 8:00	CF4	0.125099883	0.255443206	0.045073033
4/27/21 10:00	CF4	0.013019431	0.019585457	0.009921725
4/27/21 12:00	CF4	0.021641004	0.056317402	0.004063173
4/27/21 14:00	CF4	0.222811046	0.004119375	0.045073033
4/27/21 16:00	CF4	0.426854945	0.309574493	0.197395371
4/27/21 18:00	CF4	0.159586176	0.526099639	0.056790136
4/27/21 20:00	CF4	0.096361305	0.522233119	0.027497379
4/27/21 22:00	CF4	0.113604452	0.394637943	0.027497379
4/28/21 0:00	CF4	0.099235163	0.357905999	0.045073033
6/1/21 0:00	CF4	0.3245635	0.103251377	0.058660698
6/1/21 2:00	CF4	0.341267	0.11202382	0.041487846
6/1/21 4:00	CF4	0.3621464	0.117872108	0.047592733
6/1/21 6:00	CF4	0.1282976	0.07693406	0.013497515

6/1/21 8:00	CF4	0.3120359	0.17050674	0.039990421
6/1/21 10:00	CF4	0.1992874	0.14126528	0.028932512
6/1/21 12:00	CF4	0.2828048	0.11787211	0.027550274
6/1/21 14:00	CF4	0.2702772	0.13541699	0.03100587
6/1/21 16:00	CF4	0.2828048	0.199748202	0.030775497
6/1/21 18:00	CF4	0.2577496	0.138341132	0.008429307
6/1/21 20:00	CF4	0.30786	0.13541699	0.02501617
6/1/21 22:00	CF4	0.374674	0.14126528	0.028932512
6/2/21 0:00	CF4	0.534749	0.15881016	0.034231093

SRP Stream Data

Table G.0.4: SRP concentration in stream water at MFC for 6 sampling ideas throughout the 2021 Water Year

Date, Time	Location	Concentration (ppm)
11/17/20-0:00	CF1	0.05821145288
11/17/20-0:00	CF4	0.05654672825
11/17/20-6:00	CF1	0.01159916329
11/17/20-6:00	CF4	0.06154090214
11/17/20-12:00	CF1	0.04988782974
11/17/20-12:00	CF4	0.06154090214
11/17/20-18:00	CF1	0.09500769771
11/17/20-18:00	CF4	0.131377755
11/17/20-20:00	CF1	0.09831406655
11/17/20-20:00	CF4	0.1346841238
1/20/21 12:00:00 AM	CF4	0.07988727627
1/20/21 2:00:00 AM	CF4	0.08158788435
1/20/21 4:00:00 AM	CF4	0.09009092474
1/20/21 6:00:00 AM	CF4	0.07988727627
1/20/21 8:00:00 AM	CF4	0.0781866682
1/20/21 10:00:00 AM	CF4	0.07648606012
1/20/21 12:00:00 PM	CF4	0.0781866682
1/20/21 2:00:00 PM	CF4	0.0781866682

1/20/21 4:00:00 PM	CF4	0.08158788435
1/20/21 6:00:00 PM	CF4	0.0781866682
1/20/21 8:00:00 PM	CF4	0.08839031666
1/20/21 10:00:00 PM	CF4	0.08158788435
1/20/21 12:00:00 AM	CF4	0.07988727627
4/5/21 12:00:00 AM	CF4	0.03961118204
4/5/21 1:00:00 AM	CF4	0.03788436428
4/5/21 2:00:00 AM	CF4	0.03788436428
4/5/21 3:00:00 AM	CF4	0.0413379998
4/5/21 4:00:00 AM	CF4	0.03788436428
4/5/21 5:00:00 AM	CF4	0.03788436428
4/5/21 6:00:00 AM	CF4	0.0413379998
4/5/21 7:00:00 AM	CF4	0.03961118204
4/5/21 8:00:00 AM	CF4	0.03788436428
4/5/21 9:00:00 AM	CF4	0.0413379998
4/5/21 10:00:00 AM	CF4	0.0413379998
4/5/21 11:00:00 AM	CF4	0.04479163532
4/5/21 12:00:00 PM	CF4	0.04651845308
4/5/21 1:00:00 PM	CF4	0.04651845308
4/5/21 2:00:00 PM	CF4	0.0499720886
4/5/21 3:00:00 PM	CF4	0.05169890636
4/5/21 4:00:00 PM	CF4	0.0499720886
4/5/21 5:00:00 PM	CF4	0.05169890636
4/5/21 6:00:00 PM	CF4	0.0499720886
4/5/21 7:00:00 PM	CF4	0.04651845308
4/5/21 8:00:00 PM	CF4	0.04306481756
4/5/21 9:00:00 PM	CF4	0.03961118204
4/5/21 10:00:00 PM	CF4	0.0413379998
4/5/21 11:00:00 PM	CF4	0.03961118204
4/14/21 12:00:00 AM	CF4	0.02157628762
4/14/21 1:00:00 AM	CF4	0.01983429148
4/14/21 2:00:00 AM	CF4	0.01983429148

4/14/21 3:00:00 AM	CF4	0.02854427219
4/14/21 4:00:00 AM	CF4	0.02157628762
4/14/21 5:00:00 AM	CF4	0.02331828376
4/14/21 6:00:00 AM	CF4	0.02331828376
4/14/21 7:00:00 AM	CF4	0.02331828376
4/14/21 8:00:00 AM	CF4	0.02854427219
4/14/21 9:00:00 AM	CF4	0.0250602799
4/14/21 10:00:00 AM	CF4	0.03028626833
4/14/21 11:00:00 AM	CF4	0.03725425289
4/14/21 12:00:00 PM	CF4	0.03202826447
4/14/21 1:00:00 PM	CF4	0.0250602799
4/14/21 2:00:00 PM	CF4	0.05641621045
4/14/21 3:00:00 PM	CF4	0.03202826447
4/14/21 4:00:00 PM	CF4	0.03899624903
4/14/21 5:00:00 PM	CF4	0.03202826447
4/14/21 6:00:00 PM	CF4	0.03551225675
4/14/21 7:00:00 PM	CF4	0.03202826447
4/14/21 8:00:00 PM	CF4	0.0250602799
4/14/21 9:00:00 PM	CF4	0.02331828376
4/14/21 10:00:00 PM	CF4	0.02331828376
4/14/21 11:00:00 PM	CF4	0.02331828376
4/14/21 0:00:00	CF4	0.02157628762
4/27/21 12:00:00 AM	CF4	0.02303128773
4/27/21 1:00:00 AM	CF4	0.02303128773
4/27/21 2:00:00 AM	CF4	0.02303128773
4/27/21 3:00:00 AM	CF4	0.02479884329
4/27/21 4:00:00 AM	CF4	0.02656639886
4/27/21 5:00:00 AM	CF4	0.03186906554
4/27/21 6:00:00 AM	CF4	0.03010150998
4/27/21 7:00:00 AM	CF4	0.03010150998
4/27/21 8:00:00 AM	CF4	0.02479884329
4/27/21 9:00:00 AM	CF4	0.02833395442

4/27/21 10:00:00 AM	CF4	0.03010150998
4/27/21 11:00:00 AM	CF4	0.03010150998
4/27/21 12:00:00 PM	CF4	0.0336366211
4/27/21 1:00:00 PM	CF4	0.03717173223
4/27/21 2:00:00 PM	CF4	0.04247439891
4/27/21 3:00:00 PM	CF4	0.04424195448
4/27/21 4:00:00 PM	CF4	0.04600951004
4/27/21 5:00:00 PM	CF4	0.0619175101
4/27/2021 6:00:00 PM	CF4	0.03893928779
4/27/2021 7:00:00 PM	CF4	0.0336366211
4/27/2021 8:00:00 PM	CF4	0.02479884329
4/27/2021 9:00:00 PM	CF4	0.02303128773
4/27/2021 10:00:00 PM	CF4	0.02479884329
4/27/2021 11:00:00 PM	CF4	0.02303128773
4/27/2021 0:00:00	CF4	0.01949617661
6/1/21 12:00:00 AM	CF4	7.437305646
6/1/21 1:00:00 AM	CF4	BDL
6/1/21 2:00:00 AM	CF4	0.03453764321
6/1/21 3:00:00 AM	CF4	0.008072831424
6/1/21 4:00:00 AM	CF4	0.04115384615
6/1/21 5:00:00 AM	CF4	0.04280789689
6/1/21 6:00:00 AM	CF4	0.04115384615
6/1/21 7:00:00 AM	CF4	0.03949979542
6/1/21 8:00:00 AM	CF4	0.03288359247
6/1/21 9:00:00 AM	CF4	0.008072831424
6/1/21 10:00:00 AM	CF4	0.03784574468
6/1/21 11:00:00 AM	CF4	0.04115384615
6/1/21 12:00:00 PM	CF4	0.05273220131
6/1/21 1:00:00 PM	CF4	0.05604030278
6/1/21 2:00:00 PM	CF4	0.05934840426
6/1/21 3:00:00 PM	CF4	0.07423486088
6/1/21 4:00:00 PM	CF4	0.0659646072

6/1/21 5:00:00 PM	CF4	0.07754296236
6/1/21 6:00:00 PM	CF4	0.07258081015
6/1/21 7:00:00 PM	CF4	0.07423486088
6/1/21 8:00:00 PM	CF4	0.06927270867
6/1/21 9:00:00 PM	CF4	0.0659646072
6/1/21 10:00:00 PM	CF4	0.07258081015
6/1/21 11:00:00 PM	CF4	0.07588891162
6/1/21 0:00:00	CF4	0.07092675941

Appendix H: Sediment Metal Concentrations

Eight of the samples analyzed for metals in the stream had a 2 fold dilution. These samples are denoted by yellow highlights and were the only samples that had to be corrected. A few of the samples are at location CF4, however, these were not used in correlations or graphs in the main document. Aluminum was below the detection limit in a few samples. These are denoted by three asterisks and have BDL (below detection limit).

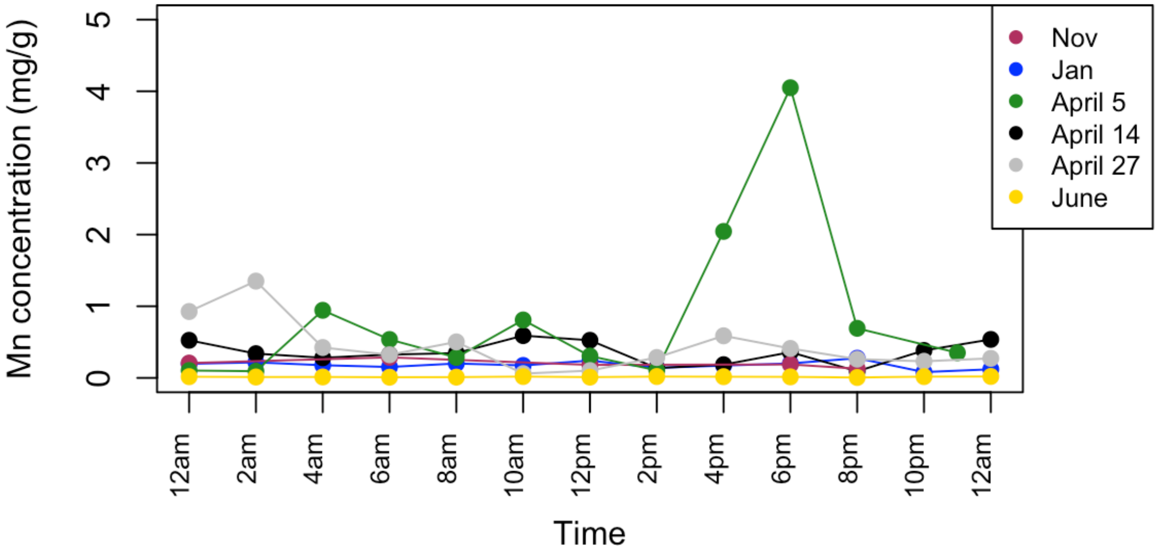


Figure H.0.1: Mn concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table H.0.1: Mn corrected stream concentration (ppm) at Missouri Flat Creek over the 2020-2021 water year

Dilution	10			Time	Date	Location
Mn ppm Uncorrected	corrected ppm	mg/g	TP ID			
0.183	1.83	0.19663324	27	12am	1/20/21	CF4
0.202	2.02	0.21704871	28	2am	1/20/21	CF4
0.165	1.65	0.17729226	29	4am	1/20/21	CF4
0.142	1.42	0.1525788	30	6am	1/20/21	CF4
0.187	1.87	0.20093123	31	8am	1/20/21	CF4
0.162	1.62	0.17406877	32	10am	1/20/21	CF4
0.225	2.25	0.24176218	33	12pm	1/20/21	CF4
0.131	1.31	0.14075931	34	2pm	1/20/21	CF4
0.16	1.6	0.17191977	35	4pm	1/20/21	CF4
0.188	1.88	0.20200573	36	6pm	1/20/21	CF4
0.256	2.56	0.27507163	37	8pm	1/20/21	CF4
0.076	0.76	0.08166189	38	10pm	1/20/21	CF4
0.112	1.12	0.12034384	39	12am	1/20/21	CF4
0.044	0.44	0.04727794	73	12am	11/17/20	CF1
0.193	1.93	0.20737822	74	12am	11/17/20	CF4
0.267	2.67	0.28689112	76	6am	11/17/20	CF4
0.112	1.12	0.12034384	77	12pm	11/17/20	CF1
0.169	1.69	0.18159026	78	12pm	11/17/20	CF4

0.335	3.35	0.35995702	79	6pm	11/17/20	CF1
0.175	1.75	0.18803725	80	6pm	11/17/20	CF4
0.424	4.24	0.45558739	81	8pm	11/17/20	CF1
0.12	1.2	0.12893983	82	8pm	11/17/20	CF4
0.086	0.86	0.10336538	117	12am	4/5/21	CF4
0.078	0.78	0.09375	118	2am	4/5/21	CF4
0.785	7.85	0.94350962	119	4am	4/5/21	CF4
0.446	4.46	0.53605769	120	6am	4/5/21	CF4
0.237	2.37	0.28485577	121	8am	4/5/21	CF4
0.673	6.73	0.80889423	122	10am	4/5/21	CF4
0.254	2.54	0.30528846	123	12pm	4/5/21	CF4
0.088	0.88	0.10576923	124	2pm	4/5/21	CF4
1.701	17.01	2.04447115	125	4pm	4/5/21	CF4
3.369	33.69	4.04927885	126	6pm	4/5/21	CF4
0.576	5.76	0.69230769	127	8pm	4/5/21	CF4
0.292	2.92	0.35096154	128	11pm	4/5/21	CF4
0.437	4.37	0.52524038	179	12am	4/14/21	CF4
0.282	2.82	0.33894231	180	2am	4/14/21	CF4
0.234	2.34	0.28125	181	4am	4/14/21	CF4
0.271	2.71	0.32572115	182	6am	4/14/21	CF4
0.288	2.88	0.34615385	183	8am	4/14/21	CF4
0.491	4.91	0.59014423	184	10am	4/14/21	CF4

0.437	4.37	0.52524038	185	12pm	4/14/21	CF4
0.114	1.14	0.13701923	186	2pm	4/14/21	CF4
0.154	1.54	0.18509615	187	4pm	4/14/21	CF4
0.299	2.99	0.359375	188	6pm	4/14/21	CF4
0.077	0.77	0.09254808	189	8pm	4/14/21	CF4
0.319	3.19	0.38341346	190	10pm	4/14/21	CF4
0.447	4.47	0.53725962	191	12am	4/14/21	CF4
0.771	7.71	0.92668269	243	12am	4/27/21	CF4
1.124	11.24	1.35096154	244	2am	4/27/21	CF4
0.353	3.53	0.42427885	245	4am	4/27/21	CF4
0.269	2.69	0.32331731	246	6am	4/27/21	CF4
0.418	4.18	0.50240385	247	8am	4/27/21	CF4
0.05	0.5	0.06009615	248	10am	4/27/21	CF4
0.085	0.85	0.10216346	249	12pm	4/27/21	CF4
0.237	2.37	0.28485577	250	2pm	4/27/21	CF4
0.489	4.89	0.58774038	251	4pm	4/27/21	CF4
0.342	3.42	0.41105769	252	6pm	4/27/21	CF4
0.218	2.18	0.26201923	253	8pm	4/27/21	CF4
0.193	1.93	0.23197115	254	10pm	4/27/21	CF4
0.227	2.27	0.27283654	255	12am	4/27/21	CF4
0.014	0.14	0.01682692	307	12am	6/1/21	CF4
0.01	0.1	0.01201923	308	2am	6/1/21	CF4

0.011	0.11	0.01322115	309	4am	6/1/21	CF4
0.008	0.08	0.00961538	310	6am	6/1/21	CF4
0.009	0.09	0.01081731	311	8am	6/1/21	CF4
0.016	0.16	0.01923077	312	10am	6/1/21	CF4
0.009	0.09	0.01081731	313	12pm	6/1/21	CF4
0.016	0.16	0.01923077	314	2pm	6/1/21	CF4
0.014	0.14	0.01682692	315	4pm	6/1/21	CF4
0.012	0.12	0.01442308	316	6pm	6/1/21	CF4
0.005	0.05	0.00600962	317	8pm	6/1/21	CF4
0.015	0.15	0.01802885	318	10pm	6/1/21	CF4
0.017	0.17	0.02043269	319	12am	6/1/21	CF4

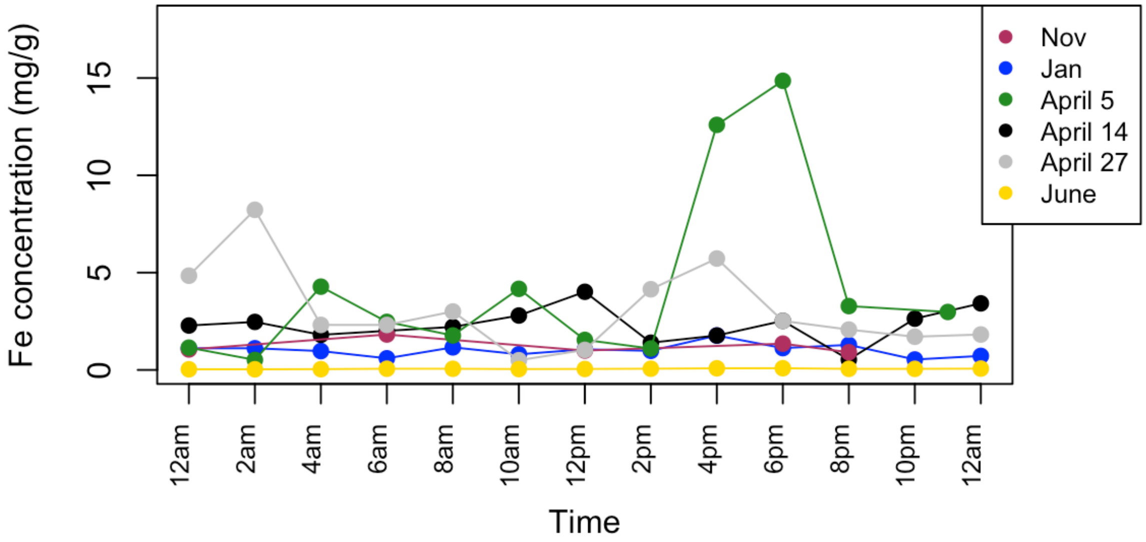


Figure H.0.2: Fe concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table H.0.2: Fe corrected sediment concentration (mg/g) at Missouri Flat Creek over the 2020-2021 water year

Dilution	10			Time	Date	Location
Iron ppm (uncorrected)	corrected ppm	mg/g	TP ID			
1.034	10.34	1.11103152	27	12am	1/20/21	CF4
1.036	10.36	1.11318052	28	2am	1/20/21	CF4
0.902	9.02	0.96919771	29	4am	1/20/21	CF4
0.556	5.56	0.5974212	30	6am	1/20/21	CF4
1.08	10.8	1.16045845	31	8am	1/20/21	CF4
0.748	7.48	0.80372493	32	10am	1/20/21	CF4
0.985	9.85	1.05838109	33	12pm	1/20/21	CF4
0.914	9.14	0.98209169	34	2pm	1/20/21	CF4
1.644	16.44	1.76647564	35	4pm	1/20/21	CF4
1.045	10.45	1.122851	36	6pm	1/20/21	CF4
1.198	11.98	1.28724928	37	8pm	1/20/21	CF4
0.499	4.99	0.53617479	38	10pm	1/20/21	CF4
0.67	6.7	0.71991404	39	12am	1/20/21	CF4
2.945	29.45	3.16439828	73	12am	11/17/20	CF1
0.98	9.8	1.0530086	74	12am	11/17/20	CF4
1.694	16.94	1.82020057	76	6am	11/17/20	CF4

1.052	10.52	1.13037249	77	12pm	11/17/20	CF1
0.926	9.26	0.99498567	78	12pm	11/17/20	CF4
1.111	11.11	1.19376791	79	6pm	11/17/20	CF1
1.257	12.57	1.3506447	80	6pm	11/17/20	CF4
1.346	13.46	1.44627507	81	8pm	11/17/20	CF1
0.846	8.46	0.90902579	82	8pm	11/17/20	CF4
0.952	9.52	1.14423077	117	12am	4/5/21	CF4
0.431	4.31	0.51802885	118	2am	4/5/21	CF4
3.56	35.6	4.27884615	119	4am	4/5/21	CF4
2.055	20.55	2.46995192	120	6am	4/5/21	CF4
1.472	14.72	1.76923077	121	8am	4/5/21	CF4
3.467	34.67	4.16706731	122	10am	4/5/21	CF4
1.284	12.84	1.54326923	123	12pm	4/5/21	CF4
0.914	9.14	1.09855769	124	2pm	4/5/21	CF4
10.477	104.77	12.5925481	125	4pm	4/5/21	CF4
12.36	123.6	14.8557692	126	6pm	4/5/21	CF4
2.73	27.3	3.28125	127	8pm	4/5/21	CF4
2.478	24.78	2.97836538	128	11pm	4/5/21	CF4
1.899	18.99	2.28245192	179	12am	4/14/21	CF4
2.053	20.53	2.46754808	180	2am	4/14/21	CF4
1.501	15.01	1.80408654	181	4am	4/14/21	CF4
1.671	16.71	2.00841346	182	6am	4/14/21	CF4

1.839	18.39	2.21033654	183	8am	4/14/21	CF4
2.326	23.26	2.79567308	184	10am	4/14/21	CF4
3.341	33.41	4.015625	185	12pm	4/14/21	CF4
1.164	11.64	1.39903846	186	2pm	4/14/21	CF4
1.471	14.71	1.76802885	187	4pm	4/14/21	CF4
2.098	20.98	2.52163462	188	6pm	4/14/21	CF4
0.444	4.44	0.53365385	189	8pm	4/14/21	CF4
2.192	21.92	2.63461538	190	10pm	4/14/21	CF4
2.846	28.46	3.42067308	191	12am	4/14/21	CF4
4.029	40.29	4.84254808	243	12am	4/27/21	CF4
6.845	68.45	8.22716346	244	2am	4/27/21	CF4
1.925	19.25	2.31370192	245	4am	4/27/21	CF4
1.924	19.24	2.3125	246	6am	4/27/21	CF4
2.498	24.98	3.00240385	247	8am	4/27/21	CF4
0.416	4.16	0.5	248	10am	4/27/21	CF4
0.855	8.55	1.02764423	249	12pm	4/27/21	CF4
3.449	34.49	4.14543269	250	2pm	4/27/21	CF4
4.763	47.63	5.72475962	251	4pm	4/27/21	CF4
2.096	20.96	2.51923077	252	6pm	4/27/21	CF4
1.724	17.24	2.07211538	253	8pm	4/27/21	CF4
1.419	14.19	1.70552885	254	10pm	4/27/21	CF4
1.514	15.14	1.81971154	255	12am	4/27/21	CF4

0.028	0.28	0.03365385	307	12am	6/1/21	CF4
0.027	0.27	0.03245192	308	2am	6/1/21	CF4
0.033	0.33	0.03966346	309	4am	6/1/21	CF4
0.051	0.51	0.06129808	310	6am	6/1/21	CF4
0.05	0.5	0.06009615	311	8am	6/1/21	CF4
0.036	0.36	0.04326923	312	10am	6/1/21	CF4
0.041	0.41	0.04927885	313	12pm	6/1/21	CF4
0.053	0.53	0.06370192	314	2pm	6/1/21	CF4
0.07	0.7	0.08413462	315	4pm	6/1/21	CF4
0.073	0.73	0.08774038	316	6pm	6/1/21	CF4
0.046	0.46	0.05528846	317	8pm	6/1/21	CF4
0.046	0.46	0.05528846	318	10pm	6/1/21	CF4
0.057	0.57	0.06850962	319	12am	6/1/21	CF4

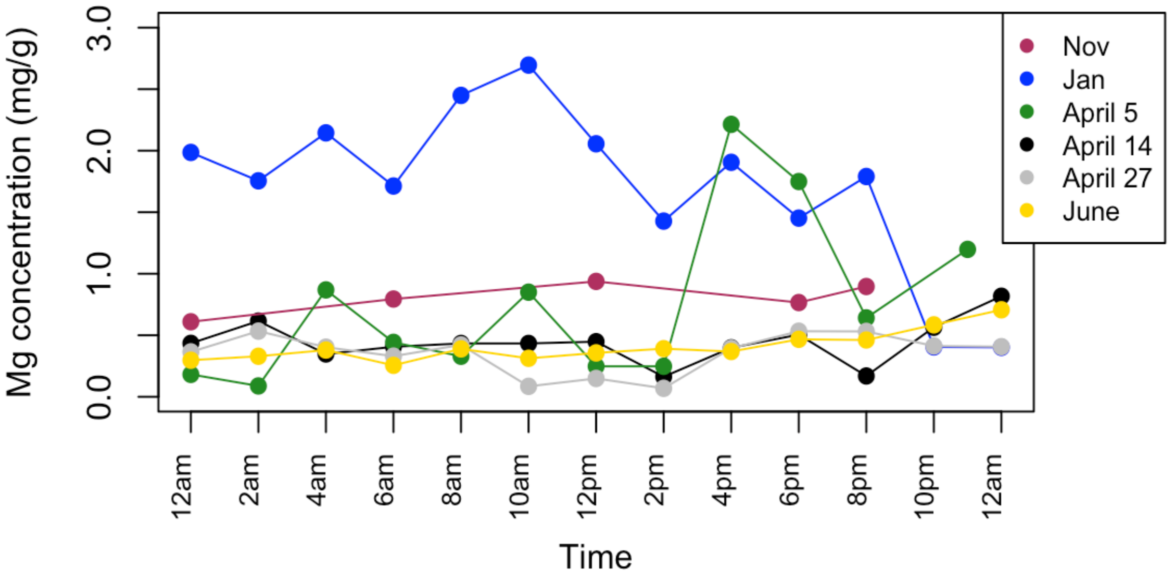


Figure H.0.3: Mg concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table H.0.3: Mg corrected sediment concentration (mg/g) at Missouri Flat Creek over the 2020-2021 water year

Sediment Mg Concentration ppm	mg/g	TP ID	Time	Date	Location
27.72	1.98567335	14	12am	1/20/21	CF4
24.5	1.75501433	15	2am	1/20/21	CF4
29.94	2.14469914	16	4am	1/20/21	CF4
23.91	1.71275072	17	6am	1/20/21	CF4
34.19	2.4491404	18	8am	1/20/21	CF4
37.63	2.69555874	19	10am	1/20/21	CF4
28.7	2.05587393	20	12pm	1/20/21	CF4
19.93	1.42765043	21	2pm	1/20/21	CF4

26.6	1.90544413	22	4pm	1/20/21	CF4
20.27	1.45200573	23	6pm	1/20/21	CF4
24.99	1.79011461	24	8pm	1/20/21	CF4
5.66	0.40544413	25	10pm	1/20/21	CF4
5.61	0.40186246	26	12am	1/20/21	CF4
1.38	0.09885387	63	12am	11/17/20	CF1
8.51	0.60959885	64	12am	11/17/20	CF4
5.07	0.36318052	65	6am	11/17/20	CF1
11.09	0.79441261	66	6am	11/17/20	CF4
7.5	0.53724928	67	12pm	11/17/20	CF1
13.09	0.93767908	68	12pm	11/17/20	CF4
10.34	0.74068768	69	6pm	11/17/20	CF1
10.69	0.76575931	70	6pm	11/17/20	CF4
11.46	0.82091691	71	8pm	11/17/20	CF1
12.51	0.89613181	72	8pm	11/17/20	CF4
2.27	0.18189103	105	12am	4/5/21	CF4
1.1	0.08814103	106	2am	4/5/21	CF4
10.84	0.86858974	107	4am	4/5/21	CF4
5.52	0.44230769	108	6am	4/5/21	CF4
4.11	0.32932692	109	8am	4/5/21	CF4
10.61	0.85016026	110	10am	4/5/21	CF4
3.09	0.24759615	111	12pm	4/5/21	CF4

3.09	0.24759615	112	2pm	4/5/21	CF4
27.63	2.21394231	113	4pm	4/5/21	CF4
21.83	1.74919872	114	6pm	4/5/21	CF4
8	0.64102564	115	8pm	4/5/21	CF4
14.95	1.19791667	116	11pm	4/5/21	CF4
5.42	0.43429487	166	12am	4/14/21	CF4
7.68	0.61538462	167	2am	4/14/21	CF4
4.34	0.34775641	168	4am	4/14/21	CF4
5.07	0.40625	169	6am	4/14/21	CF4
5.41	0.43349359	170	8am	4/14/21	CF4
5.41	0.43349359	171	10am	4/14/21	CF4
5.59	0.44791667	172	12pm	4/14/21	CF4
2.03	0.16266026	173	2pm	4/14/21	CF4
4.97	0.39823718	174	4pm	4/14/21	CF4
6.3	0.50480769	175	6pm	4/14/21	CF4
2.11	0.16907051	176	8pm	4/14/21	CF4
7.05	0.56490385	177	10pm	4/14/21	CF4
10.2	0.81730769	178	12am	4/14/21	CF4
4.55	0.36458333	230	12am	4/27/21	CF4
6.66	0.53365385	231	2am	4/27/21	CF4
5.03	0.40304487	232	4am	4/27/21	CF4
4.12	0.33012821	233	6am	4/27/21	CF4

5.26	0.42147436	234	8am	4/27/21	CF4
1.06	0.0849359	235	10am	4/27/21	CF4
1.86	0.14903846	236	12pm	4/27/21	CF4
0.86	0.06891026	237	2pm	4/27/21	CF4
4.92	0.39423077	238	4pm	4/27/21	CF4
6.65	0.53285256	239	6pm	4/27/21	CF4
6.63	0.53125	240	8pm	4/27/21	CF4
5.15	0.41266026	241	10pm	4/27/21	CF4
5.08	0.40705128	242	12am	4/27/21	CF4
3.71	0.29727564	294	12am	6/1/21	CF4
4.11	0.32932692	295	2am	6/1/21	CF4
4.74	0.37980769	296	4am	6/1/21	CF4
3.19	0.25560897	297	6am	6/1/21	CF4
4.86	0.38942308	298	8am	6/1/21	CF4
3.9	0.3125	299	10am	6/1/21	CF4
4.45	0.35657051	300	12pm	6/1/21	CF4
4.88	0.39102564	301	2pm	6/1/21	CF4
4.59	0.36778846	302	4pm	6/1/21	CF4
5.83	0.46714744	303	6pm	6/1/21	CF4
5.76	0.46153846	304	8pm	6/1/21	CF4
7.3	0.5849359	305	10pm	6/1/21	CF4
8.82	0.70673077	306	12am	6/1/21	CF4

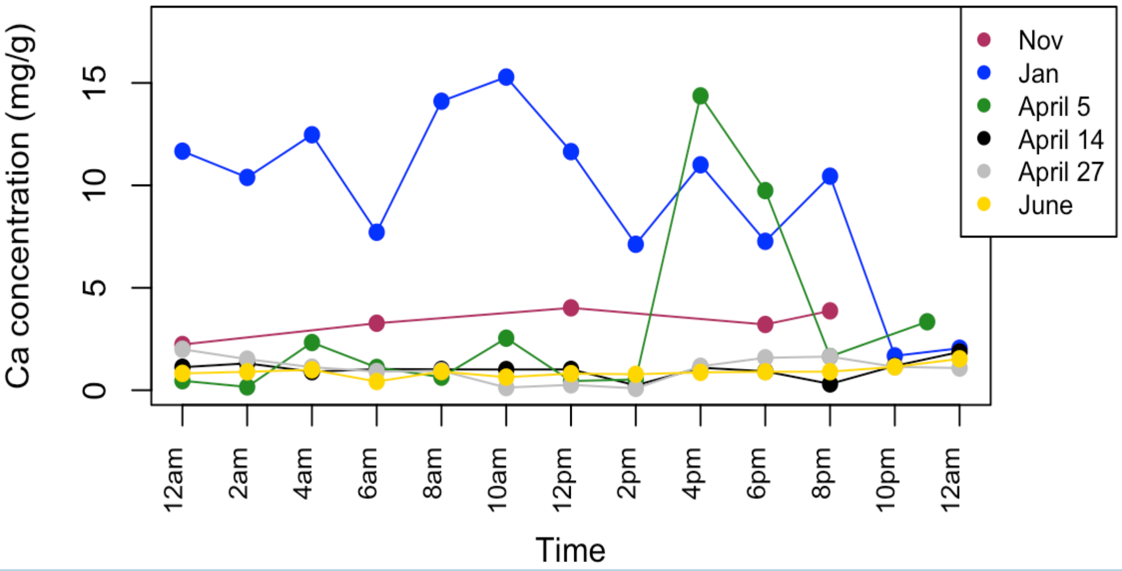


Figure H.0.4: Ca concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table H.0.4: Ca corrected sediment concentration (mg/g) at Missouri Flat Creek over the 2020-2021 water year

Ca run 6/16	mg/g	TP ID	Time	Date	Location
162.9	11.6690544	14	12am	1/20/21	CF4
145.03	10.3889685	15	2am	1/20/21	CF4
174.09	12.4706304	16	4am	1/20/21	CF4
107.67	7.71275072	17	6am	1/20/21	CF4
196.95	14.1081662	18	8am	1/20/21	CF4

213.42	15.2879656	19	10am	1/20/21	CF4
162.61	11.6482808	20	12pm	1/20/21	CF4
99.45	7.1239255	21	2pm	1/20/21	CF4
153.63	11.0050143	22	4pm	1/20/21	CF4
101.47	7.26862464	23	6pm	1/20/21	CF4
145.85	10.4477077	24	8pm	1/20/21	CF4
23.41	1.6769341	25	10pm	1/20/21	CF4
28.6	2.0487106	26	12am	1/20/21	CF4
3.35	0.23997135	63	12am	11/17/20	CF1
31.14	2.23065903	64	12am	11/17/20	CF4
14.81	1.06088825	65	6am	11/17/20	CF1
45.65	3.27005731	66	6am	11/17/20	CF4
22.5	1.61174785	67	12pm	11/17/20	CF1
56.14	4.02148997	68	12pm	11/17/20	CF4
29.95	2.14541547	69	6pm	11/17/20	CF1
44.8	3.20916905	70	6pm	11/17/20	CF4
39.93	2.86031519	71	8pm	11/17/20	CF1
54.08	3.8739255	72	8pm	11/17/20	CF4
5.77	0.46233974	105	12am	4/5/21	CF4
2.01	0.16105769	106	2am	4/5/21	CF4
29.06	2.32852564	107	4am	4/5/21	CF4
13.88	1.11217949	108	6am	4/5/21	CF4

7.93	0.63541667	109	8am	4/5/21	CF4
31.7	2.5400641	110	10am	4/5/21	CF4
5.57	0.4463141	111	12pm	4/5/21	CF4
6.56	0.52564103	112	2pm	4/5/21	CF4
179.34	14.3701923	113	4pm	4/5/21	CF4
121.62	9.74519231	114	6pm	4/5/21	CF4
20.57	1.64823718	115	8pm	4/5/21	CF4
41.7	3.34134615	116	11pm	4/5/21	CF4
14.02	1.12339744	166	12am	4/14/21	CF4
16.37	1.31169872	167	2am	4/14/21	CF4
11.25	0.90144231	168	4am	4/14/21	CF4
12.88	1.03205128	169	6am	4/14/21	CF4
12.7	1.01762821	170	8am	4/14/21	CF4
12.6	1.00961538	171	10am	4/14/21	CF4
12.68	1.01602564	172	12pm	4/14/21	CF4
3	0.24038462	173	2pm	4/14/21	CF4
13.74	1.10096154	174	4pm	4/14/21	CF4
11.52	0.92307692	175	6pm	4/14/21	CF4
3.83	0.30689103	176	8pm	4/14/21	CF4
14.82	1.1875	177	10pm	4/14/21	CF4
23.31	1.86778846	178	12am	4/14/21	CF4
24.96	2	230	12am	4/27/21	CF4

18.93	1.51682692	231	2am	4/27/21	CF4
14.02	1.12339744	232	4am	4/27/21	CF4
11.4	0.91346154	233	6am	4/27/21	CF4
11.86	0.95032051	234	8am	4/27/21	CF4
1.63	0.13060897	235	10am	4/27/21	CF4
3.29	0.26362179	236	12pm	4/27/21	CF4
1.14	0.09134615	237	2pm	4/27/21	CF4
14.57	1.16746795	238	4pm	4/27/21	CF4
19.77	1.58413462	239	6pm	4/27/21	CF4
20.46	1.63942308	240	8pm	4/27/21	CF4
14.24	1.14102564	241	10pm	4/27/21	CF4
13.52	1.08333333	242	12am	4/27/21	CF4
10.26	0.82211538	294	12am	6/1/21	CF4
11.22	0.89903846	295	2am	6/1/21	CF4
12.47	0.99919872	296	4am	6/1/21	CF4
5.29	0.42387821	297	6am	6/1/21	CF4
11.37	0.91105769	298	8am	6/1/21	CF4
7.95	0.63701923	299	10am	6/1/21	CF4
10.11	0.81009615	300	12pm	6/1/21	CF4
9.73	0.77964744	301	2pm	6/1/21	CF4
10.87	0.87099359	302	4pm	6/1/21	CF4
11.24	0.90064103	303	6pm	6/1/21	CF4

11.31	0.90625	304	8pm	6/1/21	CF4
14.2	1.13782051	305	10pm	6/1/21	CF4
19.12	1.53205128	306	12am	6/1/21	CF4

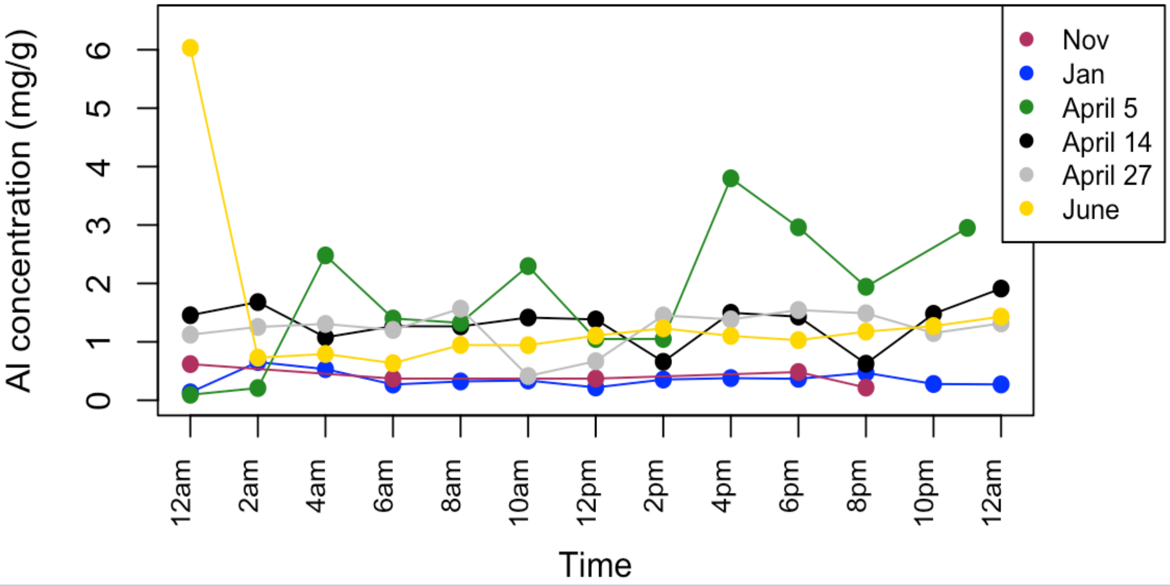


Figure H.0.5: Al concentrations in the sediment for 24 hours on 6 sampling days throughout the 2020-2021 water year at Missouri Flat Creek

Table H.5: Al corrected sediment concentration (mg/g) at Missouri Flat Creek over the 2020-2021 water year

	10x Dilution/30x dilution (highlighted)					
Uncorrected ppm	Aluminum Corrected	mg/g	TP ID	Time	Date	Location
0.126	1.26	0.13538682	2	12am	1/20/21	CF4
0.609	6.09	0.65436963	1	2am	1/20/21	CF4
0.496	4.96	0.53295129	3	4am	1/20/21	CF4
0.251	2.51	0.26969914	4	6am	1/20/21	CF4
0.3	3	0.32234957	5	8am	1/20/21	CF4
0.315	3.15	0.33846705	6	10am	1/20/21	CF4
0.204	2.04	0.21919771	7	12pm	1/20/21	CF4
0.33	3.3	0.35458453	8	2pm	1/20/21	CF4
0.353	3.53	0.37929799	9	4pm	1/20/21	CF4
0.342	3.42	0.36747851	10	6pm	1/20/21	CF4
0.438	4.38	0.47063037	11	8pm	1/20/21	CF4
0.259	2.59	0.27829513	12	10pm	1/20/21	CF4
0.252	2.52	0.27077364	13	12am	1/20/21	CF4
0.046	1.38	0.1482808	53	12am	11/17/20	CF1
0.192	5.76	0.61891117	54	12am	11/17/20	CF4
0.179	1.79	0.19233524	55	6am	11/17/20	CF1
0.115	3.45	0.37070201	56	6am	11/17/20	CF4

0.144	1.44	0.15472779	57	12pm	11/17/20	CF1
0.15	3.45	0.37070201	58	12pm	11/17/20	CF4
0.191	4.32	0.46418338	59	6pm	11/17/20	CF1
0.202	4.5	0.48352436	60	6pm	11/17/20	CF4
0.078	5.73	0.61568768	61	8pm	11/17/20	CF1
0.174	2.02	0.21704871	62	8pm	11/17/20	CF4
0.608	0.78	0.09375	93	12am	4/5/21	CF4
0.361	1.74	0.20913462	94	2am	4/5/21	CF4
2.063	20.63	2.47956731	95	4am	4/5/21	CF4
1.165	11.65	1.40024038	96	6am	4/5/21	CF4
1.102	11.02	1.32451923	97	8am	4/5/21	CF4
1.911	19.11	2.296875	98	10am	4/5/21	CF4
0.872	8.72	1.04807692	99	12pm	4/5/21	CF4
0.873	8.73	1.04927885	100	2pm	4/5/21	CF4
3.161	31.61	3.79927885	101	4pm	4/5/21	CF4
2.463	24.63	2.96033654	102	6pm	4/5/21	CF4
1.616	16.16	1.94230769	103	8pm	4/5/21	CF4
2.455	24.55	2.95072115	104	11pm	4/5/21	CF4
1.211	12.11	1.45552885	153	12am	4/14/21	CF4
1.398	13.98	1.68028846	154	2am	4/14/21	CF4
0.896	8.96	1.07692308	155	4am	4/14/21	CF4
1.055	10.55	1.26802885	156	6am	4/14/21	CF4

1.052	10.52	1.26442308	157	8am	4/14/21	CF4
1.178	11.78	1.41586538	158	10am	4/14/21	CF4
1.151	11.51	1.38341346	159	12pm	4/14/21	CF4
0.548	5.48	0.65865385	160	2pm	4/14/21	CF4
1.246	12.46	1.49759615	161	4pm	4/14/21	CF4
1.191	11.91	1.43149038	162	6pm	4/14/21	CF4
0.521	5.21	0.62620192	163	8pm	4/14/21	CF4
1.231	12.31	1.47956731	164	10pm	4/14/21	CF4
1.591	15.91	1.91225962	165	12am	4/14/21	CF4
0.934	9.34	1.12259615	217	12am	4/27/21	CF4
1.044	10.44	1.25480769	218	2am	4/27/21	CF4
1.087	10.87	1.30649038	219	4am	4/27/21	CF4
1.001	10.01	1.203125	220	6am	4/27/21	CF4
1.305	13.05	1.56850962	221	8am	4/27/21	CF4
0.345	3.45	0.41466346	222	10am	4/27/21	CF4
0.556	5.56	0.66826923	223	12pm	4/27/21	CF4
1.208	12.08	1.45192308	224	2pm	4/27/21	CF4
1.151	11.51	1.38341346	225	4pm	4/27/21	CF4
1.285	12.85	1.54447115	226	6pm	4/27/21	CF4
1.238	12.38	1.48798077	227	8pm	4/27/21	CF4
0.957	9.57	1.15024038	228	10pm	4/27/21	CF4
1.095	10.95	1.31610577	229	12am	4/27/21	CF4

5.02	50.2	6.03365385	281	12am	6/1/21	CF4
0.607	6.07	0.72956731	282	2am	6/1/21	CF4
0.659	6.59	0.79206731	283	4am	6/1/21	CF4
0.528	5.28	0.63461538	284	6am	6/1/21	CF4
0.787	7.87	0.94591346	285	8am	6/1/21	CF4
0.784	7.84	0.94230769	286	10am	6/1/21	CF4
0.92	9.2	1.10576923	287	12pm	6/1/21	CF4
1.025	10.25	1.23197115	288	2pm	6/1/21	CF4
0.916	9.16	1.10096154	289	4pm	6/1/21	CF4
0.856	8.56	1.02884615	290	6pm	6/1/21	CF4
0.977	9.77	1.17427885	291	8pm	6/1/21	CF4
1.056	10.56	1.26923077	292	10pm	6/1/21	CF4
1.191	11.91	1.43149038	293	12am	6/1/21	CF4

Appendix I: Stream Metal Correlations

Table I.0.1: Stream Metal Correlations for the Winter Sampling Season

winter	Stream Al	Stream Mn	Stream Fe	Stream Mg	Stream Ca
pH	0.47·	-0.44·	0.26	-0.52*	-0.60*
DO	-0.63**	0.32	-0.75***		
Temp	0.64**	-0.36*	0.62*	-0.38	-0.51*
SRP-Ca/Mg				-0.0064	-0.018
SRP-Al	0.21				
SRP-Fe/Mn	-0.043	0.056	0.069		
Al sediment	-0.12				
Fe sediment	0.023	0.056	-0.24		
Mn Sediment		-0.20	-0.21		
Ca Sediment				0.16	0.072
Mg Sediment				0.15	0.07
Stream SRP	-0.67**	0.26	-0.78***	0.28	0.42

Table I.0.2: Stream Metal Correlations for the Spring Sampling Season

spring	Stream Al	Stream Mn	Stream Fe	Stream Mg	Stream Ca
pH	0.079	-0.65***	0.38*	-0.36*	-0.27·
DO	0.18	-0.43**	-0.27·		
Temp	-0.068	-0.73***	0.48**	-0.37*	-0.29·
SRP-Ca/Mg				0.055	0.037
SRP-Al	-0.29				
SRP-Fe/Mn		0.063	-0.18		
Al sediment	0.36*				
Fe sediment	0.14	-0.16	-0.18		
Mn Sediment		-0.095	-0.26		
Ca Sediment				-0.17	-0.16
Mg Sediment				-0.13	-0.13
SRP Stream	0.58***	-0.66***	-0.20	-0.46**	-0.40*

Table I.0.3: Metal Correlations for the Summer Sampling Season

Summer	Stream Al	Stream Mn	Stream Fe	Stream Mg	Stream Ca
pH	0.16	-0.84***	0.27	0.077	0.094
DO	-0.14	-0.37	-0.17	0.31	0.24
Temp	0.29	-0.76**	0.53	-0.098	-0.013
SRP-Ca/Mg	N/A			-0.027	-0.006
SRP-Al	0.11				
SRP-Fe/Mn	N/A	-0.28	0.35		
Al sediment	0.38				
Fe sediment		-0.34	0.48		
Mn Sediment		-0.44	-0.094		
Ca Sediment				0.074	0.11
Mg Sediment				0.18	0.24
Summer SRP	0.25	-0.19	0.78**	-0.77**	-0.66*

Appendix J: Seasonal Correlations with Abiotic Factors

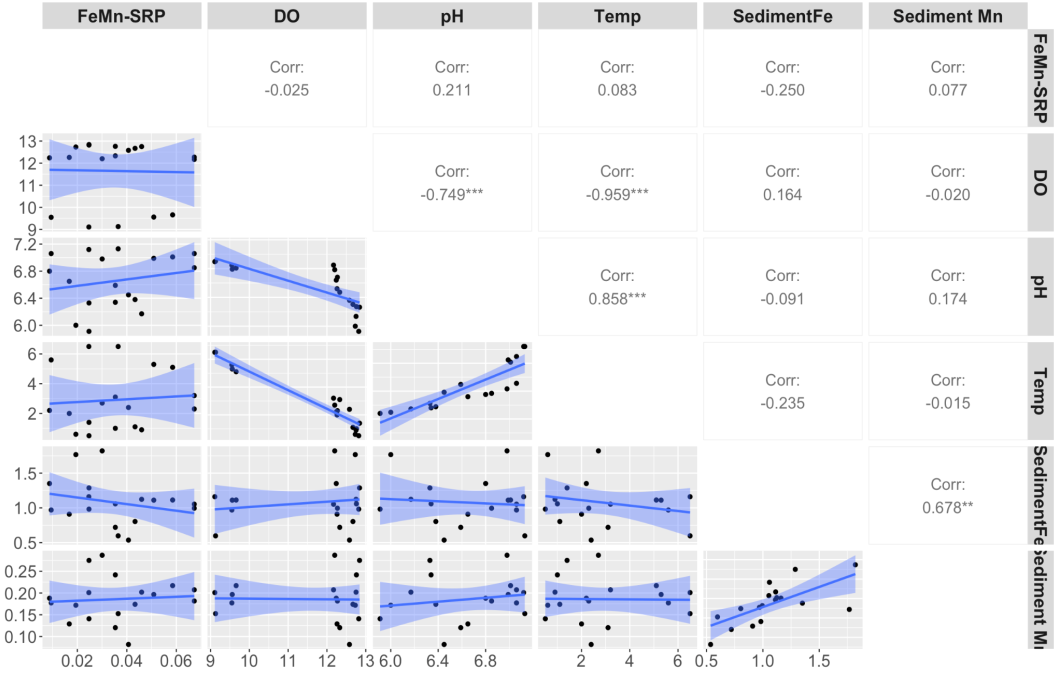


Figure J. 0.1: Correlation matrix between abiotic factors and SRP bound to Fe and Mn during winter sample dates at Missouri Flat Creek.

There were no significant correlations between any of the abiotic factors and extractable soil P or other metals during the winter (i.e., November and January) sample dates (Figure 2.16). However, there was a significant correlation (0.678; p-value < 0.0001) between the Fe and Mn concentration in the bed sediments. There was a non-significant correlation between the extractable soil P from the Fe/Mn metals in the soil and Fe concentration in the soil. There was a -0.75 correlation between stream Fe and dissolved oxygen (p value <0.001). There was also a -0.78 correlation between stream Fe and stream SRP (p value <0.001).

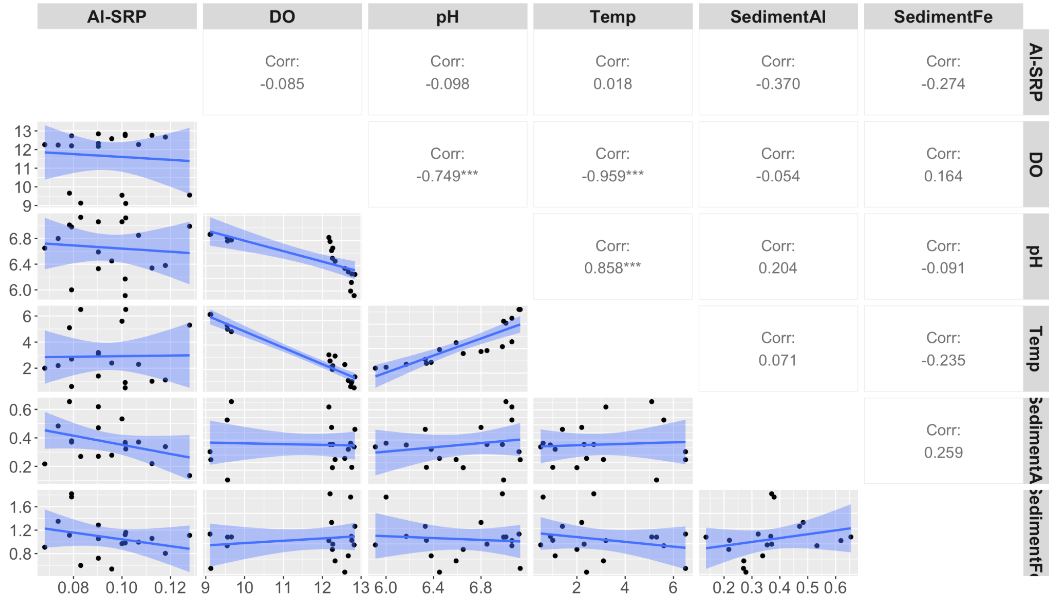


Figure J.0.2: Correlation matrix between abiotic factors and SRP bound to Al during winter sample dates at Missouri Flat Creek.

Similar to Fe/Mn-SRP, the Al-SRP was not correlated with pH, temperature, or dissolved oxygen during the winter sampling dates (Figure 2.17). Sediment [Al] and [Fe] were also not correlated with pH, temperature, dissolved oxygen during this time period. There was a weak, non-significant relationship between Al and Fe in the sediments as well as between Al/Fe in the sediments and Al-SRP. There was no evidence of any correlation between stream concentrations of Al and Fe with the Al and Fe in the sediments. There was a -0.63 correlation between stream Al and dissolved oxygen (p value <0.01), and 0.64 correlation between stream Al and temperature (p value <0.01), and -0.64 correlation between stream Al and stream SRP (p value <0.01).

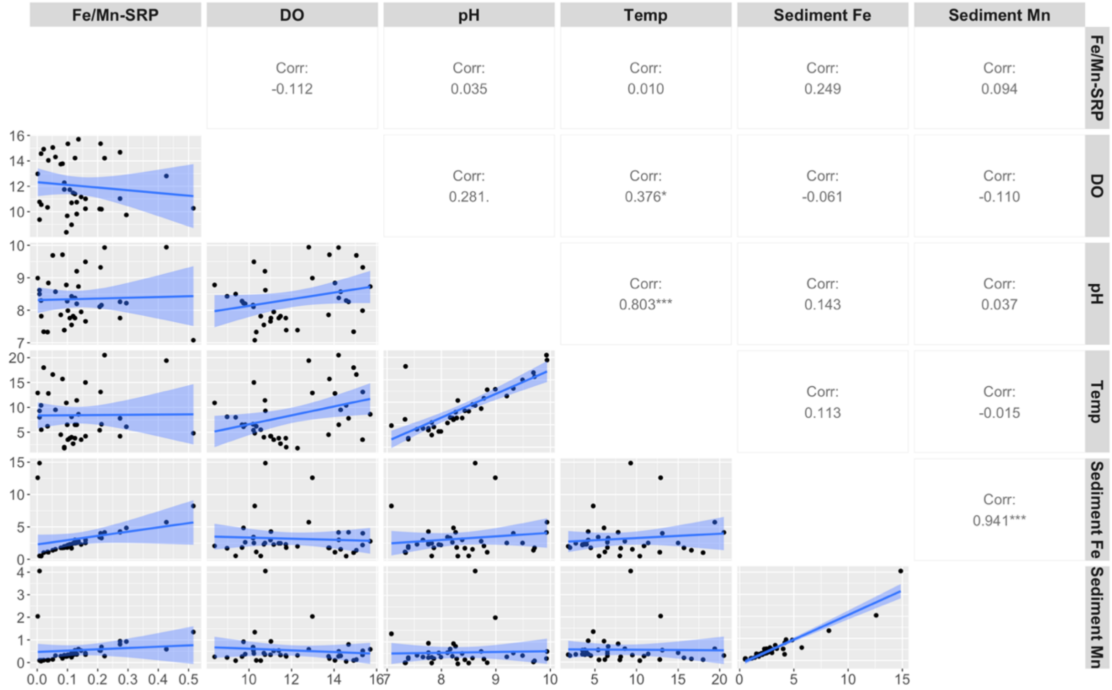


Figure J.0.3: Correlation matrix between abiotic factors and SRP bound to Fe and Mn during spring sample dates at Missouri Flat Creek.

Similar to winter, there were no significant correlations between SRP-Fe/Mn and pH, dissolved oxygen, and temperature during these sampling dates. There was more Fe in the sediments than Mn and more Mn in the stream than Fe. Similar to the Ca and Mg, there were two unusual high points for Fe and Mn in the sediments from the same day and time. Removal of these two points increased the correlation to 0.91 and 0.80 between sediment Fe and Fe/Mn-SRP and sediment Mn and Fe/Mn-SRP, respectively. The p- level increased to 0.001. There was a 0.38 correlation between stream Fe and pH (p value <0.05), a -0.27 correlation between stream Fe and DO (p value <0.1), and a 0.48 correlation between stream Fe and temperature (p value <0.01). There was a -0.65 correlation between stream Mn and pH (p value <0.001), a -0.43 correlation between stream Mn and DO (p value <0.01), a -0.73

correlation between stream Mn and temperature (p value <0.001), and a -0.66 correlation between stream Mn and Stream SRP (p value <0.001).

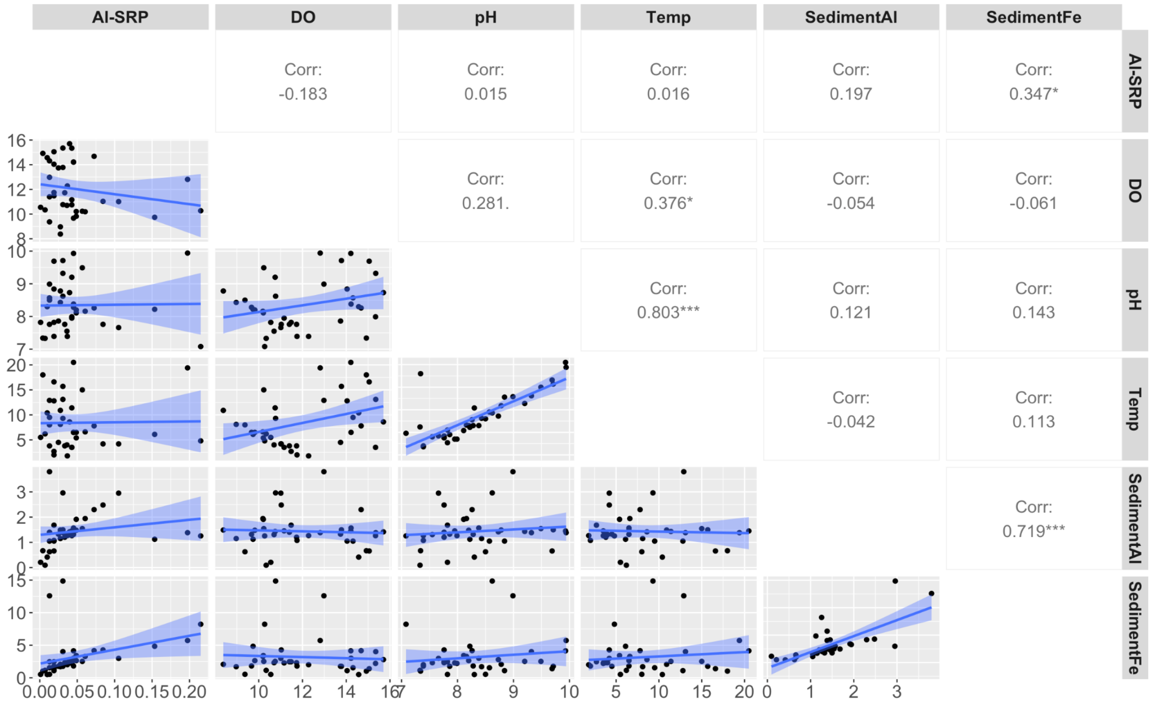


Figure J.0.4: Correlation of potential relationships between abiotic factors and of SRP bound to Al in the spring at Missouri Flat Creek

Similar to winter data, in the spring there were no statistically significant abiotic correlations that explain Al-SRP sorption patterns. There was, however, an association between Al in the sediment with SRP bound to Al. There was a statistically significant correlation between Fe in the sediment and Al-SRP. Similar to other ions, there are two unusual high points for Al and Fe in the sediments on April 5th at 4pm and 6pm. Removal of these two points increases the correlation to 0.88 and 0.35 between sediment Fe and Al-SRP and sediment Al and Al-SRP, respectively. The p- level increased to 0.001 and 0.05, respectively. There was a 0.36 correlation between stream Al and stream sediment (p value <0.05), and a 0.58 correlation between stream Al and stream SRP (p value <0.001).

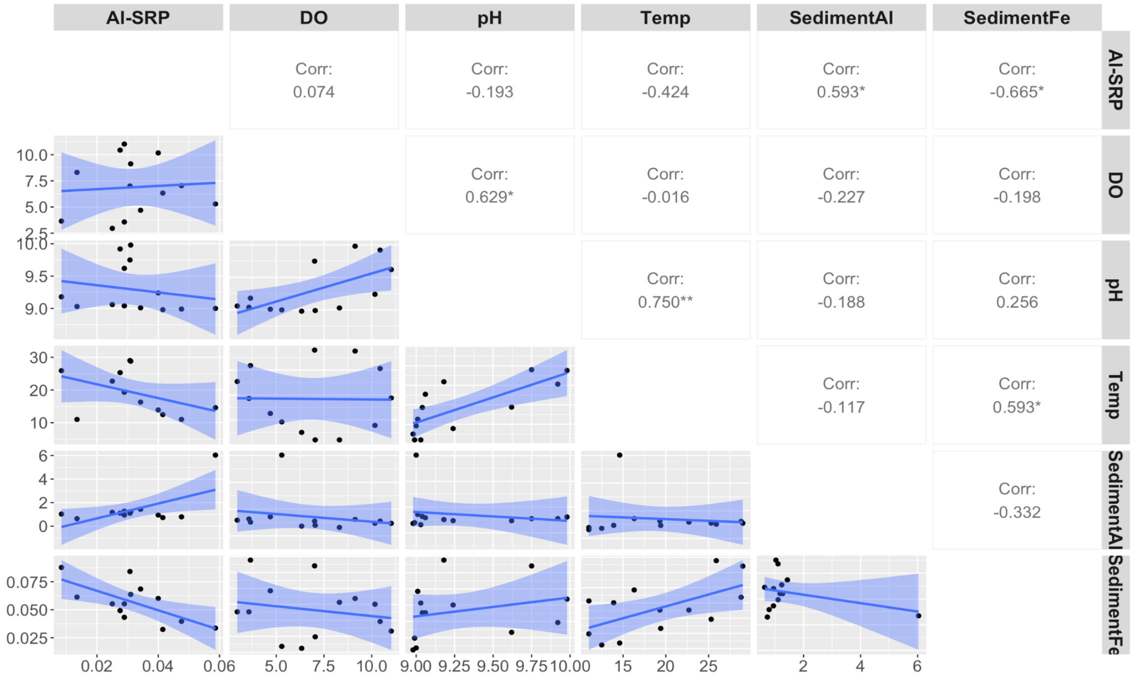


Figure J.0.5: Correlation matrix relationships between abiotic factors and of SRP bound to Al in the summer at Missouri Flat Creek

In the summer, extractable Al-SRP exhibits no significant correlation between temperature, dissolved oxygen, and pH. Although the correlation between temperature and Summer Al-SRP was not statistically significant, there was a medium strength association between temperature and Al-SRP. There was a correlation between concentrations of Al sediment and Fe sediment. Sediment Al is positively correlated with Al-SRP and sediment Fe is negatively correlated with Al-SR. There were no statistically significant correlations between stream Al and Fe concentrations and the sediment concentrations.

Appendix K: Lesson Plan with Next Generation Science Standards

Name	Tia Ogus
Lesson #, Lesson Title	Phosphorus in Stream Ecosystems
Date (including day of week)	
Grade Level & Class Title	Junior/Seniors in high school
Period or Block (# of minutes)	

Learning Goal
Students will develop different lab and sampling skills and have a basic understanding of how nutrients affect an agricultural stream. Students will understand water and phosphorus cycling.
Central Focus
The students can understand the importance and difference between total phosphorus and soluble reactive Phosphorus. Students will be able to sample and analyze water. --------COVID Method------ The students can understand the importance of TP monitoring and remediation methods
Standards
● HS-ESS2-5: The students can learn part of the standards in "ESS2.C- dissolved and transport materials" ● ELA-WHST.9-12.7: Students will write a report synthesizing their results ● Math HSN.Q.A.3: Choose a level of accuracy appropriate to limitations on measurement when reporting quantities. (HS-ESS2-5). Students will report values in sig figs, and calculate the total load ● HS-ESS2-2.: "The Roles of Water in Earth's Surface Processes". The students can understand how sediment and erosion from nearby areas can lead to an increase in sediment and dissolved P and nutrients. Students will understand how erosion can affect and pollute the hydrological cycle. Students can learn how erosion affects the stream and how the water/ pollutants travel.

Learning Objectives and Assessments	
Learning Objectives	Assessment Plan
1. Understand the basic water cycle and how nutrients affect the	1. Read a document and create a simple drawing of how P may

hydrological cycle (e.g. sedimentation, runoff, etc) 2. Students understand why it is important to sample water, understand how to pick sample location, and understand how P changes downstream. 3. Students can understand how to analyze SRP in a lab setting 4. Students can understand how the SRP concentration changes downstream, how to use excel and analyze what the result means. 5. Students can calculate the daily load by using streamflow and concentration 6. Students can understand external and internal sources of SRP ------- COVID Methods------- 1. 1-2 the same 2. Students can understand a reaction between Alum and TP and the importance of remediation efforts 3. Students can understand how P may be released from sediments. 4. Students can understand the importance of DO and pH	enter the stream and where it can end up 2. Students will learn how to collect water samples at every said distance. This will enable them to evaluate if P changes downstream and synthesize reasons why the concentration changes. 3. Students can run lab tests according to the EPA standards or a P test kit to determine the TP and SRP concentration. 4. Create an excel graph comparing TP and SRP concentration. 5. Students can use a formula to calculate the SRP daily load and analyze what that means for the local stream. 6. Students can write a lab report with an introduction, methods, results, and discussion section. Alternatively, a quiz may be given. ------ COVID Method------ 1. Add Al salt to core and compare how TP concentration changes 2. Measure DO with a DO probe at each site.

Instructional Strategies and Learning Tasks (Procedures & Timelines)		
Time	Instructional Strategies/Learning Tasks/Questions to Ask	Adaptations/Modifications
1 hour	Students draw processes of the hydrological cycle in one color (e.g. evaporation, runoff) in one color. In another color indicate how P may be transported via water and how P enters the system (e.g. P can enter through sedimentation, ag runoff, etc and may end in GW/stream and travel to bigger bodies of water.	
1 hour	Teachers will pick sample locations based on accessibility. Students will have their individual	The number of sample sites depends on the

	water bottle (clean-acid washed if possible ahead of time). They will go to their given spot and collect their one water sample. The student will rinse the bottle twice and then fill the bottle up on the third time. I recommend using a 125mL bottle. The student will place samples in a cooler.	sample location and how many students. For example, is the site easily accessible and are there at least 5 students. I recommend the distance between each sample site is every 10 feet. -------COVID Protocol------ Because of COVID, it is best to have students outside to maintain social distancing. Sediment with overlying water will be collected in a small pipe (e.g. from any building supply). There will be two collected at each site. As these are more time consuming, only have three sites. Possibly one before the WWTP and two after the WWTP.
3 hours	Students will analyze SRP as follows. As only one batch of color reagent is needed, the teacher can create the reagent while students watch/ help with certain parts. The kids will then add their sample to the cuvette and then add color reagent to their sample. All the samples can be run on the spectrometer in the same run. Students will record every TP and SRP value.	I hope that students have the opportunity to do the SRP colorimetric method, however, one can use the Hatch Kit https://www.hach.com/phosphorus-orthophosphate-reactive-test-kit-model-po-19/product?id=7640214958 https://www.hach.com/phosphorus-reactive-and-total-tntplus-vial-test-lr-0-15-4-50-mg-l-po-25-

		tests/product?id=7640196815 --------COVID Protocol----- Students will test Phosphorus concentration of overlying water in one sediment core from each site. Next add aluminum salts (10:1 Al:P) (weare gloves and goggles) to the second sediment core from each site. Wait 5 minutes and add measure and measure P concentration. If students can measure DO at each site.
30 min	The teacher will give a brief demonstration on how to create a graph on excel. If students do not have access to excel, they can create a graph on google docs. Students will input the concentration of TP and SRP in two separate columns. The distance at which concentration was collected is in a separate column. Then using the graph function, one can create a graph.	Students can use excel, however, if students do not have access to excel, google sheets. However, I recommend using a scatter/line plot. ------- COVID Protocol------ Students will have to create graphs of DO, TP (without Alum addition), TP (with Alum Addition)
30 min	Using the average P concentration and streamflow (either from USGS-Palouse River or calculate streamflow during lab) one can calculate the daily load. In the discussion section	Some sites have a USGS streamflow gauge (Paradise Creek at UI) or one can calculate

	of the lab report, one can analyze what the number means.	streamflow when collecting water.
how much time to put together a report	In the introduction explain the difference between TP and SRP, the phosphorus and water cycle, how nutrients affect stream ecology (ie algae), and the objectives of this report. A methodology section including a site description and what they did in the field and lab. A results section with the TP and SRP vs Distance graph and the daily load calculation. There will be a brief paragraph explaining what the graph explains. A discussion section explaining any SRP and TP trends, how much TP consists of SRP and what does that mean, and any analysis. They can do some research to support their theories.	------COVID Protocol------- Students will write a report explaining the importance of TP and alum, the phosphorus and water cycle, how nutrients affect stream ecology (ie algae), and the objectives of this report. A methodology section including a site description and what they did in the field. Graphs will be included in the results section. A discussion section explaining any DO and TP trends, how alum addition affected the TP concentration and what does that mean, and any analysis. They can do some research to support their theories.

Materials and Resources
○ waders ○ 125mL acid washed poly-etheylne bottle **The following is needed if following Kit Protocol for SRP** ○ https://www.hach.com/phosphorus-orthophosphate-reactive-test-kit-model-po-19/product?id=7640214958 (or any kit one can find, as long as it is not strip test) **The following is needed if Following EPA Protocol for SRP** ○ Spectrometer (if following SRP EPA Protocol) ○ Sulfuric Acid

- Ammonium Molybdate
- Antimony Potassium Tartate
- Ascorbic Acid
- Acetone
- Phosphorus Potassium Monobasic

  The following is for TP
- https://www.thomassci.com/Laboratory-Supplies/Water-Quality-Test-Kits/_/Phosphorus-TNTplus-HR?q=Hach%20Phosphorus%20Test%20Kit

- **The Following is needed for COVID adaption**
- pipe for core,
- gloves/goggles
- Al sat
- TP concentration strips
- DO probe

Assessment Rubric:

Grade	5	4	3	2	1
Hydrological/P cycle Drawing	All components of both cycles are there, with brief description. Effort is shown.	1-2 Components of the cycles are missing. Description is present, but only 90% complete. Effort is shown.	3-4 components of the cycle are missing. Description is only 70-80% complete.	Several components are missing that cycle is incomplete. Only 50% of the description is complete.	Most parts of the cycle are incomplete. Lack of effort shown.
Introduction	Introduction includes full background to the project (check lab manual for full list of what is included), rationale, and objectives. The student goes above and beyond.	Introduction is slightly lacking in either the background, rationale, or objective. The student shows great effort.	Introduction is missing one component (background, rationale, objective).	Introduction is not grammatically correct. Introduction lacks several aspects of each of the components.	Introduction is extremely weak, does not flow or make sense grammatically. Does not answer the questions or include the parts.
Method	Near perfection grammatically. Addresses the important part of the lab and field methods. Included a site description. Student shows extreme effort.	Some grammar mistakes. Addresses 95% of the field and lab methods. Includes site description. Student shows great effort.	Method section is slightly choppy. Addresses 75-80% of field, lab and site methods.	Method section is poor grammatically. Missing 50% of components	Method section missing less than 50% aspects. Lack of Effort shown.
Results	Graph is black and not flashy. Has appropriate axis labels, size, units, description. Daily Load calculation is correct	Graph is black and not flashy. Missing one of the labels or units. Daily Load calculation is correct.	Graph is flashy and missing (1-2) appropriate labels, size, units etc. Daily Load calculation missing one component .	Graph is not correct. Missing 2-3 of the appropriate labels, size, units. Daily Load calculation missing	Missing graph and calculation

Discussion	Student analyzes results, discusses probable reasons, synthizes what result means for Stream. Has some research to support article	Student shows great effort. 80-95% of components are there. Some grammatical errors. Has research articles.	70-80% of components are there. Paragraphs not descriptive and a little choppy.	50-69% of the discussion components are missing. Significant Grammatical errors.	No effort show. Discussion is only a few sentences.

Alternative methods for summer:

Collecting 2 samples (water and sediment) at each location . One sample will be analzyed for TP as typical, the other sample will be exposed to Alum ~10:1. How does phosphorus concentration differ.ent . Near wastewater treatment plant.

TP reduction is almost immediate.

How does DO change over stream?

Appendix L: Student Quiz

Quiz

1. What are the different forms of phosphorus that may be present in the stream?
2. What can contribute to P release from sediments to the overlying water?
3. What is the oxidation number of phosphate?
4. What is Eutrophication and how is it affected by Phosphorus? What are some water quality issues?
5. What is a total maximum daily load? Is it the same for every stream?
6. Why is streamflow important when monitoring water quality?
7. Why is aluminum sulfate important in reducing P (can you explain in chemical terms)?
8. Why are dilutions for standards important for determining the concentration of P?
9. List the components of the water cycle and P cycle? How does P end up in streams?
10. What is one interesting thing you learned? (only on after quiz)

Appendix M: Specific Lab and Field Methods to follow for students

Lab and Field Procedures

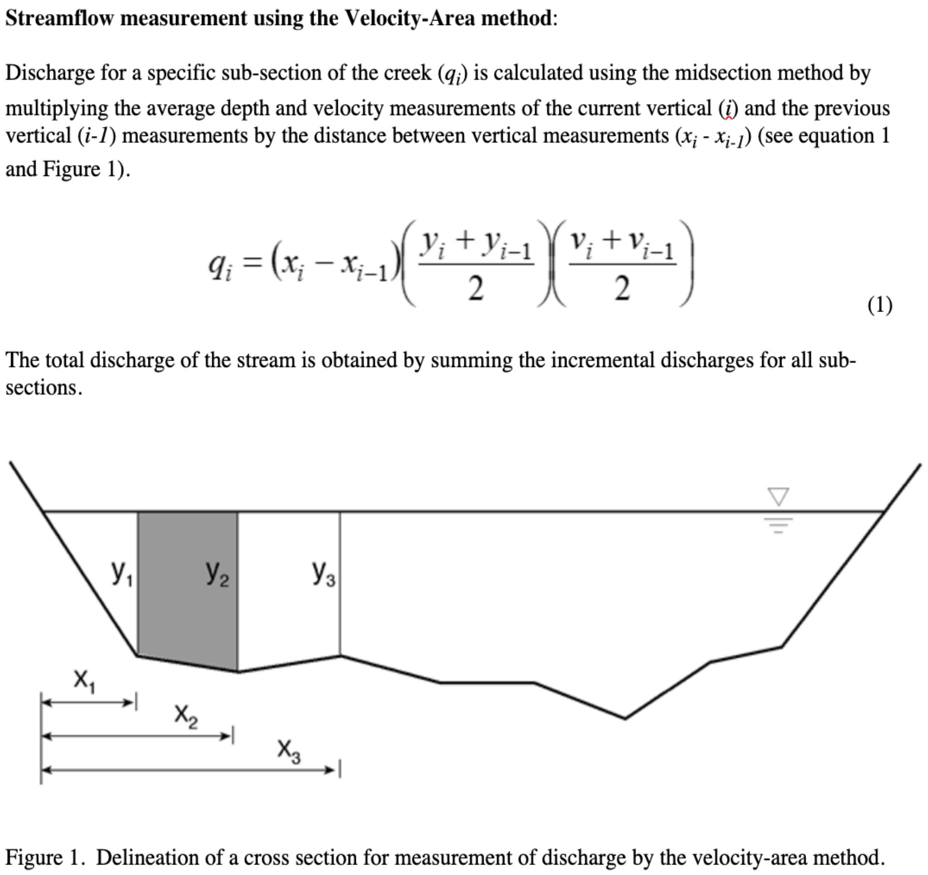
Materials:

- DI Water
- ~30 125mL Polyethylene bottles
- Syringe Filter casings with 0.45um filters
- KH_2PO_4
- 2.5M H_2SO_4
- Ammonium Molybdate Solution
- 0.1M Ascorbic Acid Solution
- Potassium Antimonyl Tartrate
- Waders
- Alum
- Notebook
- Streamflow meter
- Centrifuge Tubes
- Transfer pipettes
- Gloves
- Goggles
- Volumetric Pipettes
- Volumetric Flasks (12 50mL),
- Cuvettes

Field Methods

1. **Velocity Meter:**

   Each meter is set up differently. The teacher will know ahead of time the specific settings needed to run the meter. One student will wear waders and measure the width of the stream, while another student will record other data. Each group should record approximately 10 values across the stream. Next, the student in the stream will face the meter upstream, which will measure the flow of the stream and the depth of the stream. One student will read the flow, while another student records the data. At each site, the group should record the depth, the width of the site (i.e. if the stream is 5 meters, and you measure at widths 1,1.5, 2,2.5 etc), and the flow. Below is a figure adopted from Erin Brooks (University of Idaho)explaining how to calculate discharge



Streamflow measurement using the Velocity-Area method:

Discharge for a specific sub-section of the creek (q_i) is calculated using the midsection method by multiplying the average depth and velocity measurements of the current vertical (i) and the previous vertical ($i-1$) measurements by the distance between vertical measurements ($x_i - x_{i-1}$) (see equation 1 and Figure 1).

$$q_i = \left(x_i - x_{i-1}\right)\left(\frac{y_i + y_{i-1}}{2}\right)\left(\frac{v_i + v_{i-1}}{2}\right) \tag{1}$$

The total discharge of the stream is obtained by summing the incremental discharges for all sub-sections.

Figure 1. Delineation of a cross section for measurement of discharge by the velocity-area method.

2. Stream Sampling

A) Grab Samples: Collect a grab sample from your sample site for SRP Analysis

Each group should write their group's initials on a bottle. Take one 125mL polyethylene bottle and rinse twice in the stream water. On the third time fill the bottle completely full. Try to avoid touching the inside of the cap with your hand. Place the sample in a cooler

B) Sediment Core: Collect a sediment core to be processed with alum and water

Take a sediment core by using a pipe. First, take a little piece of the sediment and put it in a centrifuge tube (clearly labeled with your group info). Add ~ 25mL of DI water to the centrifuge tube and shake the centrifuge tube (try to shake as hard as you can) for 2 minutes. Pour the water from the centrifuge tube into a clearly labeled polyethylene bottle. Clearly mark the bottle with your group's information and with H20 treatment. Repeat this process again for a second time. While some people are working on the first step, the rest of the group can add stream water to the sediment and pipe and then add the appropriate amount of alum to the water (9.6mg Al: 1 mg P). Wait a minute and then take a new water sample. Clearly mark this polyethylene bottle with your group's information and alum treatment.

3. **Describe and take pictures of your site (i.e. what was the weather, what was the surrounding environment, was there algae in the stream etc)**

Lab Methods:

Analyze your three water samples (Stream samples, sediment-H20 sample, and sediment-alum sample) on the spectrometer. Using a standard curve and absorbance values of the samples, you can determine the P concentration of the samples.

Filtering:

The filters will be prepared ahead of time. To make the casings, the o ring will go on the top (where you can attach the syringe) of the filter. Next add a PES 0.45um filter (shiny side up) on top of the o ring. Finally screw the bottom of the filter on to the top of the filter. There is a picture below to help with setting up these casings. I recommend having half the group members work on filtering all your samples.

Standards:

I recommend having half the group members work on creating the standards. To create the stock solution, pre dry KH2PO4 (Teachers perform ahead of time). Then create a 10ppm solution of stock P standard. Use this stock to create 5 diluted standards using a serial dilution. Create the following concentrations:

0.01 ppm
0.05ppm
0.1 ppm
0.5 ppm
1 ppm

<u>I recommend using a 25mL flask</u>. One should add 2.5mL of the 10ppm stock to a flask and then fill the flask with water to the line to create the 1ppm standard. Add 12.5mL of the 1ppm standard to a new flask and then fill the flask with water to the line to create the 0.5ppm standard. Add 5mL of the 0.5ppm standard to a new flask and then fill the flask with water to the line to create the 0.1ppm standard. Add 12.25mL of the 0.1ppm standard to a new flask and then fill the flask with water to the line to create the 0.05ppm standard. Add 5mL of the 0.05ppm standard to a new flask and then fill the flask with water to the line to create the 0.01ppm standard.

Samples:

Make an analytical ID for your group's samples (This way it is easier to write the sample number on the cuvette). Add ~2.5mL of each filtered sample to a cuvette. I suggest having replicates of each of your three samples. You should have six samples to run in total.

Color Reagent:

The color reagent was made ahead of time:

Add in the specific order:

Add 5ml of 2.5 M Sulfuric Acid
Add 1.5mL of 20g/500mL Ammonium Molybdate Solution
Add 3.0mL of 0.1M Ascorbic Acid Solution
Add 0.5mL of Potassium Antimonyl Tartrate

Then add ~ 0.4mL of color reagent to each sample and standard.

Set the spectrometer to 880nm.

1. Run a blank (pure DI) and a method blank (DI with color reagent).

2. Run the standards on the cuvette and make sure the r-squared value is strong.
3. Run the samples and duplicates

Plot the standard concentrations on the x axis and the absorbance values on the y axis. Using the equation of the line (y=mx+b or Absorbance=(slope of the line *concentration/unknown)+ y intercept of the line), determine the concentration of the rest of the samples. The slope, y intercept, and r squard value can easily be found on excel using the function =slope, =yintercept, =rsq respectively.

Appendix N: Student Group Results

Group 1

Concentration	Absorbance		
0.01	0.474	0.9888295393	rsq
0.1	0.51	0.4799657313	intercept
0.5	0.566	0.183314953	slope
1	0.665		
sample	0.567	**0.4747799743**	**ppm**

Group 2

concentration	Absorbance		
0.01	0.50817	0.7639808845	rsq
0.1	0.51	0.5237327043	intercept
0.5	0.808	0.3268566352	slope
1	0.795		
sediment	0.528	0.01305555774	Ppm concentration

Group 3

Concentration	Absorbance		
0.01	0.059	0.997624315	rsq
0.1	0.078	0.05904713475	intercept
0.5	0.131	0.1514356901	slope
1	0.212		
water sample	0.094	0.2308099579	
sediment sample	0.216	1.036432463	