# SEDIMENT-PHOSPHORUS RESPONSE TO REDUCED POINT SOURCE LOADING IN THE JAMES RIVER WATERSHED, SOUTHWEST MISSOURI

A Masters Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science, Geospatial Sciences in Geography and Geology

By

Adam Dale Mulling

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Geography, Geology, and Planning

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## **ABSTRACT**

Eutrophication of lakes due to increased loading of nutrients negatively affects water quality, warranting worldwide efforts to reduce the limiting nutrient in most lakes, phosphorus (P). Reduced water quality in the James River Arm (JRA) of Table Rock Lake, Missouri led to a total maximum daily load for the James River addressing excess nutrient loads. In 2001, upgrades at a major sewage treatment plant (STP) reduced its phosphorus loading by 90%. This project aims to quantify the spatial and temporal distribution of sediment P in the James River Basin by (1) quantifying present sediment-P concentrations in the basin, (2) quantifying and describing the spatial patterns of sediment-P reduction, and (3) investigating the link between upstream sediment and P sources, and the JRA sediment-P response. Sediment collected from in-channel, overbank, and lake bottom locations was analyzed for geochemistry, organic carbon, and sediment size. Lake sedimentation zones are identified based on physical and chemical sediment characteristics, and lake morphometry. Sediment-P concentrations are highest immediately downstream of the STP and in the JRA. Within the JRA, sediment-P concentrations are strongly linked to depth and Fe. Sediment-P concentrations have decreased in all zones downstream of the STP since 2001, with an average decrease of 33% in the JRA in response to point source loading reductions. Longitudinal sediment P/Al trends suggest current P concentrations in the JRA are less influenced by point source P than in 2001.

**KEYWORDS**: sediments-lake, phosphorus, reservoirs, eutrophication, nutrients, geochemistry

This abstract is approved as to form and content

Dr. Robert Pavlowsky Chairperson, Advisory Committee Missouri State University

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## **CHAPTER 1**

## INTRODUCTION

Eutrophication through nutrient enrichment negatively affects marine, freshwater, and terrestrial ecosystems around the world. It diminishes water quality through increased algal and plant biomass, reduced water clarity, altered biodiversity, and reduced aesthetic value (Smith, Tilman, and Nekola, 1999). Reduced water quality can also impact regional economies by reducing the recreational value of waterways and increasing the cost of water treatment. Nutrient-loading reductions are a major focus globally in the effort to improve water quality (Jeppesen et al., 2005). In the United States, nutrient contamination is the cause of 303(d) impaired waters including more than 150,000 km of rivers and more than 12,000 km<sup>2</sup> of lakes (U.S. EPA, 2013). Widespread eutrophication in the United States has spurred large-scale initiatives to reduce anthropogenic nutrient loading. There have been many attempts to improve the water quality of lakes including combinations of watershed nutrient loading reduction, biomanipulation, and physicochemical methods (Jeppesen et al., 2005).

Many Midwestern lakes are phosphorus (P) limited, resulting in the implementation of best management practices (BMPs) that focus on P reduction and management (Conley et al., 2009; Jeppesen, Søndergaard, Meerhoff, Lauridsen, and Jensen, 2007; Jones and Knowlton, 1993; Søndergaard, Jensen, and Jeppesen, 2003). Efforts to reduce P loading to lakes are expensive, and the impacts of those efforts are difficult to see and measure on small (< decade) time scales (Jeppesen et al., 2007). Even though lake restoration projects have been in existence for more than 30 years, more

needs to be known about the spatial and temporal response of sediment P transport and sedimentation to reduced nutrient loads. Several studies have shown the importance of sediment P to water quality (Marsden 1989; Søndergaard et al., 2003; Håkanson and Jansson, 1983).

# **Sediment Phosphorus**

Phosphorus is a reactive element, interacting with sediment, organic matter, and water throughout a watershed (Boström, Andersen, Fleischer, and Jansson, 1988).

Dissolved orthophosphate is bioavailable, and this fraction of the total P is generally the most reactive, incorporating with sediment quickly. Sediment P occurs in several forms, influenced by environmental, chemical, and biological factors (Håkanson and Jansson, 1983). Sediment P can be divided into two major groups, inorganic and organic.

Inorganic P forms include allogenic and non-allogenic apatite phosphorus. Non-apatite inorganic P forms are generally associated with inorganic constituents, including Fe and Al hydroxides and calcite precipitates. Non-apatite inorganic P also includes P adsorbed onto sediment particles. Organic P describes many forms of P, but can be summarized as P incorporated into dead organisms or part of humic compounds (Håkanson and Jansson, 1983).

Within a watershed, sediment P is generally associated with bed, overbank, suspended, and upland sediment sources. During baseflow, bed and suspended sediment P concentrations are commonly acting in equilibrium to dissolved P concentrations in the water column (House, Denison, and Armitage, 2000). During storm flow, upland sediment is mobilized and transported to the waterways by erosion processes. Sediment-P

stored in bed sediments can also be mobilized during storm flow. Suspended sediment-P associated with storm flow can have many pathways including, deposition on floodplain, bench, bar, and/or bed surfaces, or transportation to a more permanent sediment sink such as a lake or reservoir (Thornton, 1990b).

Once P enters a lake or reservoir, internal cycling processes become more important. Sediment P settles out of the water column, naturally sorted by grain-size and density. Dissolved P is utilized by primary producers, turning dissolved P into organic P. Oxic lake conditions limit P release from the sediments, while anoxic conditions drive sediment-P release (Correll, 1998). Resuspension of sediment can also mobilize P, and can be caused by natural or anthropogenic phenomenon. Aquatic plants can also redistribute P, described by Wetzel (2001) as the macrophyte pump. Many other factors influence P cycling in lakes; however the general pattern of down-lake P cycling, particularly in reservoirs, is primarily a result of P mobilization due to resuspension or anoxic conditions (Kennedy and Walker, 1990).

# **Management and Reduction of Phosphorus**

Phosphorus is an essential nutrient for life and is found naturally throughout the world (Correll, 1998). Anthropogenic alteration of the concentration and distribution of P is common and can be divided into two source categories—point source and nonpoint source. Point-source locations are places where the substance of concern (in this study, P) is released from a place that can be represented by a point, such as a discharge pipe, or animal feedlot. Common P point sources include wastewater effluent and runoff from waste-disposal sites, animal feedlots, mines, oil fields, and large construction sites, as

well as storm sewer outfalls from cities with populations greater than 100,000 (Smith et al., 1999). Nonpoint source locations are places where P is released by a larger geographic area, conceptualized as a polygon, such as pastures or urban areas. Common P nonpoint sources include failing septic systems and runoff from agriculture, pastures, rangelands, abandoned mines, small construction sites, and storm sewer outfalls from smaller cities—those with populations under 100,000 (Smith et al., 1999).

Point Source Management. Reduction of point source P for lake restoration began with the work by Edmondson (1970). In response to eutrophic conditions in Lake Washington, particularly reduced clarity and increased algae blooms, the city of Seattle diverted sewage from the lake. This resulted in increased water clarity, and reduced primary producer biomass, successfully restoring Lake Washington (Edmondson, 1991). Reducing point source P loading quickly became recognized for effectively reducing eutrophication throughout many first-world countries (Schindler, 2006).

Nutrient reduction from point sources, particularly sewage treatment plants, has been a major strategy in lake restoration efforts (Schindler, 2006). These strategies have been implemented by governments and agencies around the world (Jeppesen et al., 2005). Generally, these strategies involve biological or chemical removal of nutrients prior to discharge, a process called tertiary treatment. Biological and chemical removal of P from wastewater involves settling out P as a solid, followed by appropriate disposal. In the biological removal system, microorganisms are initially stressed in an anaerobic environment. Then they are subjected to aerobic conditions, where they utilize large amounts of dissolved P. Finally, sedimentation processes remove the P from the water

column (Van Haandel and Van der Lubbe, 2007). Chemical removal methods involve additions of aluminum sulfate (alum), causing flocculation of P.

Nonpoint Source Management. Nonpoint-source, P-reduction strategies tend to be more difficult to implement than point-source reduction strategies. Nonpoint-source P from different land-uses (e.g., pasture, agriculture, and lawn) are generally managed by encouraging proper stewardship of the land by landowners (Carpenter et al., 1998). Some watershed groups offer free soil testing to aid in the appropriate application of fertilizers. In some situations, poor land-use practices in the past have created a legacy of nutrient-rich sediment on the land surface that can become mobile during storm events. The buildup of nutrients, combined with the sporadic mobility of the nutrients, creates a longer geomorphic lag between the initiation of a nonpoint-source P reduction effort and its desired effect in both sediment and water column (Carpenter et al., 1998).

Effectiveness of Nutrient Load Reduction Strategies. The effectiveness of nutrient load reduction strategies is often evaluated using water-quality, as opposed to sediment-quality, variables (Jeppesen et al., 2005). Jeppesen et al. (2005) provides a synthesis of lake responses to reduced nutrient loading involving 35 case studies. The results of this study suggest recovery generally occurs over 10-15 years, delayed by internal loading, where P is released into the overlying water column from the sediments. Although internal loading commonly affects the recovery time of lakes, sediment-quality is less commonly used to evaluate the effectiveness of nutrient load reduction strategies. Several studies have investigated temporal and spatial changes in lake bottom sediment-P concentrations in response to reduced nutrient loading (Anderson and Rippey, 1994; Heaney, Corry, and Lishman, 1992; Søndergaard, Kristensen, and Jeppesen, 1993; Van

der Molen, Portielje, Boers, and Lijklema, 1998). These studies conclude that sediment-P concentrations decrease, albeit slowly, in response to nutrient load reduction strategies.

Much of the scientific literature regarding nutrient reduction strategies and their effectiveness focus on water quality improvements, leaving sediment quality unstudied (Jeppesen et al., 2005). Water quality is easier to measure and managers are generally more interested in the water component than the sediment component. This has led to a scientific gap regarding nutrient-load reductions and the associated sediment-P concentration reductions. While many studies have investigated the distribution of sediment P in response to nutrient-load reduction (Anderson and Rippey, 1994; Heaney et al., 1992; Søndergaard et al., 1993; Van der Molen et al., 1998), few have incorporated a watershed-size approach to identifying how sediment P distribution has changed both temporally and spatially.

# Nutrient Problems in the James River Basin and Table Rock Lake

This study focuses on the Ozark region of Missouri, where both water and sediment quality problems exist. A total maximum daily load (TMDL) for one of the major tributaries of Table Rock Lake (the James River) exists and a TMDL for the lake is in progress (U.S. EPA, 2001). The Springfield area in southwest Missouri has been a source of contamination to the James River and Table Rock Lake (U.S. EPA, 2001); however steps have been taken over the past 40 years to improve both sediment and water quality. According to the U.S. Environmental Protection Agency (2001), eutrophic conditions in Table Rock Lake, located in southwest Missouri, led to point source nutrient-load reductions in the watershed. Specifically, Springfield's Southwest

Wastewater Treatment Plant (SSWTP) reduced its P loading by 90% in 2001 (Obrecht, Thorpe, & Jones, 2005).

Water quality in the James River has been recorded since the mid-1960s. The completion of SSWTP in the 1950s resulted in low dissolved oxygen in Wilson's Creek and the James River, warranting water-quality assessments through the 1960s and 1970s (U.S. EPA, 2001; Kerr, 1969). Upgrades at SSWTP in 1977 were evaluated by a study indicating dissolved-oxygen levels had increased (U.S. EPA, 2001; Berkas, 1982). By the late 1980s, decreased water clarity and increased algae in Table Rock Lake shifted water quality concerns to Table Rock Lake.

Knowlton and Jones (1989) documented the distribution of nutrients, phytoplankton, and dissolved oxygen in Table Rock Lake. The results of this study suggested the James River was a major source of nutrients to the lake. Large-scale algae blooms in the 1990s increased awareness of the diminished water quality in Table Rock Lake. The Lakes of Missouri Volunteer Program (LMVP) began sampling Table Rock Lake in 1999, measuring water-quality variables such as nitrogen, phosphorus, chlorophyll a, and Secchi transparency (LMVP, 1999). Annual reports of their data are publicly available on their website. The results of the first year suggested eutrophic conditions in the James River Arm.

A TMDL for the James River was completed in 2001 and a TMDL for the lake is in progress (U.S. EPA, 2001). The results of the James River TMDL showed about 29% of the total P load can be attributed to known point source locations, predominantly sewage treatment plants (STPs). The largest STP in the watershed, SSWTP, discharges 11 times more effluent than the other STPs combined. The TMDL estimates 92,000

kg/year of P is released from SSWTP, compared to the total point source P loading value entering the JRA of 112,000 kg/year.

In order to improve water quality conditions in Table Rock Lake, SSWTP completed tertiary treatment upgrades in 2001, utilizing both biological and chemical P removal strategies. The combination of removal strategies allows the facility to more consistently achieve low P concentrations in its effluent. Wastewater treatment processes at SSWTP are discussed in more detail in Chapter 3.

The effects of nutrient reduction on water quality were assessed in 2005 using data collected by the LMVP (Obrecht et al., 2005). The results of this study showed significant improvements in chlorophyll a, nutrient, and Secchi transparency values. The conclusions of this study suggest large-scale point-source P reductions have reversed eutrophication in Table Rock Lake.

The majority of published studies on water quality in the James River basin have ignored the interactions of water with sediment; however, several master's theses have focused on sediment-P problems in the James River basin. Frederick (2001) documented the spatial distribution of channel sediment P in the James River basin above the James River Arm (JRA) of Table Rock Lake. This study showed that proximity to a P point source was a key variable in P-contaminated sediment. Owen (2003) investigated the spatial distribution of sediment P in the JRA. Both of these studies predate the upgrades at SSWTP, providing an extensive database of sediment geochemistry and P distribution in the James River basin. This database provides the opportunity to use a sediment-quality approach to evaluate point-source nutrient loading reductions in the James River Basin by advancing the concepts developed by Frederick (2001) and Owen (2003).

# **Purpose and Objectives**

This research aims to quantify the spatial and temporal changes of sediment and sediment P in response to point-source P reductions in the James River watershed.

Specifically, the purpose is to address the lack of knowledge and advance the concepts of Frederick (2001) and Owen (2003) regarding recent developments in water and sediment quality management. The objectives of this study are to:

- 1) Quantify 2013 sediment-P concentrations in Wilson's Creek, the James River and the JRA and link them to spatial and geochemical variables.
- 2) Quantify and describe the spatial patterns of sediment-P reduction in the James River and JRA in response to SSWTP nutrient load reductions.
- 3) Investigate the link between upstream sediment and P sources, and the JRA sediment-P response.

# **Benefits of this Study**

This study aims to benefit the scientific community and the local community by updating the sediment record for the watershed, evaluating the impact of upgrades at SSWTP, and identifying current locations with high-sediment P concentrations. The sediment record in the James River basin has been recorded historically through several studies (Frederick, 2001; Owen, 2003; Rodgers, 2005). In order to study the temporal changes occurring within the watershed, the sediment record has been updated for three major sections of the watershed, including Wilson's Creek, the James River, and the JRA.

Locally, upgrades at SSWTP and the surrounding STPs have improved water quality in Table Rock Lake and the JRA (Obrecht et al., 2005). Yet, as sediment in the James River basin is remobilized, transported, and deposited it is important to understand the legacy of the sediment. This study provides a snapshot of the current sediment-P distribution as well as the opportunity to quantify the impact of major point-source reduction on sediment quality.

Another benefit of this research is the potential to identify areas within the James River watershed that warrant future or continued study. Since the general pattern of sediment-P concentrations should be decreasing over the last 12 years; an increased sediment-P concentration in the watershed could signify areas where more research is warranted.

Finally, this research will provide an example of using a watershed-scale sediment-quality approach to evaluate nutrient load reductions. Studies like this are relatively uncommon, however they are an effective means of evaluating nutrient management strategies over decadal time scales.

# **CHAPTER 2**

# SEDIMENT PHOSPHORUS DEPOSITION IN RESERVOIRS

The interactions between P and sediment allow researchers to investigate transport and distribution patterns of P within stream and lake sediments. The P cycle describes a natural change from sediment to dissolved P, and dissolved to sediment P (Figure 1) (Correll, 1998; Søndergaard et al., 2003). When a directional flow is applied to the cycle, such as a stream, net transport of P is downstream in a process called nutrient spiraling (Dorioz, Cassel, Orand, and Eisenman, 1998; Newbold, Elwood, O'Neill, and Van Winkle, 1981). This process is also valid in reservoir systems (Correll, 1998; Kennedy and Walker, 1990; Søndergaard et al., 2003). Anthropogenic P loading is

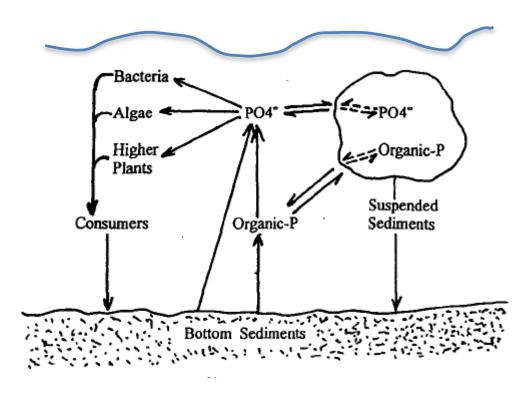


Figure 1. The phosphorus cycle in stream and lake systems (modified from Correll, 1998).

recorded throughout the watershed as part of this cycle. The natural cycling of anthropogenic P allows investigations of source-to-sink pathways of sediment P.

This chapter has four major objectives. First, it will define the P system, discussing chemical and physical properties of P as well as geochemical and physical associations between sediment and P. Second, it will discuss the transport pathways, including sections on stream and lake processes. Third, it will describe the effect of P-management strategies on sediment P reductions. Lastly, it will review sediment-P trends and concentrations in response to reduced nutrient loading from the literature.

# **Sediment Phosphorus System**

Understanding sediment P cycling within a watershed involves knowledge of sediment P properties, both physical and chemical, as well as source, transport, and sink processes. The physical and chemical properties of sediment P set up geochemical and physical associations between sediment and P that allow investigation into source transport and sink processes.

**Properties of Sediment Phosphorus.** The reactive nature of P encourages interactions between sediment and dissolved P within a watershed. Bio-available P is in the dissolved form; however, much of the P within a watershed is bound to and part of the sediment (Correll, 1998). Sediment P is made up of several forms of P, which are determined by factors such as origin, sediment composition, clay mineralogy, sediment size, and organic matter content (Horowitz and Elrick, 1987; Hupfer and Lewandowski,

2008; Wang and Morrison, 2014; Zhu et al., 2013). Within this study, sediment P will include all forms of particulate P.

Dissolved P is a negatively charged ion, adsorbing onto a variety of sediment sites. Generally, P adsorption is a function of decreasing grain size, including clays, carbonates, organic matter, Fe oxides, and Al oxides in the smallest sediment fraction (Håkanson and Jansson, 1983; Wang and Morrison, 2014). The relationship between adsorption sites and grain size is primarily a function of sediment surface area (Horowitz, 1991). Increased sediment surface area and adsorption sites are a common theme when investigating P associated with Al and Fe oxide sediment coatings (Håkanson and Jansson, 1983).

Associations of Sediment Phosphorus. The interactions between sediment and P develop relationships and associations between P and geochemical and physical variables. Increased P adsorption on fine-grained sediment would suggest correlations between the concentrations of P, and Al, and Fe. Clay minerals are aluminosilicates, composed primarily of Al, Si, and O. Many other metals and nonmetals are constituents of different clay mineral structures, including Fe. Precipitation of P salts, particularly with Fe and Ca, can influence sediment P geochemical associations (Dodds and Whiles, 2010).

One common method of utilizing the relationship between sediment and adsorbed compounds is to normalize to a conservative element, generally Al and Ti (Horowitz, 1991). Al normalizations make the assumption that sediment source and watershed processes have remained relatively constant through time. The conservative nature of Al stems from its uniform flux from sediment and rock sources within a watershed

(Horowitz, 1991). If this assumption is not met, patterns and trends are still important; however, sediment source changes will influence the observations.

Fe is a common component of fine-grained sediment and the water column.

Fe(III) ions will bond with P to form ferric phosphate precipitate in oxic environments

(Dodds and Whiles, 2010). This form of P is relatively stable. However, in anoxic

environments, Fe(III) reduces to Fe(II), which is soluble, releasing P back into the water

column (Dodds and Whiles, 2010). Fe(III) reduction can play an important role in P

mobilization in lake sediments, particularly when hypolimnetic water is hypoxic during

stratification.

Mn also has the potential to accumulate P. Mn oxides are commonly a coating on sediment particles, and tend to be amorphous or poorly crystallized, allowing significant adsorption of P. The association of P with Mn is similar to that of Fe, where solubility is determined by oxidation state and environment (Håkanson and Jansson, 1983).

Organic matter is also commonly associated with P. Aquatic organic matter has large surface areas and high adsorption capacity (Horowitz, 1991). Within a watershed, organic matter is a common component of the sediment. In lake systems, organic matter can accumulate in deeper areas as a result of anoxic hypolimnetic conditions slowing organic matter decay (Dodds and Whiles, 2010).

# **Phosphorus Transportation in Streams**

Phosphorus transportation in streams is controlled by sediment and water-transport mechanisms. Dissolved P moves through a watershed with the flow of water, interacting along the way with bed, bank, and suspended sediment (Ekka, Haggard,

Matlock, and Chaubey, 2006). Two different flow regimes alter the flowpath of P and sediment through a watershed—baseflow and storm flow (Dorioz et al., 1998). Within these different flow regimes, there are several pathways for sediment and P to disperse from source to sink. These pathways and sediment interactions will be discussed in this section.

Baseflow-Sediment P Transportation. Baseflow conditions in a stream refer to low-flow conditions where water in the stream is provided by groundwater contributions (Knighton, 1998). Suspended sediment concentrations are lower during baseflow than during storm flow. This relationship is especially noticeable in the Ozark Plateau region where baseflow conditions are known for their very low suspended sediment (Adamski, Peterson, Freiwald, and Davis, 1995). While there is little suspended sediment in the Ozarks, water is interacting with both bed and bank sediment.

Sediment P accumulation during baseflow occurs where fine-grain sediments accumulate in the channel and in wetted bank deposits. As dissolved P is moving through the watershed, it is adsorbing onto fine-grained sediment, developing equilibrium conditions between dissolved P concentrations and sediment-bound P concentrations (Ekka et al., 2006). This process accumulates P in sediments that are transient within the stream bed, and easily erodible on the banks, setting the stage for transport during the next storm flow.

During baseflow conditions, sources of P are limited to point-source discharges.

Generally, in the Ozarks, the largest P loads during baseflow are from STPs (Ekka et al., 2006). The effluent is primarily composed of dissolved P as it is released into the stream,

allowing interaction with bed, bank, and suspended sediment downstream (Ekka et al., 2006).

Storm-Flow Sediment P Transportation. Storm events transport the majority of sediments, with a maximum sediment transport occurring during bankfull conditions (Leopold, 1995). During a storm event, sediment is mobilized from both in and out of the channel. Sediment from the land surface is eroded by two major processes—rill and sheet erosion. In the James River Basin, this accounts for an estimated 89% of in-channel sediment (Kiner and Vitello, 1997). Other sediment contributions in the James River Basin include streambank erosion (3%) and construction/urbanization (7%) (Kiner and Vitello, 1997).

Storm flows that overtop the banks store sediment on the land surface, on floodplains, on benches, and sometimes on terrace surfaces (Knighton, 1998). Floodplain and bench deposits record the geochemical and physical characteristics of the sediment. As the stream level decreases after a storm, fine-grained sediment is also temporarily stored in low-energy portions of the channel, including bar tails and pools (Knighton, 1998). The fine-grained, in-channel sediment provides adsorption sites for P and other compounds (Horowitz, 1991).

During storm-flow conditions, both point and nonpoint-source P is moving through the watershed. Nonpoint-source P previously stored on the land surface can be transported with sediment by overland flow, including sheet and rill erosion.

Construction sites and urban areas also contribute sediment and P during storm events (Dorioz et al., 1998). Stream-bank erosion additionally contributes sediment and P previously stored by the stream. During a storm event, point-source P temporarily stored

in bed and bank sediments is flushed through the watershed, and combines with nonpoint-source P (Dorioz et al., 1998).

#### **Reservoir Sedimentation**

Sedimentation in reservoirs occurs as a function of flow velocity, lake morphometry, sediment supply, and primary production. Within the reservoir, sedimentation is generally considered in terms of longitudinal trends and lateral trends. Reservoirs are unique in that they tend to occupy stream basins, resulting in high shoreline length, high shoreline development index, shallow mean depth, and high overall productivity (Dodds and Whiles, 2010). Reservoirs also have larger drainage basins than natural lakes, suggesting higher nutrient loads, and higher productivity (Dodds and Whiles, 2010).

Longitudinal Sedimentation Zones. The three longitudinal depositional zones are the riverine, transition, and lacustrine (Figure 2) (Thornton, 1990a). Flow velocity slows in the riverine zone, depositing bed load and coarser suspended sediment. These deposits are deltaic in nature, comprised of mixed sediment, and have high sedimentation rates (Morris and Fan, 1998). Delta deposits grow both up-lake and down-lake with constant lake levels. Suspended allochthonous and autochthonous sediment are deposited in the lacustrine zone. The finest particles settle to the lake bottom in areas associated with the lowest flow velocities. The transition zone divides the riverine and lacustrine zones, and is composed of a mix of bed load and suspended load sediment. Turbidity currents and density flows can move coarser sediment from the riverine delta into the transition and lacustrine zones (Håkanson and Jansson, 1983; Morris and Fan, 1998).

Sedimentation depositional features can vary from reservoir to reservoir (Figure 3). These patterns can exist simultaneously or exclusively in reservoir systems (Morris and Fan, 1998).

Lateral Sedimentation Processes. Lateral sedimentation processes focus sediment to the deepest areas, leveling the lake bottom surface (Figure 4). Three distinct processes are involved (Morris and Fan, 1998). First, density deposits focus sediment based on their travel path, the thalweg. Water flow within a reservoir is focused in the deepest part of the cross section, generally the historic stream thalweg. Sediment travelling with the flow is more likely to settle out of suspension within this zone.

Second, vertical sediment concentrations and fall velocities are greatest in the deepest section. Within the deepest part of the reservoir cross section, sediment accumulates and settles out of suspension faster than in shallower parts. Third, based on the cross-section depth, more sediment overlays the deepest section. Sediment quantity, as mass, is maximized in the water column in the deepest part of the cross section.

Sedimentation Trends in Managed Reservoirs. In managed reservoir systems, changing lake levels can alter the longitudinal morphology and sedimentation patterns in several ways. Varying lake levels can result in multiple deltas or the absence of a morphologic delta. Low lake levels can result in the reworking of past deltas, moving bed load material down-lake via head cutting (Morris and Fan, 1998). Flood events can also affect the longitudinal morphology. High sediment loads associated with floods have been shown to move the delta and build up large amounts of sediment. Subsequent low lake levels rework this material down-lake, smoothing the overall lake-bottom gradient (Galay, Okaji, and Ntshino, 1995; Morris and Fan, 1998).

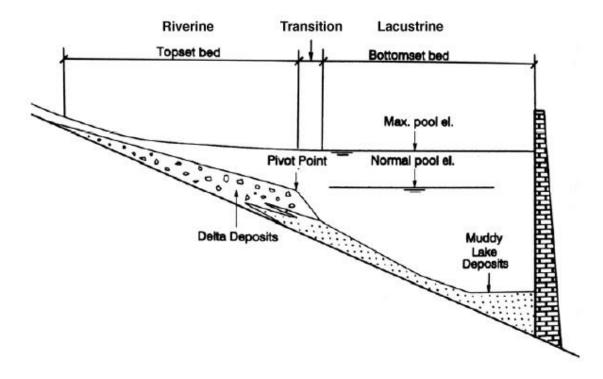


Figure 2. Longitudinal depositional zones within a reservoir (modified from Morris and Fan, 1998).

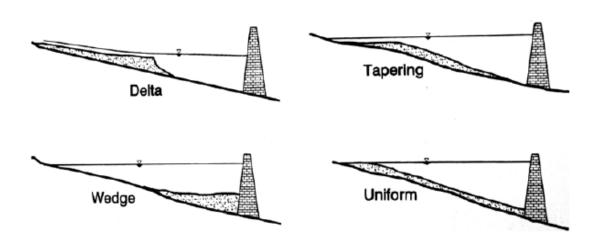


Figure 3. Longitudinal depositional profiles within a reservoir (from Morris and Fan, 1998).

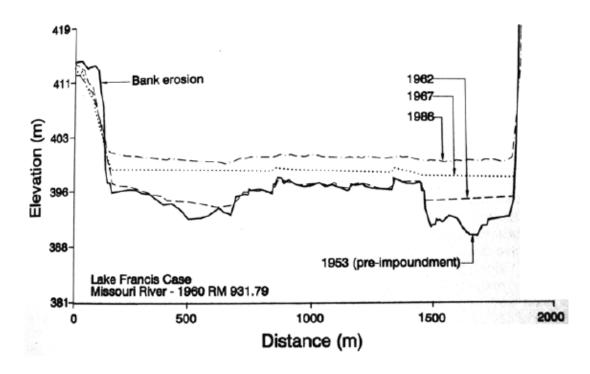


Figure 4. Lateral depositional profile of a reservoir (from Morris and Fan, 1998).

# **Sediment Phosphorus Deposition in Reservoirs**

Sediment P deposition patterns are similar to general sedimentation patterns, however sediment P cycling plays an important role. Reservoirs are generalized as traps or sinks for sediment and sediment P; however, it is possible for sediment P to dissolve and remobilize, becoming a source of nutrients to the water column (Dodds and Whiles, 2010; Håkanson and Jansson, 1983). Sediment-P dissolution is controlled by a complex set of variables including sediment composition, external load, catchment hydrology, lake morphometry, and biogeochemical reactions (Hupfer and Lewandowski, 2008). Once dissolved, P can be transported to the water column by diffusion, bioturbation, gas ebullition, or wind-induced turbulence (Håkanson and Jansson, 1983). The internal cycling and storage of P within lakes and reservoirs is generally referred to as internal

loading (Dodds and Whiles, 2010). Internal loading of P-rich sediments creates a lag between watershed-P load reductions and water/sediment quality improvements (Søndergaard et al., 2003). The cycling process of sediment P within reservoir systems focuses P-rich sediment toward the dam, in the deepest parts of the reservoir.

# **Effects of Best Management Practices on Sediment P Reductions**

Best management practices refer to water and sediment pollution control strategies. BMPs in response to nutrient enrichment are usually nutrient-load-reduction strategies, as well as treatment of nutrient-rich water (Meals, Dressing, and Davenport, 2010). Natural wetlands and other productive environments can be effective sediment and nutrient traps (Knox, Dahlgren, Tate, and Atwill, 2008). BMPs are specifically aimed at improving water quality, however the interactions between sediment P and dissolved P lead to improvements in both sediment and water quality. BMPs affect sediment P concentrations both spatially and temporally.

Spatial Changes in Sediment Phosphorus. The effects of BMPs on the spatial distribution of sediment P depend on whether or not the BMP is aimed at point or nonpoint source P. BMPs reduction of point-source P will have the largest effect locally, immediately downstream of the point source (Meals et al., 2009). This type of spatial change will be observable first in water quality, second in bed sediment, and third in overbank deposits. Bed sediments responding to reduced-point-source P will release P to the water column during baseflow and become part of the suspended sediment load during storm flow. Once the sediment has responded to reduced-point-source P, the

reduced-point-source load should be recognizable in storm-flow sediments stored on floodplains or in lakes/reservoirs.

The impact on water and sediment quality in response to BMPs efforts to reduce nonpoint-source P are often difficult to assess due to the large geographic extent and long lag times associated with these types of strategies (Meals et al., 2009). Examples of nonpoint-source P reduction BMPs include, but are not limited to, fertilizer application education, stormwater management, upland erosion mitigation, livestock exclusion from streams, and riparian zone restoration (Meals et al., 2009). Spatially, BMPs of this nature should reduce sediment-P concentrations geographically close to where they are implemented. Fluvial processes during storm events mobilize, mix, transport, and deposit sediment, spreading the BMP effect throughout the downstream reaches of the watershed. This reworking and mixing of the sediment develops a time lag between BMP initiation and measureable improvement (Meals et al., 2009).

Temporal Changes in Sediment Phosphorus. The temporal response of sediment-P concentrations to BMPs is dependent on the P source type. Point-source-reduction BMPs tend to have a faster response time, when compared to nonpoint-source-reduction BMPs (Meals et al., 2009). This is due to the transient nature of stored sediment P within the channel. Sediment-P concentrations in bed sediments release P in response to point-source P reduction during baseflow, while P-rich sediment is reworked during storms (Dorioz et al., 1998; Meals et al., 2009).

Sediment and water quality response to nonpoint-source P-reduction strategies is slow, on the order of decades (Meals et al., 2009). This lag between BMP implementation and measureable response is related to watershed variables including

hydrology, vegetation, transport pathways, hydraulic residence time, sediment sorption capacity, and ecosystem/hydrologic linkages (Meals et al., 2009). Assessment and monitoring programs often find BMPs of this nature to be unsuccessful, partly because of the long lag times and partly because of poorly designed monitoring or assessment programs (Meals et al., 2009).

# **Sediment Phosphorus Concentrations**

Stream and lake sediment P concentrations have been investigated around the world, measuring point and nonpoint source nutrients as well as background nutrient concentrations. Table 1 lists several sediment P studies and their respective average sediment P values. Average sediment P concentrations are elevated in areas receiving point and nonpoint source P. Total P concentration analyses vary between the studies, making comparisons difficult. Additionally, spatial variables such as watershed size, land-use, and climate likely vary significantly between the studies.

Based on the results from Table 1, along with the sedimentation principles presented in this chapter, sediment-P concentrations in the JRA should show significant reduction between 2001 and 2013. Sediment-P concentrations should be reduced nearly to equilibrium. Sedimentation trends within the JRA should be similar in 2013 to 2001, with increased fine-grained sedimentation in the deepest part of the cross-section and lake. This selective fine-grained sedimentation should be accompanied by the highest concentrations of sediment-P. This would suggest the largest reductions in sediment-P should be in the deepest parts of the lake cross-section, and in the deepest parts of the lake.

Table 1. Sediment-phosphorus concentrations from stream and lake sediments

Study	P Source	Sediment Type	Grain-Size Fraction	Extraction Method	Sediment P Concentration (ppm)
1	Point - STP	Stream Bed	< 200 um	Sequential Extraction	1,210
1	Nonpoint	Stream Bed	< 200 um	Sequential Extraction	590
1	N/A	Stream Bed	< 200 um	Sequential Extraction	420
2	Point and Nonpoint	Lake Bottom	-	Sequential Extraction	4,152
2	Nonpoint	Lake Bottom	-	Sequential Extraction	3,791
3	Point and Nonpoint	Lake Bottom	-	Total (a)	529
4	Point and Nonpoint	Lake Bottom	-	Inorganic and Organic (b)	750
5	Point and Nonpoint	Bench	< 10 um	XRF	1590
6	Point - Dairy	Stream Bed	-	Sequential Extraction	343
6	Point - Dairy	Overbank	-	Sequential Extraction	568
7	Point and Nonpoint	Lake Bottom	-	Sequential Extraction	2,900
8	Point and Nonpoint	Lake Bottom	-	Aqua Regia ICP-MS	641
9	N/A	Lake Bottom	-	Aqua Regia ICP-MS	458
9	Point and Nonpoint	Lake Bottom	-	Aqua Regia ICP-MS	3,382
10	Point and Nonpoint	Lake Bottom	-	Sequential Extraction	315
11	Point and Nonpoint	Lake Bottom	-	Sequential Extraction	1,793

<sup>1 –</sup> Dorioz et al., 1998; 2 – Heaney et al., 1992; 3 – Juracek, 1998; 4 – Liu et al., 2009;

<sup>5 –</sup> Olley and Caitcheon, 2000; 6 – Reddy et al., 1995; 7 – Spears et al., 2007;

<sup>8 –</sup> Trolle et al., 2009; 9 – Trolle et al., 2009; 9 – Wang and Morrison, 2014;

<sup>10 –</sup> Zhu et al., 2013; a – Fishman and Friedman, 1989; b – Ruban et al., 2001

<sup>-</sup> Grain-size fraction not listed

#### **CHAPTER 3**

## STUDY AREA

This study focuses on the James River Basin, including both river and reservoir portions of the basin. The James River Basin is located in southwest Missouri, draining portions of Greene, Webster, Wright, Christian, Lawrence, Barry, and Stone counties (Figure 5). The James River empties into Table Rock Lake, an impoundment on the White River. Table Rock Lake is a United States Army Corps of Engineers (USACE) reservoir and was completed in 1959 to provide economic opportunities, protection from White River floods, and electricity (USACE, 1985). Springfield is the only large metropolitan center within the James River watershed, with a population of about 160,000 in the city, and 437,000 in the metro area (U.S. Census Bureau, 2010). The population has doubled in Springfield over the past 60 years (U.S. Census Bureau, 2010). This chapter describes the characteristics of the James River Basin, the JRA of Table Rock Lake, and the connectedness of the SSWTP with these two areas.

## The James River Basin

The James River Basin drains about 3,770 km<sup>2</sup> and is been divided into two subareas for this study (Figure 6). The Upper James River Basin drains 2,500 km<sup>2</sup> or 67% of the study area. This distinction separates the reservoir and river sections of the watershed. The JRA of Table Rock Lake begins about seven kilometers downstream of Galena, Missouri, based on the power pool elevation of 278.9 m above sea level. The Upper James River Basin includes about 157 km of stream from the headwaters near Seymour

to the JRA boundary. The Upper James River Basin was further divided into three sections in relation to the confluence of two important James River tributaries—Wilson's Creek, and the Finley River. The Upper James River extends from river kilometer 157 to 64. The Middle James River is from kilometer 64 to 47, and the Lower James River extends from kilometer 47 to 0, at the JRA lake boundary.

Wilson's Creek drains much of the city of Springfield, and enters the James River near river kilometer 64. The SSWTP discharges effluent into Wilson's Creek about 12

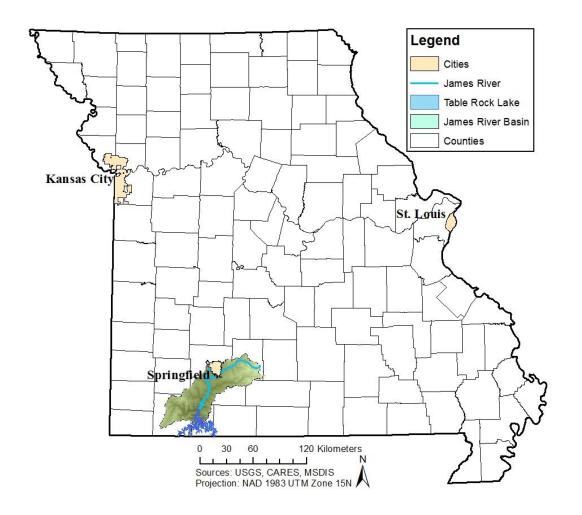


Figure. 5. Location of the James River Basin within the state of Missouri.

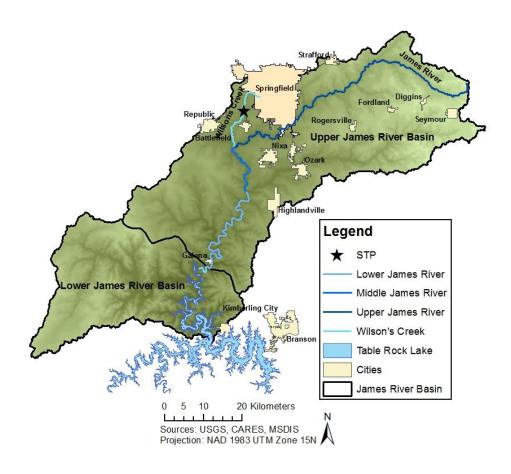


Figure 6. The Upper and Lower James River Basin separate the river and lake portions of the watershed.

km upstream of the James River and Wilson's Creek confluence. For this study, Wilson's Creek has been divided into two sections, above and below the SSWTP. Wilson's Creek represents a major source of contaminated sediment to the James River. Above the SSWTP, Wilson's Creek is ephemeral; flow is absent in much of the stream under baseflow conditions. Below the SSWTP, stream discharge is primarily effluent.

The Finley River is the largest tributary of the James River, draining about 715 km<sup>2</sup>. The confluence of the Finley River and James River is at river kilometer 47. Four municipal wastewater treatment plants discharge effluent into the Finley River.

Geology and Soils. The James River Basin is located within the Ozark Plateau Province, a region of uplifted sedimentary rocks. Within the Ozark Plateau Province, the James River flows through the Springfield Plateau section (Adamski et al., 1995). The bedrock geology of the James River Basin is primarily Mississippian in age (Figure 7). Ordovician strata in this study area are part of the Ibesian series, and include the Smithville, Powell, Cotter, and Jefferson City dolomites. These units are associated with the southern end of the study area within the Lower James River Basin. Mississippian

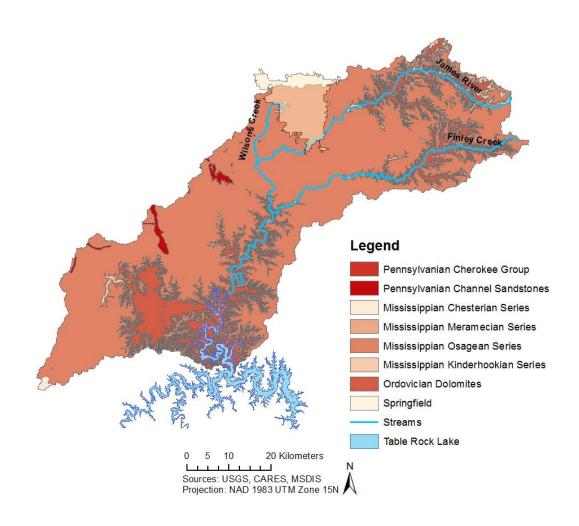


Figure 7. Geology of the James River Basin.

aged rocks include formations in the Chesterian, Meromecian, Osagean, and Kinderhookian series. These are all primarily limestone, with occasional shale units. The Pennsylvanian strata in this study area are part of the Middle series and include cyclic shale and limestone deposits including some sandstone (Thomson, 1986).

The abundance of limestone in this region creates a unique karst topography including caves, sinkholes, and springs. These features play an important role in connecting surface water and groundwater. Intermittent and ephemeral streams are common in the Ozarks, where surface water can easily infiltrate the shallow carbonate aquifers (Adamski et al., 1995). Karst features including estevelles heavily influence Wilson's Creek. Estevelles act as springs and swallow holes depending on the water table. During much of the year the estevelles are keeping Wilson's Creek dry, while during wet periods, they are increasing flow (Thomson, 1986).

Soils in the James River Basin can be generalized as combinations of loess, colluvium, and residuum. Loess, if present, is generally in the A and/or B horizons, originating as wind-blown glacial sediment of Pleistocene age. Colluvium is a common component of soils in the steeper areas of the James River Basin. Residuum, the chemical weathering residue, can contain variable amounts of chert, depending on the local limestone source. The Natural Resources Conservation Services (NRCS) soil database lists 11 soil associations in the James River Basin. Soils in the Upper James River Basin, on the Springfield Plateau, are formed in colluvium and residuum and occupy low to moderate slopes on the uplands. These soils include Tonti-Goss-Alsup, Ocie-Moko-Gatewood, Pembroke-Keeno-Eldon-Creldon, Viraton-Ocie-Mano, Wilderness-Viraton, and Wilderness-Tonti. They tend to be deep or very deep and moderately to well drained

(NRCS, 2015). Chert fragment content within the soils range from 0 to 80%, and clay content ranges from 15-85%. Soils in the Lower James River Basin are also formed in colluvium and residuum and occupy low to high slopes. These soils include Hector-Cliquot-Bolivar, Keeno-Hoberg-Creldon, Nexa-Jay-Clarksville-Captina, Ocie-Mano-Gatewood-Alred, Ocie-Moko-Gatewood, Rueter-Moko-Clarksville, and the Wilderness-Tonti. They also tend to be deep or very deep, but some are excessively drained (NRCS, 2015). Chert fragment content in the soils range from 0-80%, and clay content ranges from 15-85%.

Climate and Hydrology. The James River Basin is located within the humid continental region, where temperatures average 3°C in January and 30°C in July (Adamski et al., 1995). The average precipitation per year is about 105 cm, and tends to fall in intense storm events. The greatest rainfall usually occurs in late spring, while the late winter months are usually the driest (Adamski et al., 1995). These storm events, combined with the geology, lead to flashy runoff events (Jacobson and Gran, 1999).

Land Use History. Settlement of southwest Missouri began in the early 1800s, with the transformation of forest to pastures and fields (Jacobson and Primm, 1997). Timber production from the 1870s to the 1960s increased upland erosion and began to alter the hydrology of the Ozark streams. Additionally, livestock production in southwest Missouri has increased through much of the 20<sup>th</sup> Century, creating disturbance zones in the streams through damaged riparian zones. These land-use changes have made stream hydrographs flashier and increased the amount of chert gravel in stream channels (Jacobson and Primm, 1997).

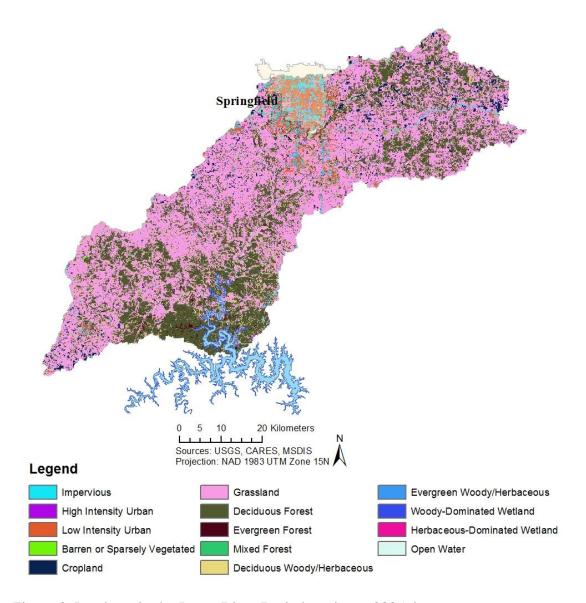


Figure 8. Land-use in the James River Basin based on a 2005 dataset.

Currently, the James River Basin is more than 50% grassland and cropland, about 35% forest, and 7% urban land use (Figure 8). These values are based on the most recent 2005 land use land cover dataset. Urban areas are clustered around the city of Springfield, with some urbanization around Table Rock Lake.

## The James River Arm of Table Rock Lake

The James River empties into the JRA of Table Rock Lake about 7 km below the town of Galena (Figure 9). The transition between lake and river is defined as lake-river kilometer zero in this study. Several additional tributaries flow into the JRA, the largest of which is Flat Creek (Figure 9). The JRA drains into the main arm, White River, of Table Rock Lake about 64.5 km down-lake of the river-lake boundary.

Table Rock Lake is managed by the USACE, resulting in predicable, but variable lake levels. The power pool lake level is 278.9 m, above sea level. Lake levels tend to peak in winter or spring and decrease in summer, with an average yearly fluctuation of five meters (Knowlton and Jones, 1989). Table Rock Lake has a high shoreline development index and a large watershed-to-volume ratio (Table 2), both of which are indicators of productive lakes (Dodds and Whiles, 2010). The high length and overall size of the lake promote sedimentation in certain regions, creating large longitudinal gradients in trophic state, from hypereutrophic to oligotrophic (Knowlton and Jones, 1989). The lake is warm monomictic, mixing from late fall to early spring, with a summer thermocline ranging from 7-12 m in depth (Knowlton and Jones 1989).

The JRA of Table Rock Lake accounts for approximately 20% of the total lake area and about 30% of the total flow, making the JRA the largest tributary by flow. Residence times in the JRA range seasonally from 107 days between April and June to 321 days between July and September (Knowlton and Jones, 1989). Approximately 2,500 km<sup>2</sup> of the Ozark Highland Province drains into the JRA before flowing into Table Rock Lake (Knowlton and Jones, 1989).

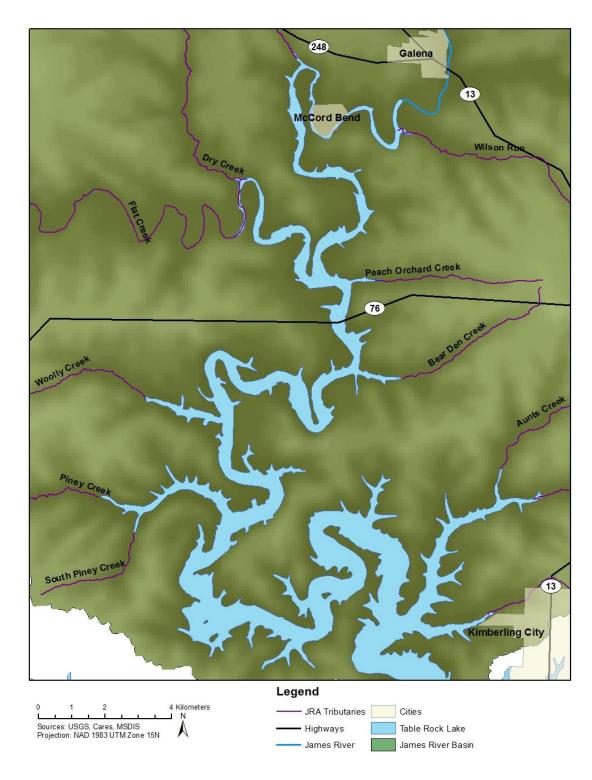


Figure 9. The James River Arm of Table Rock Lake, with landmarks at power pool (278.9 m msl) lake level.

Table 2. Lake Morphometry of Table Rock Lake and the JRA at power pool lake level (278.9 m msl)

_ F	/	
Characteristic	Table Rock Lake	James River Arm
Drainage Area (km²)	10,412	3,770
Surface Area (km <sup>2</sup> )	174	34
Volume (km <sup>3</sup> )	4	0.42
Average Depth (m)	24	12
Maximum Length (km)	91	65
Average Width (m)	571	346
Maximum Depth (m)	77	48
Shoreline length (km)	1,199	243
Watershed area/ Lake volume	2,438	9,015
Shoreline Development Index	45	21

Poor water quality in Table Rock Lake, particularly in the JRA, led to the development of a TMDL for the James River, which the Environmental Protection Agency (EPA) accepted in 2001. Prior to the 2001 upgrades, 27% of the P entering Table Rock Lake was estimated to come from the SSWTP (U.S. EPA, 2001). The Missouri Clean Water Commission implemented a phosphorus limit of 0.5 mg/L for all STP facilities releasing more than 85,000 liters per day to Table Rock Lake. The phosphorus limit affected 13 point-source locations.

# **Springfield's Southwest Wastewater Treatment Plant**

The SSWTP is located in southwest Springfield and discharges effluent into Wilson's Creek. Wilson's Creek is an ephemeral stream; just upstream of the SSWTP there is generally no flow. During baseflow conditions, the SSWTP provides all of the water in Wilson's Creek.

The plant was completed in 1958 with a flow capacity of 45 million liters per day. Expansions and major improvements were completed in 1978 and 1993, increasing capacity to 160 million liters per day. By 2001, biosolid and chemical P removal upgrades were implemented, providing significant nutrient removal (City of Springfield, 2012). The plant is divided into two parallel facilities, which differ in their removal of nutrients. On one side of the plant, biological P removal is accomplished by moving microorganisms back and forth between anoxic and oxic environments. While in the anoxic environment, stress causes certain bacteria to release stored P. On the other side of the plant, a chemical treatment process using the addition of alum (aluminum sulfate) to flocculate P is used to remove P (City of Springfield, 2012).

These upgrades have had a significant effect on reducing nutrient concentrations in the effluent. At the SSWPT outfall, the median total monthly discharge of total P was 12,402 kg between July 1992 and February 2001 (Obrecht et al., 2005). From March 2001 to September 2003, the median total monthly discharge of total P had dropped by nearly 90% to 1,217 kg (Obrecht et al., 2005). Obrecht et al. (2005) also measured the effects of the plant's P reductions in the JRA of Table Rock Lake. Their findings suggest P reductions at the SSWTP shifted the trophic state at two sites, from hypereutrophic to eutrophic and from eutrophic to mesotrophic. Secchi depth increased throughout the JRA.

Although SSWTP is not the only point P source in the watershed, it is by far the largest (U.S. EPA, 2001). The calculated annual P loading from SSWTP was 92,450 kg/year prior to the 2001 upgrades. Contributions of point source P from other locations in the watershed only accounted for 19,148 kg/year, or about 21% of the total (U.S. EPA, 2001).

### **CHAPTER 4**

### **METHODS**

This study involved field, laboratory, statistical, and GIS methods. The sampling design was developed using three previous studies within the James River Basin as references (Frederick, 2001; Owen, 2003; and Rodgers, 2005). Field methods included lake-bottom, floodplain, bar-tail, and bench-sediment sampling. Sample site locations were collected using GPS. Sediment samples were prepared in the laboratory and analyzed for chemical composition, grain size, and organic matter content. Statistical analysis using SPSS involved descriptive and comparative methods, including scatter-plots and Pearson correlation matrices. GIS analysis was completed using ArcMap 10.2.

## **Field Methods**

Samples collected from the James River and Wilson's Creek focused on identifying different depositional environments, and therefore different contamination sources. Channel sediment samples from bar tails were collected using an entrenchment tool to scrape fine-grained channel material into plastic collection bags. A bar tails is the downstream end of a bar, where fine-grained material can be deposited. Bench and floodplain sediment samples were collected from the unconsolidated surface sediment using an entrenchment tool. At each location the site ID, date, and depositional feature were identified on the sample bag and a GPS coordinate was recorded. Duplicate samples were collected every 10 sites to analyze within-site variability. Samples were collected in

2014 on February 19 and 20, 2014 during baseflow conditions. Sample location data are listed in Appendix A.

Sediment sample sites on the James River were selected from the work by Frederick (2001) based on accessibility and reproducibility. Sediment samples were collected from 11 sample sites (Figure 10). Five sample sites were selected on Wilson's Creek—two above and three below SSWTP—replicating sample locations in work by Rodgers (2005) and Frederick (2001) (Figure 11).

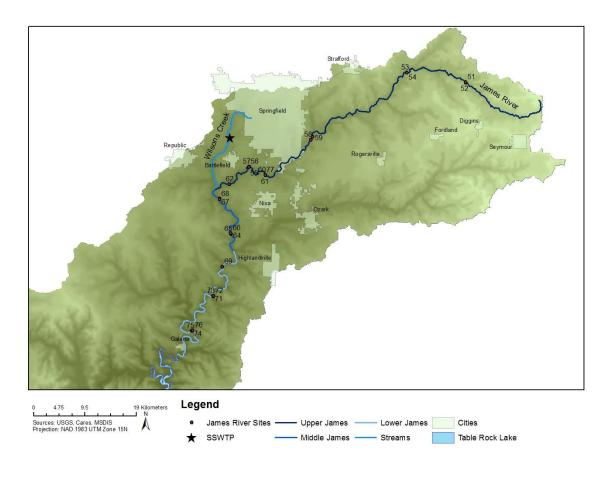


Figure 10. Sediment sample sites on the James River are separated into three zones, the Upper, Middle, and Lower James River.

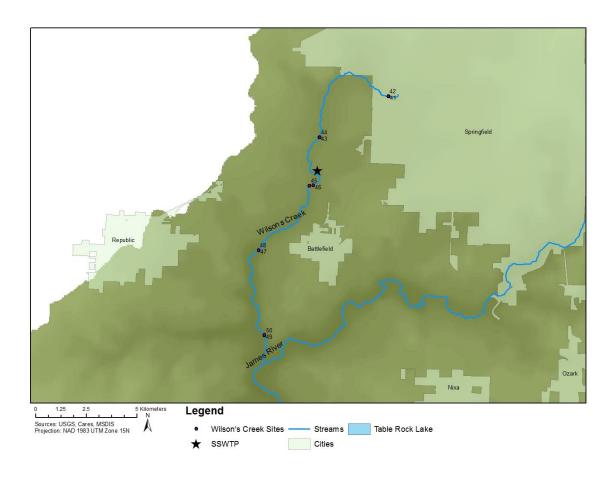


Figure 11. Sediment sample sites on Wilson's Creek are separated into two zones, above and below SSWTP.

An Ekman spring-loaded grab sampler was used to collect the top 10 centimeters of lake-bottom surface sediment from the JRA of Table Rock Lake (Blomqvist, 1985). Longitudinal sediment samples were collected at the deepest part of the lake, using a Lowrance Mark 4 sonar depth finder as a guide. At each site, the sediment was collected in plastic bags, with the date, depth, and site description written on the bag. Field notes were taken to include any additional site-specific data such as observed bank material and failed sample locations. The depth finder was used to collect and store depth information for the sample locations and lake cross sections. GPS coordinates for sample locations

were recorded using a Trimble GeoXL with post processing accuracy of < 1 m. Duplicate samples were collected from every 10<sup>th</sup> sample site. Longitudinal sampling occurred on November 11, 14, and 19, 2013, while lateral sampling occurred on July 28 and 31, 2014. Sample location data are listed in Appendix A. In order to account for potential changes in sediment P concentrations due to sampling at two different times, five transect samples were selected to overlap longitudinal samples. Average relative percent difference of P for all samples was 8% and all were below 20% (Table 3).

Sediment sample sites on the JRA were identified from work by Owen (2003). Forty sites were selected to investigate the longitudinal variability and seven transects were selected to investigate the lateral variability (Figure 12). Sediment samples along each transect were collected at roughly equal distance between the collectable portions of the lake bottom, ranging from 4 to 10 samples per transect (Figure 13).

# **Laboratory Methods**

Laboratory analysis of the sediment samples involved both in-house and external components. Sediment characteristics and geochemistry data are summarized in

Table 3. Relative percent difference between samples collected in summer and fall.

	Relative Percent Difference				
Transect	P	Al	Fe	Mn	Ca
1	17	-25	-20	-12	30
3	-1	-11	-2	-2	-9
4	-13	-17	-16	-31	-19
5	-4	-2	-10	39	2
7	4	-6	6	-5	6

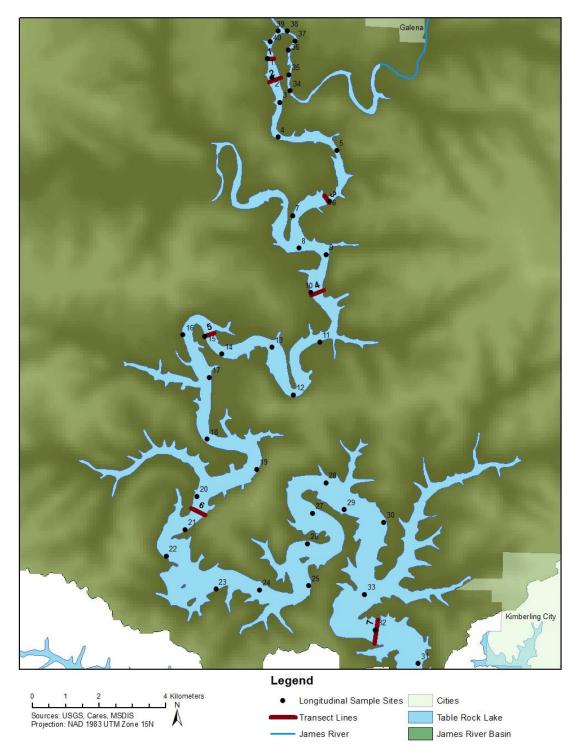


Figure 12. Sediment sample sites on the JRA.

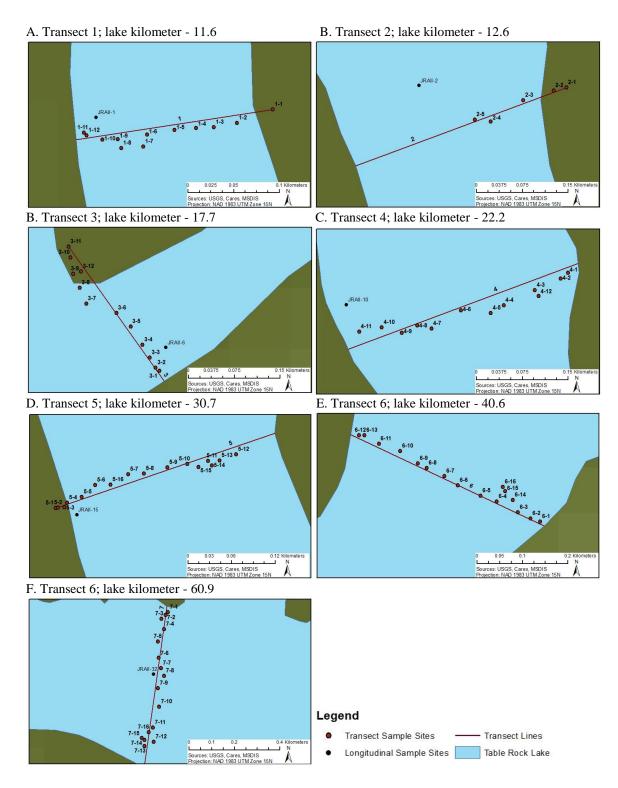


Figure 13. Lateral sediment sample sites on the JRA.

Appendix B. The sediment samples were received in the lab in quart-size zip-top bags and placed in a 60°C oven until dry, about 3 to 10 days. Once dry, the samples were disaggregated by mortar and pestle and sieved to less than 2 mm. Sediment greater than 2 mm was discarded after the mass was recorded. Stream sediment greater than 2 mm was composed primarily of chert and limestone. Lake sediment greater than 2 mm was minimal; however, chert, limestone, and sandstone were collected.

Geochemical Composition. A subsample from each site was sent to ALS Chemex for ICP analysis using an aqua regia (HCl: HNO<sub>3</sub> 3:1) acid-extraction method. This method quantifies the concentration of acid-extractable P and 31 other elements. Extraction of P by the aqua regia method provides P concentrations that are close to the total P in the sediment (Kulhánek, Balik, Černý, and Vaněk, 2009).

Organic Carbon. Organic carbon content was determined using two in-house methods. A loss-on-ignition (LOI) method modified from Dean (1974) was used in previous studies (OEWRI, 2007a). This method was replicated in the current study to validate the newer organic-carbon-analysis method using an Elementar Carbon-Nitrogen-Sulfur (CNS) analyzer (OEWRI, 2007b). Loss-on-ignition procedures included weighing a 5 g subsample and combusting the sample in a 600°C muffle furnace for six hours to remove organic matter. The pre- and post-burn weights were used to quantify organic content. CNS analysis combusts a sediment subsample of 20 mg, loaded into tin boats. One subsample was analyzed as is to determine total carbon. A second subsample was combusted for three hours at 450°C prior to analysis of inorganic carbon content. Organic carbon was calculated as the difference between total and inorganic carbon.

The results of each method were compared in order to further understand the relationship between LOI and CNS derived carbon data (Figure 14). Carbon content measured using the LOI method is on average 2.95 times higher than CNS derived data. This relationship will allow further comparison between this study and prior work in the area utilizing the older LOI method.

Grain Size. Particle size was determined using two in-house methods. Lake bottom sediment grain size was determined using the hydrometer method and a laser particle size analyzer (Gee and Bauder, 1986; OEWRI, 2008). Pretreatment of sediment samples for both analyses included organic matter digestions in a 30%  $H_2O_2$  and 1% acetic acid solution. The sediment was dispersed in a 5% sodium-hexametaphosphate solution prior to analysis. A 40 g subsample was used for the hydrometer method and readings were taken at 63  $\mu$ m, 32  $\mu$ m, 16  $\mu$ m, 8  $\mu$ m, 4  $\mu$ m, and 2  $\mu$ m size fractions based on sediment settling velocities. After the hydrometer readings, the sediment was wet sieved to 63  $\mu$ m, and the remaining sand fraction was weighed to further quantify the sand content. A 0.20 g subsample was analyzed using a Beckman-Coulter LS 13 320 laser-diffraction particle-size analyzer equipped with the aqueous liquid module for sediment suspension (OEWRI, 2008).

The results of each method were compared in order to further understand the relationship between the two methods (Figure 15). Both methods produce similar clay content results, however sand and silt relationships are not very strong. This is likely due to measurement errors of sand and silt sized grains near the 63 µm cutoff. The error does not appear to be systematic.

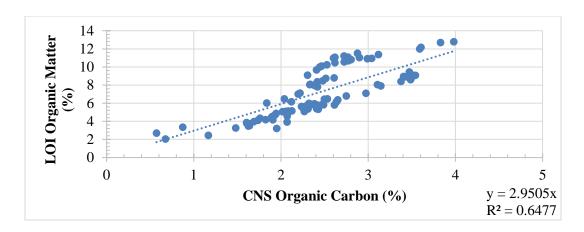
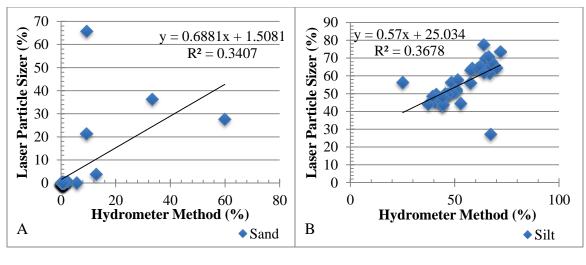


Figure 14. Comparison of loss-on-ignition and CNS method analysis of organic carbon content.



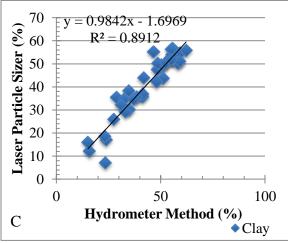


Figure 15. Comparison of hydrometer and laser particle sizer method analysis of sediment grain size.

# **Computer Methods**

After the analyses were completed for the sediment samples, work began using Excel, ArcMap 10.2, SPSS, and GPS Utility. Excel was used as the primary spreadsheet database for all of the sample information. ArcMap 10.2 was used for all GIS analyses and map making. SPSS was used for both descriptive and inferential statistical analyses. GPS Utility was used to retrieve and process the GPS waypoint data from the Lowrance Mark 4 depth finder.

GPS. Waypoint data were stored on the depth finder and transferred to a micro-SD memory card. GPS Utility was able to open the Lowrance .usm data files and convert them to ArcMap .shp files. The data were exported in metric units and the UTM coordinate system. Location data collected on the Trimble GeoXL were processed in Pathfinder, improving the accuracy of each measurement.

GIS. GIS was used to develop maps of the study area and sample sites. Data were downloaded and retrieved from MSDIS, CARES Maproom, USGS, and the Missouri State University Department of Geography, Geology, and Planning network drive. The National Hydrology Dataset was used for flowpath determination. Lake bathymetry data were mosaicked with terrestrial DEM data to develop a 10 m DEM image for the watershed. The spatial resolution of the DEM was not high enough to accurately describe temporal changes between this study and the older bathymetry data.

**Statistics.** SPSS software was used for statistical analysis of the data. In order to investigate associations between P and other sedimentation variables, a Pearson correlation matrix was constructed using both physical and chemical variables to identify P relationships. Box plots were created to show geochemical differences between

sedimentation zones and/or depositional environments. One-way ANOVA was used to identify statistically significance between sediment sample groups. The Pearson correlation matrix and box plots were also used as a comparison tool for identifying differences between pre- and post-upgrade sedimentation patterns. Linear regression modeling was used to investigate spatial and geochemical predictors for the spatial distribution of sediment-P, Al, P:Al, and P:Al:Fe. SPSS was also used for general descriptive statistical analyses of the raw data.

Stream Gage Analysis. The United States Geological Survey (USGS) monitors a stream gage on the James River at Galena, site number 07052500, and water chemistry and sampling condition information are available online. Variables including discharge, suspended solids, unfiltered Al, filtered Al, filtered P, unfiltered P, and sampling condition were downloaded from the USGS website on December 15, 2014. Particulate Al and P were calculated as the difference between unfiltered and filtered concentrations. These data are listed in Appendix F. Element concentrations below the detection limit were chosen to be half of the detection limit, while estimated values were listed as is.

In order to investigate temporal changes in Al concentrations, pre- and post-upgrade sampling events were separated for comparative analysis. Sample events were also categorized by discharge, using the hydrologic condition code to separate high (storm) discharge samples from low (baseflow) discharge samples. The data were grouped by pre- and post-upgrade with 2002 as the cutoff. Suspended Al was calculated using by subtracting the filtered Al concentration, or dissolved Al, from the unfiltered Al concentration, or total Al. Comparisons between pre- and post-upgrade samples were

used to test the hypothesis that the mean value of Al concentrations was lower following SSWTP treatment procedure upgrades.

### **Previous Studies**

This project was designed as one part of an overall watershed-monitoring goal.

The sample design of this research was created to update the sediment P database for three major sections of the watershed including Wilson's Creek, the James River, and the JRA to the main stem of Table Rock Lake. Three previous studies were used to develop the sample design framework in order to assess the temporal and spatial variations associated with upgrades at the SSWTP.

James River Basin Sediment Survey. Frederick (2001) used a watershed-scale approach to investigate the spatial relationships between P sources and sediment P contamination trends in the James River Basin. The study focused on the James River above the JRA and its major tributaries. In-channel sediment samples were collected from bar tails during baseflow conditions in 1999. Sediment samples were dried at 60°C, disaggregated by mortar and pestle, and sieved to less than 2 mm. ICP analysis was performed by Chemex Labs using an aqua regia digestion. Grain-size analysis was performed in-house using the hydrometer method (Gee and Bauder, 1986). Organic matter content was determined in-house using the loss-on-ignition method (Dean, 1974). Frederick (2001) used GIS to assess the influence of spatial variables, such as land cover and proximity to a point source, on sediment P contamination. This study highlights the role of sediment in P dispersal and determined that organic matter, forested land cover,

and the point-source-loading index were the key variables when predicting sediment P concentrations.

Of the 80 sites Frederick (2001) sampled, 14 locations were selected for replication in this study. These data were manually entered into Excel for comparative analysis and are listed in Appendix C. Six sample sites are within the Upper James River zone and are used to investigate sediment source changes and sediment P background levels. Two sample sites are within the Middle James River zone and are used to investigate the interaction between Wilson's Creek and the James River. Three sample sites are within the Lower James River zone and are used to investigate the dilution effects of the Finley River as well as sediment P transport through the James River. Two sample sites are below SSWTP on Wilson's Creek and one sample site is above SSWTP.

James River Arm Sediment Survey. Owen (2003) analyzed the spatial distribution of P in lake-bottom sediments of the JRA in order to quantify the importance of anthropogenic P contributions to the lake. The study included both longitudinal and lateral sedimentation analyses and identified key variables associated with P distribution. Sediment samples were collected with an Ekman grab sampler in 2001. Samples were dried at 60°C, disaggregated by mortar and pestle, and sieved to less than 2 mm. ICP analysis was performed by Chemex Labs using an aqua regia digestion. Grain size and organic matter content were determined using the same in-house procedures as Frederick (2001). This study found lake depth, Mn, and Ca were key variables describing the spatial distribution of sediment P in the JRA.

Forty sample sites from the JRA were selected from Owen (2003) to investigate longitudinal sedimentation changes within the lake. Additionally, six transect locations

were replicated. The data from Owen (2003) were accessible in digital form and are summarized in Appendix D.

Wilson's Creek Sediment Survey. Rodgers (2005) collected channel and overbank sediment samples in the summer of 2003 and 2004 to determine the spatial distribution of sediment-bound Hg in Wilson's Creek watershed. Sediment samples were collected from 66 locations, including channel, overbank, and land-surface sediment from each location. Sediment samples were dried at 60°C, disaggregated by mortar and pestle, and sieved to less than 2 mm. ICP analysis was performed by Chemex Labs using an aqua regia digestion and grain size and organic matter were determined using the same in-house procedures as Frederick (2001) and Owen (2003).

Of the 42 sites Rodgers (2005) sampled, five were replicated in this study. Three of these sites were shared between the Rodgers (2005) and Frederick (2001) studies.

Three sample sites are below SSWTP, and two are above. Data from Rodgers (2005) were manually entered and are summarized in Appendix E.

#### **CHAPTER 5**

### RESULTS AND DISCUSSION

The results of this study are described in this chapter, with an emphasis on both the current distribution of sediment-P in the James River Basin, as well as how it has changed in response to upgrades at SSWTP. Specifically, this section will define sedimentation zones in the JRA, describe current longitudinal and lateral sedimentation patterns in the JRA, investigate P source and transport factors, quantify temporal sedimentation changes, and link these results to STP upgrades in the James River Basin.

### **Sedimentation Zones of the James River Arm**

Sedimentation patterns in the JRA were investigated in order to identify sedimentation zones based on lake morphometry, as well as geochemical and physical properties of the sediment. Defining sedimentation zones in a reservoir system is important in order to predict and explain spatial and temporal changes in sediment and sediment-P patterns. A longitudinal depth profile was created using depth values recorded on the depth finder during sediment sampling (Figure 16). The lake-bottom gradient is about 0.00079. Several bends in the lake approach 180 degrees, possibly affecting currents and flow velocities within the lake (Figure 12).

Longitudinal Sediment Trends. Longitudinal sediment texture patterns indicate the majority of sand sized particles are deposited above lake kilometer 14 (Figure 17). Clay content increases down-lake, suggesting longitudinal sorting and fine-grain sediment focusing in the deepest part of the lake. Clay content plateaus around 52% in

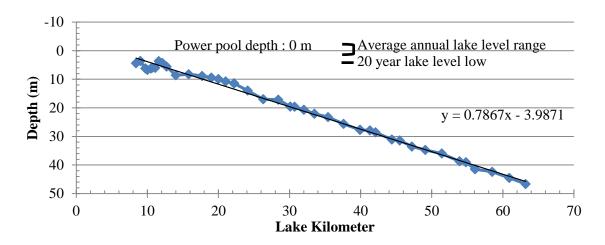


Figure 16. Longitudinal depth profile of the JRA.

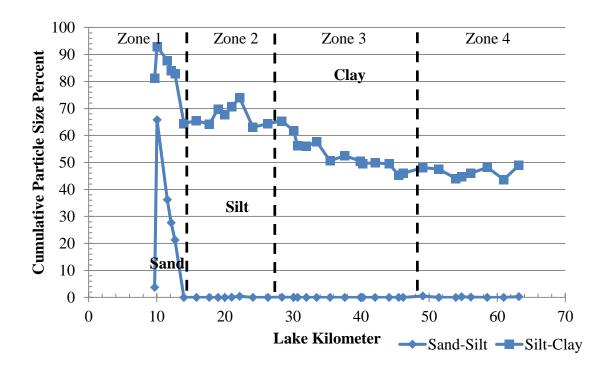


Figure 17. Longitudinal sediment grain-size distribution in the JRA.

the lower portion of the JRA. Organic matter content increases down-lake, with a sharper increase in the lower portion of the lake (Figure 18). Longitudinal geochemical trends are also apparent in the JRA, with systematic down-lake increases in Al and Fe concentrations, and a fluctuating Mn trend (Figure 19). Concentrations of Al, Fe, and organic carbon are expected to increase down-lake, associated with increases in fine-grained sediment abundance (Morris and Fan, 1998). Inorganic carbon content increases down-lake until around lake kilometer 50, where concentrations decrease (Figure 18). Ca concentrations increase through much of the lake, and decrease below lake kilometer 50 (Figure 19). The similarities between inorganic carbon and Ca trends are expected, relating to the dominance of CaCO<sub>3</sub> in the sediment and bedrock of the region.

Sedimentation Zone Characteristics. The sedimentation patterns and geochemical trends were used to identify four sedimentation zones (Figure 20). These zones are based on the longitudinal sedimentation models described by Morris and Fan (1998) (Figures 2 and 3). Longitudinal geochemical changes between the sedimentation zones are significant (Figure 21). Figure 22 shows significant correlation between Al, and Fe, organic carbon, and clay (Figure 22).

Zone One. Zone one extends from lake kilometer 0 to 14 and is characterized by increased sand and variable concentrations of Al, Fe, Ca, Mn, and carbon (Figures 17, 18, 19, and 20). Zone one is classified as a riverine zone, where particle settling due to decreased stream velocities create a diverse sediment load, building up the delta deposits (Morris and Fan, 1998).

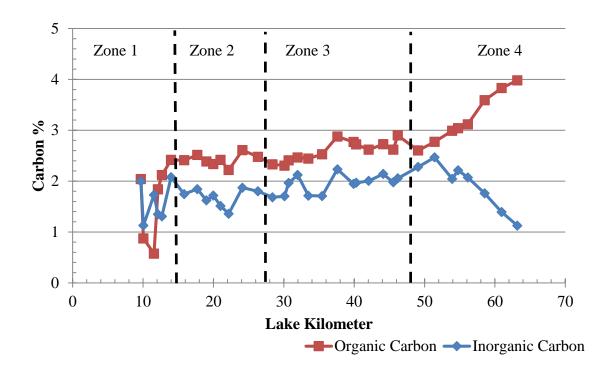


Figure 18. Longitudinal percent carbon of the JRA.

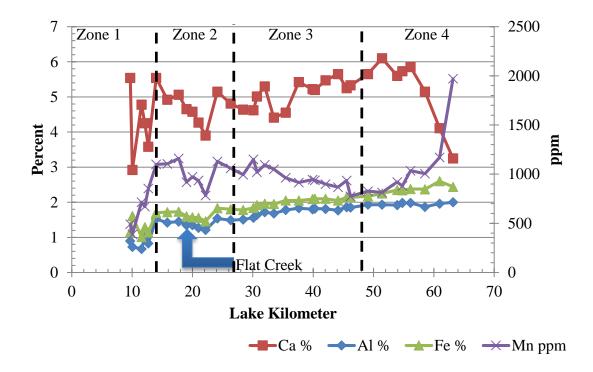


Figure 19. Longitudinal sediment geochemistry of the JRA.

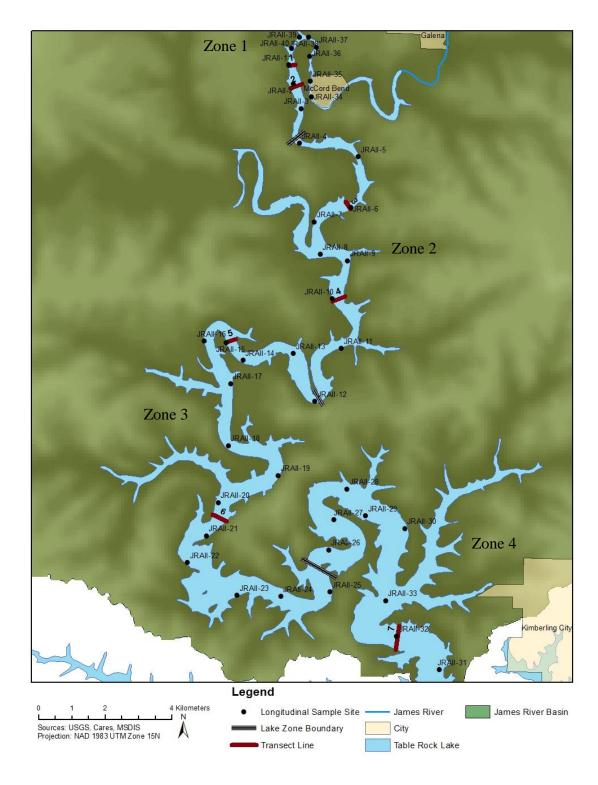


Figure 20. Sedimentation zones of the JRA of Table Rock Lake.

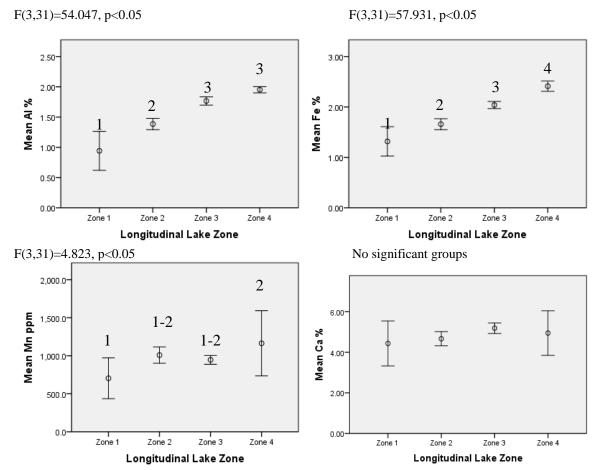


Figure 21. Longitudinal geochemical characteristics of the JRA by sedimentation zone. Error bars represent 95% confidence interval of the mean for each metal. Results from one-way ANOVA test show significant means between groups. Sample size for each zone: zone one, 6; zone two, 8; zone three, 15; and zone four, 6.

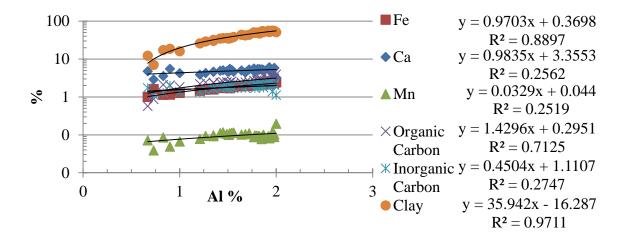


Figure 22. Geochemical trends of sediment variables with change in Al concentration in the JRA.

Zone Two. Zone two extends from lake kilometer 14 to 27 and is characterized by increased concentrations of clay, Al, and Fe, while concentrations of inorganic carbon, Ca and organic carbon remain statistically unchanged (Figures 17, 18, and 19). Geochemical patterns within zone two show decreasing down-lake concentrations of inorganic carbon, Mn, and Ca below lake kilometer 19, where Flat Creek enters the JRA (Figures 18, and 19). This zone is classified as the transition zone, where the diverse riverine sediment has been exhausted, and suspended sediment dominates the lake-bottom sediment (Morris and Fan, 1998).

Zone Three. Zone three extends from lake kilometer 27 to 48 and is characterized by increasing concentrations of Al, Fe, Ca, carbon, and clay, and steady concentrations of Mn (Figures 17, 18, and 19). This zone is classified as the lacustrine zone, where development and deposition of autochthonous sediment begins (Morris and Fan, 1998).

Zone Four. Zone four extends from lake kilometer 48 to the end of the JRA and is characterized by increasing concentrations of Al, Fe, Mn, and organic carbon, decreasing Ca, and inorganic carbon, and stable clay (Figures 17, 18, 19). The sharply increasing concentration of Mn and organic carbon, combined with the sharp decrease in Ca and inorganic carbon suggests a new sedimentation zone within this zone. It is still classified as lacustrine using the Morris and Fan (1998) classification scheme, however distinct differences exist between sedimentation zones three and four. Hypothetical lake circulation models developed by Knowlton and Jones (1989) suggest water from the White River arm enters the JRA through the thermocline during summer stratification conditions. The influence of these two water masses mixing could explain sediment trends, particularly the rapid increase in Mn in the down-lake portion of zone four.

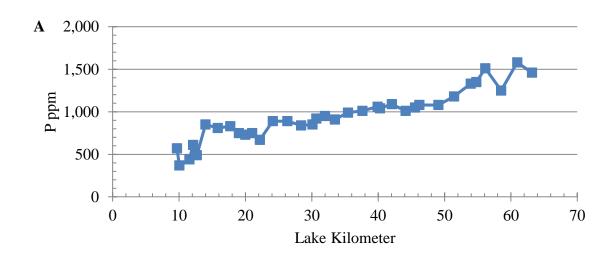
These lake zones will be used throughout the study to compare spatial and temporal trends of sediment and sediment-P. Defining these zones is important because sedimentation and chemical processes vary spatially within a lake system. Understanding these differences will be useful in explaining spatial and temporal patterns in the following sections.

# **Spatial Sediment Trends in the James River Arm**

Longitudinal sediment trends within the JRA followed the theory presented in Chapter 2, with the highest concentrations of P in the deepest down-lake portions of the lake. Sediment-P trends within the JRA are described both longitudinally and laterally within this section. Owen (2003) used regression analysis to investigate sedimentation trends and patterns. The same variables and methods will be used to develop current regression models and are presented in this section.

Longitudinal Sediment Trends. Longitudinal sediment trends were briefly discussed in the previous section while defining lake sedimentation zones. Increased variability of Al, Fe, and Mn in zone one is expected, as a range of sediment sizes are entering from the river (Figure 21). Increased concentrations of Al, and Fe suggest increased fine-grained sedimentation compared to zone one. The average Fe concentration is the only significant geochemical parameter within this zone. The significance of Fe and not Al could suggest Fe enrichment in this zone due to anoxic conditions seasonally. Zone four has a significant average Fe concentration, and a significant Mn average compared to zone one. The significance of these variables within zone four suggests the influence of redox reactions.

Sediment-P concentrations increase down-lake, with an average concentration of 948 ppm (Figure 23). The sediment P values in this study are within the range (315 – 4,152 ppm) of published values for lake-bottom sediment (Table 1). Field duplicate analysis for the JRA (n=4) shows low cv%, suggesting at-a-site variability is minimal (Figure 23). Sediment P variability within each sedimentation zone is relatively low, with maximums in zones one and four (Figure 24). The increased variability in zone one is most likely due to the increased sediment diversity, particularly the sand portion.



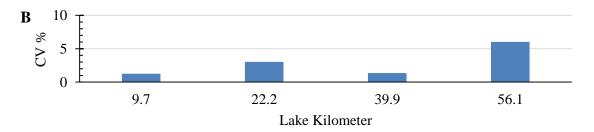


Figure 23. Longitudinal sediment-P trends of the JRA. A) Sediment-P concentrations. B) Within zone sediment-P variability.

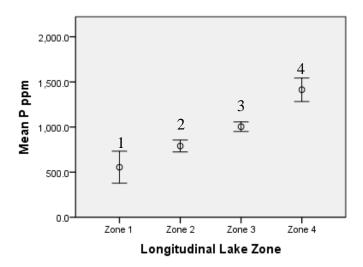


Figure 24. Longitudinal sediment-P concentrations by lake sedimentation zone. Error bars represent 95% confidence interval for the mean. Mean phosphorus concentrations are significantly different in each sedimentation zone, F(3,31)=65.811, p<0.05.

Increased sediment P variability in zone four could be due to additional sources of P, or sediment-P cycling processes. Additional sources of P could include Aunt's Creek, the main stem of the lake, or resuspended sediment from up-lake. Sediment-P cycling processes associated with seasonal anoxia in the hypolimnion could also enrich sediment-P within the deepest portions of the lake. Aunt's Creek drains 64 km² of mostly forested land, however there is development within this sub-watershed. The hypothetical inflow of White River water into the JRA during summer stratification (Knowlton and Jones, 1989) could provide additional sediment-P to the lower part of zone four. Finally, physical and geochemical redistribution of sediment P from up-lake zones could focus sediment P in zone four.

**Lateral Sediment Trends.** Transect specific data are summarized in down-lake order in Figures 25, 26, 27, 28, 29, 30, and 31. Each transect is oriented so that looking down-lake, the left bank corresponds to zero. Figures are divided into four parts. Part a

shows sample locations along each transect, with unsuccessful sample sites noted. Part b notes the sediment-P concentration at each site along each transect. Parts c and d show the relationship between clay content and depth, and sediment-P and depth respectively.

Transects one and two are within sedimentation zone one, the riverine zone (Figure 25 and 26). The right bank on transect one was primarily gravel bottom, most likely colluvium from the bedrock bluff. Sediment P and percent clay increase with depth in this zone, suggesting increased fine-grain sedimentation in the deepest part of the cross section. This suggests focusing of fine grain material is important to sediment P sedimentation in this zone.

Transects three and four are in sedimentation zone two, the transition zone (Figures 27 and 28). The deepest part of the lake transitions from the left to the right between these two transects. Sediment P and percent clay increase with depth in transect three (Figure 27), however these relationships break down in transect four (Figure 28). The consistency of percent clay in relation to depth could be related to several factors including lake morphometry and anthropogenic variables. Transect four could be affected by sediment from Flat Creek, entering about two kilometers up-lake. Flat Creek is the largest tributary of the JRA, draining 840 km². Flat Creek sediment associated with a secondary delta or storm pulses could result in local reduction of the clay content downlake of Flat Creek. Sedimentation in the Flat Creek cove of the JRA should be deltaic in nature and include coarse-grained sediment. Owen (2003) found increased sand concentrations in JRA sediments immediately down-lake of Flat Creek, as well as in the cove itself. Another possibility is anthropogenic in nature. The topographic feature to the

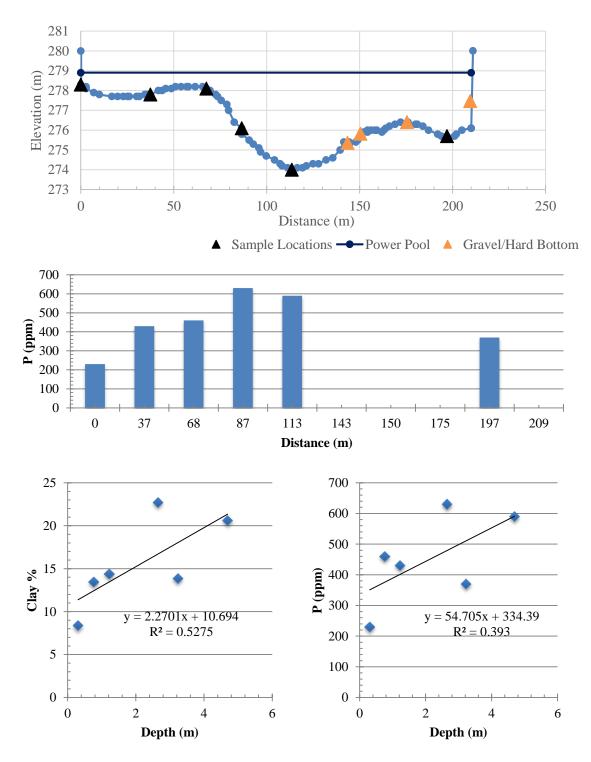


Figure 25. Transect one of the JRA within sedimentation zone one at lake kilometer 11.6. Lake left is the east bank of the JRA at this location.

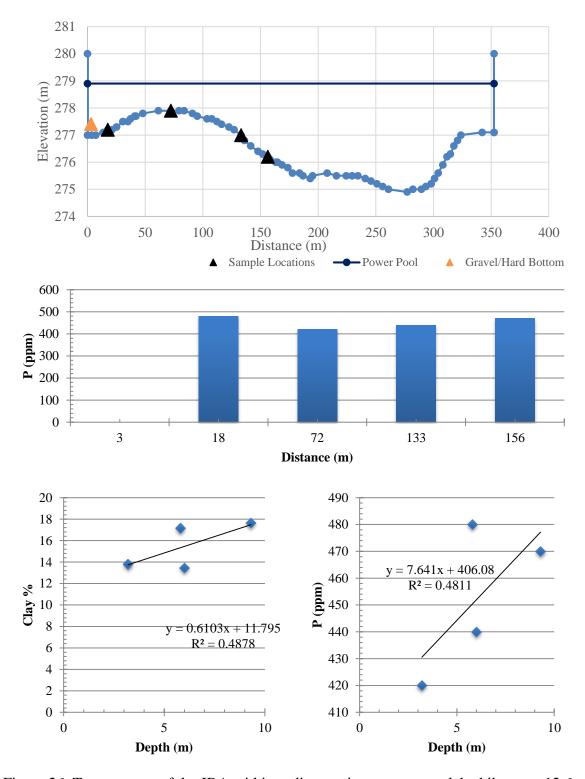


Figure 26. Transect two of the JRA within sedimentation zone one at lake kilometer 12.6. Lake left is the east bank of the JRA at this location.

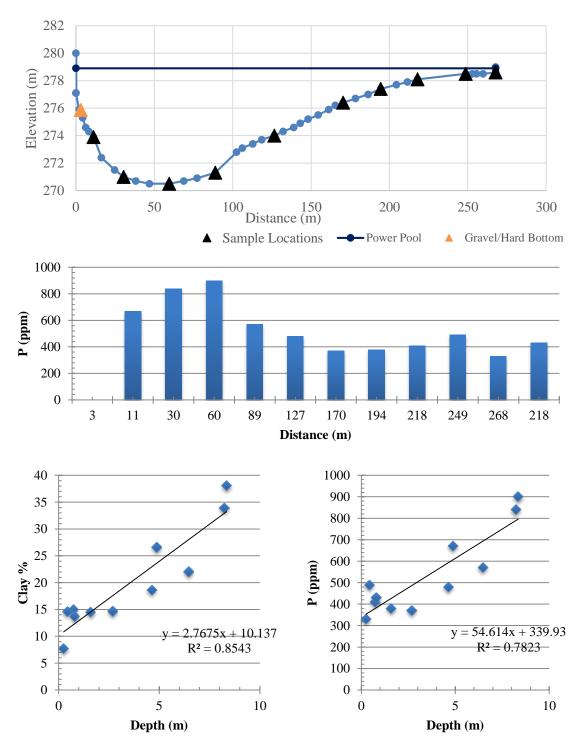


Figure 27. Transect three of the JRA within sedimentation zone two at lake kilometer 17.7. Lake left is the southeast bank of the JRA at this location.

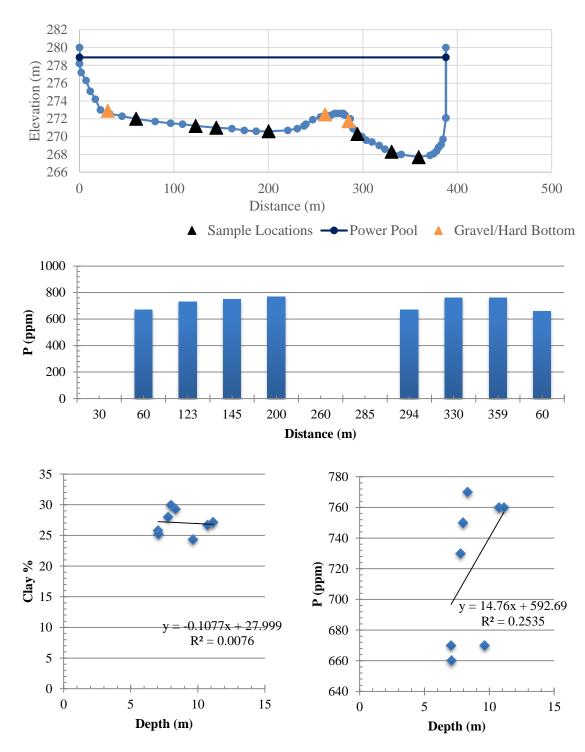


Figure 28. Transect four of the JRA within sedimentation zone two at lake kilometer 22.2. Lake left is the east bank of the JRA at this location.

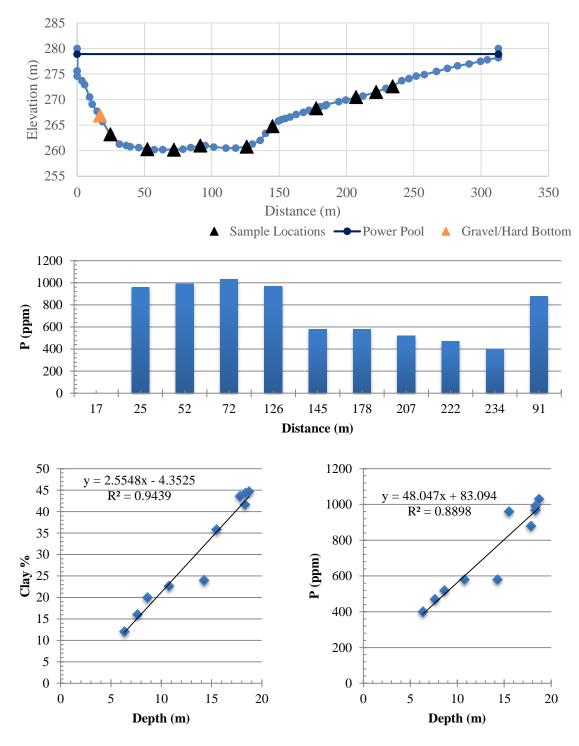


Figure 29. Transect five of the JRA within sedimentation zone three at lake kilometer 30.7. Lake left is the west bank of the JRA at this location.

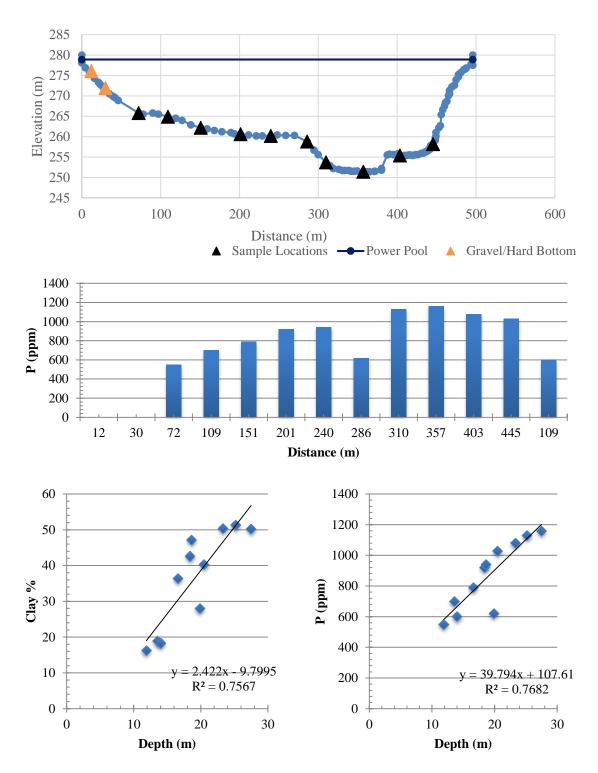


Figure 30. Transect six of the JRA within sedimentation zone three at lake kilometer 40.6. Lake left is the east bank of the JRA at this location.

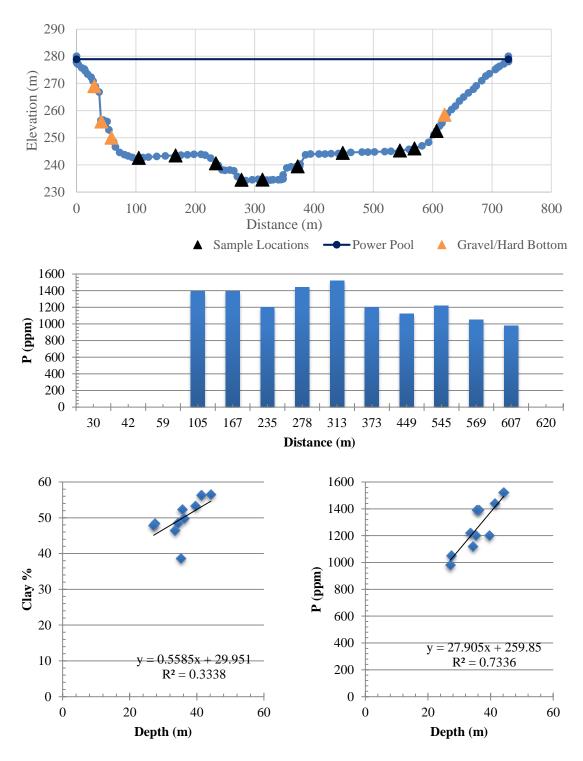


Figure 31. Transect seven of the JRA within sedimentation zone four at lake kilometer 60.9. Lake left is the north bank of the JRA at this location.

left of the main channel was unsampleable, due to hard, compact material at the lakebottom surface. Aerial photos show an old bridge crossing the James River before the lake was completed. This mound, and the associated stream basin could have been altered before impoundment, resulting in abnormal sedimentation dynamics.

Transects five and six are in sedimentation zone three, the lacustrine zone (Figures 29 and 30). Depth and percent clay relationships are very strong in this zone; particularly in transect five ( $r^2$ =0.94). Depth and sediment-P concentration relationships are also strong in transects five and six, with  $r^2$  values of 0.89 and 0.77 respectively. The strength of these relationships in this zone suggests preferential fine grain sedimentation in the deepest part of the lake cross-section influences sediment-P distribution within this zone. The underwater channel morphology in transect six clearly shows the drown-valley topography, including a terrace and separate floodplain surface on the right (Figure 30).

Transect seven is located within sedimentation zone four, the lacustrine zone (Figure 31). Percent clay and sediment-P concentrations are elevated throughout this transect when compared to the other six. Concentrations of sediment-P and clay are still strongly associated with depth, even though both are consistently high in this zone.

Drowned-valley channel morphology is even more defined in this transect, with floodplains flanking the old river channel, and paired terrace surfaces.

Multiple Regression Analysis of Sediment Phosphorus. Multiple regression analysis was used to further quantify the spatial distribution of sediment-P. The models use all sediment samples from the JRA, focusing on the variables listed in the Pearson

correlation matrix (Table 4). The Pearson correlation matrix was used to identify potential errors associated with co-variation between variables. The simplest model, one parameter depth, explains 88% of the variability (Table 5). Depth accounts for variations in fine-grained sedimentation and potential redox gradients. The thermocline depth in the lake is estimated at 7-12 m (Knowlton and Jones, 1989). This suggests that portions of the lake below 12 m in depth could be influenced by seasonal hypoxia of the hypolimnion, geochemically redistributing sediment-P.

The one parameter geochemical regression equation using Fe to predict P explains 87% of the variability, accounting for the influence of fine-grained sedimentation on the spatial distribution of sediment-P, with significant covariance (0.925) between Al and clay, as well as geochemical redistribution processes (Table 4 and 5). The two-parameter geochemical regression equation, using Mn and clay concentrations, explains 91% of the variability. Manganese concentrations account for oxide coatings and their ability to adsorb and redistribute P with fine-grained sediment in the water column and lake bottom. Calcium may explain the spatial distribution of evaporative precipitation of calcite, as well as the inorganic apatite phosphorus form. The best regression equation utilizes depth and Mn concentration, explaining 92% of the variability. While this model explains the highest amount of sediment-P variability, depth, the simplest and easiest obtainable variable, explains nearly 88% of the variance. As a management tool, the depth model makes predicting sediment-P concentrations in the JRA simple and relatively accurate. Finally, the strong relationship between sediment P and Al suggests that P:Al may be useful in reducing P variability, allowing insight into P enrichment zones.

Table 4. Pearson correlation matrix for JRA sediment parameters

	Distance	Depth	OC	OM 0/	Al	Ca	Fe	Mn	P	Sand	Silt	Clay
Distance	km	m	%	%	%	%	%	ppm	ppm	%	%	%
km	1	.937	.757	.645	.753	.194	.776	.459	.843	313	616	.801
Depth (m)		1	.801	.801	.836	.141	.872	.613	.937	388	659	.902
OC %			1	.818	.761	.115	.734	.617	.854	519	408	.807
OM %				1	.703	.072	.731	.639	.809	471	486	.831
Al %					1	.409	.947	.724	.926	612	491	.958
Ca %						1	.301	.081	.237	449	.104	.311
Fe %							1	.735	.933	413	659	.925
Mn ppm								1	.734	438	352	.688
P ppm									1	515	578	.947
Sand %										1	337	604
Silt %											1	547
Clay %												1

**Bold.** Correlation is significant at the 0.01 level (2-tailed). Organic carbon (OC) was determined using the CNS method

Organic Matter (OM) was determined using the LOI method

n=95

Table 5. Linear regression models for sediment-P concentration prediction

Model	$\mathbb{R}^2$	SE	Sig.	$\mathbf{b}_0$	<b>b</b> 1	b <sub>2</sub>
1 Parameter Depth	0.88	112	0.00	442.74	Depth (m) 22.85	
1 Parameter Geochemical	0.86	121	0.00	-74.106	Al (%) 622.191	
2 Parameter Geochemical	0.91	97	0.00	88.09	Mn (ppm) 0.172	Clay (%) 17.794
2 Parameter Depth- Geochemical	0.92	92	0.00	275.733	Depth (m) 19.024	Mn (ppm) 0.282

## **Watershed Source and Transport Factors**

In order to quantify the spatial and temporal effects of SSWTP on sedimentation patterns and trends within the watershed, the current patterns and trends must be examined. This section will describe the current geochemical patterns in Wilson's Creek and the James River, and investigate downstream sediment geochemistry trends from SSWTP to the main arm of Table Rock Lake.

Sediment Trends Above the James River Arm. Physical and geochemical characteristics of the sediment in Wilson's Creek and the James River vary significantly by geographic zone. Channel sediment tends to be coarser in the James River than in Wilson's Creek (Figure 32). The lowest sand content is found in the Upper Wilson's Creek zone, where silt is the dominant grain size. Clay and silt are found in relatively low percentages in James River channel sediments ranging from 0 to 17%. Floodplain and bench sediment tend to be silt rich in the Upper James River and Wilson's Creek with silt content ranging from 15-75% (Figure 33). Sand is found in high percentages in the Middle and Lower James River, ranging from 28-100%.

The sediment patterns suggest that fine-grained sediment supply from Wilson's Creek is diluted with sand, exhausted relative to higher coarse sediment supplies in the James River, or selectively transported through the Middle and Lower James River Zones. Selective transportation of fine grained sediment through the Middle and Lower James River could be due to higher flow regimes during baseflow conditions limiting the amount of in-channel storage of fine-grained sediment. The average discharge from 1922 to 2015 at the James River at Galena USGS gage is 28 m³/s. Likely the flow velocity associated with this discharge is large enough to keep fine-grained sediment suspended.

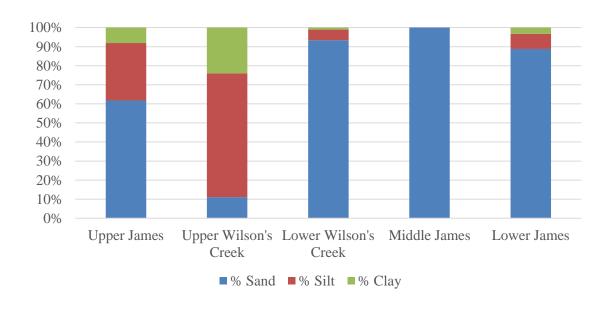


Figure 32. Average grain size distribution of channel-bed sediment from the Upper James River Basin. Total n=16, Upper James n=6, Upper Wilson's Creek n=2, Lower Wilson's Creek n=3, Middle James n=2, Lower James n=3.

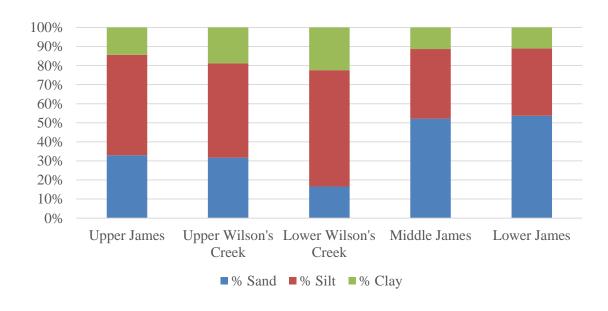


Figure 33. Average grain size distribution of floodplain and bench sediment from the Upper James River Basin. Total n=19, Upper James n=9, Upper Wilson's Creek n=2, Lower Wilson's Creek n=3, Middle James n=2, Lower James n=3.

Geochemical trends of Al, Fe, Mn and Ca in Wilson's Creek and the James River are shown in Figure 34. High concentrations of Al, Fe, Mn and Ca with high variability are present in sediments from Wilson's Creek. The concentrations are elevated above SSWTP, suggesting they are related to urban influence or other land-use sources and not SSWTP inputs. Concentrations of Al, Fe, Mn and Ca remain the same throughout the James River. Elevated average concentrations of Al, Fe, Mn, and Ca are found in Wilson's Creek. Elevated average concentrations of Al, Fe, and Mn in Wilson's Creek are likely due to increased fine-grained sediment within both channel and overbank

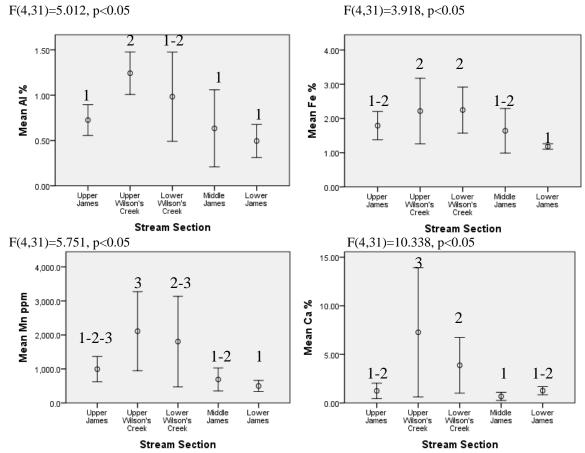


Figure 34. Geochemical characteristics of the Upper James River Basin separated by stream section. Sediment is from bed, bench, and floodplain surfaces. Total n=36, Upper James n=13, Upper Wilson's Creek n=4, Lower Wilson's Creek n=6, Middle James n=5, Lower James n=8.

sediment in this zone (Figures 32 and 33). The higher concentrations of Ca in Wilson's Creek could be due to increased karst influence on the stream.

Watershed-Scale Longitudinal Trends. The JRA and Wilson's Creek are the primary zones of sediment-P enrichment (Figure 35). This is expected, as sediment from Wilson's Creek is influenced by a major point source, and the JRA will act as a sediment, and therefore a sediment-P sink. Sediment-P concentrations are lowest in the James River, with a slight increase below Wilson's Creek. Separating the floodplain and channel sediment data allows further insight into sediment-P trends in the watershed (Figure 36). Sediment-P concentrations increase in both floodplain and bed sediment immediately below SSWTP, and decrease below the confluence with the James River.

Floodplain sediment-P concentrations remain higher than bed sediments through the James River, likely due to geochemical enrichment by increased sorption by clay and silt in floodplain deposits. Observing the downstream trends of SSWTP's sediment P signal, dilution is seen at the confluence of both the James and Finley Rivers (Figure 36). Channel sediment-P concentrations downstream of the Finley River are consistently low.

## **Geochemical Ratios**

In order to further quantify the sediment-P enrichment due to SSWTP, geochemical ratios are investigated. Normalizing downstream sediment-P trends with percent Al and clay allow insight into sediment and P source effects on sediment-P concentrations. These normalization curves are aimed at identifying sediment and P source effects, as well as geochemical redistribution effects on sediment-P concentrations.

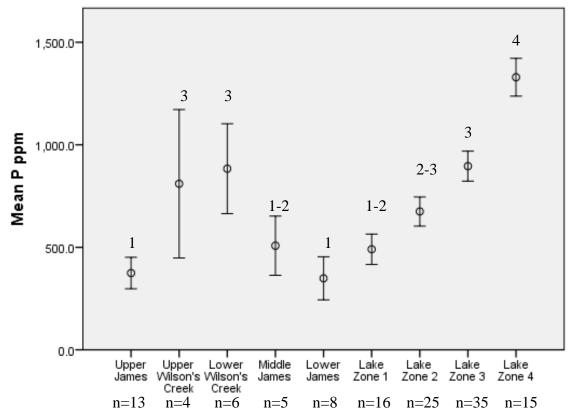


Figure 35. Phosphorus in the James River Basin by sedimentation zone. Error bars represent the 95% confidence interval for the mean. Statistical significance of the means was analyzed using one-way ANOVA, resulting in F(3,31)=65.811, p<0.05.

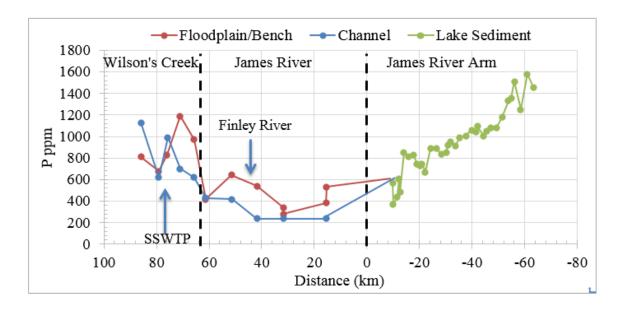


Figure 36. Longitudinal sediment-P trends in the James River Basin.

Phosphorus/Aluminum. Sediment-P normalized to Al shows increased separation between floodplain and channel P/Al values for the stream portions of the watershed (Figure 37). Elevated ratios are observed downstream of SSWTP in both floodplain and channel sediment. Channel sediment in the Middle James River is recording SSWTPs P signal. Channel sediment P/Al are elevated below SSWTP, and are reduced after the confluence with the Finley River. Elevated floodplain sediment P/Al in Lower Wilson's Creek drops off after the confluence with the James River, suggesting dilution of the SSWTP source sediment by sediment in the James River.

Longitudinal floodplain sediment P/Al trends show little variability throughout the watershed, with slight elevation below SSWTP and in zone four of the JRA. Floodplain sediment is deposited during storm events, when sediment and P sources from

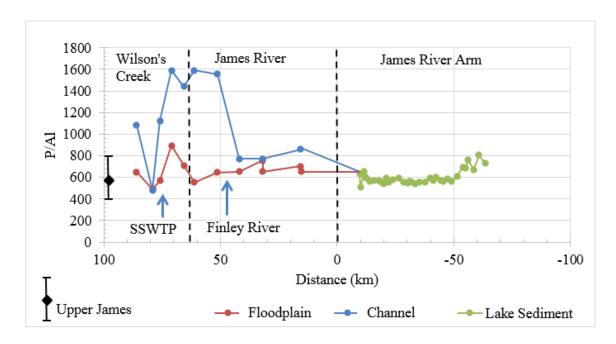


Figure 37. Longitudinal profile of P normalized to Al in the James River Basin.

the entire watershed are active, including both point and nonpoint sources. This suggests that the JRA sediment P/Al is influenced moreso by storm flow than baseflow conditions. The fact that P/Al values in the JRA are similar to floodplain values throughout the watershed and that P/Al values are consistent through much of the JRA suggest SSWTP P enrichment is not measureable in the JRA using this method.

Phosphorus/Clay. Downstream sediment-P normalized to clay patterns show low ratios in the stream portions of the watershed and high ratios in the lake portions (Figure 38). The major increase in P/clay from the stream to JRA sections of the watershed shows increased P per clay content in the JRA. This is likely due to geochemical redistribution, mixing and concentrating P onto the supply of fine-grained sediment of the JRA. Elevated P/Clay are observed immediately downstream of SSWTP in Wilson's Creek channel sediments, but are reduced after the confluence with the James River.

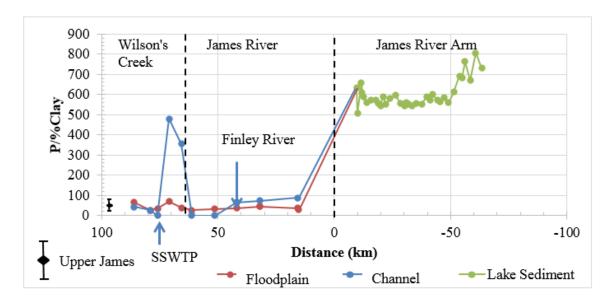


Figure 38. Longitudinal profile of P normalized to clay in the James River Basin.

This suggests P enrichment below SSWTP, however the signal is diluted, or exhausted by the James River. Sediment P/clay increases below the confluence with Finley River, suggesting either increased P or reduced clay concentrations in sediment from the Finley River.

Channel sediment P/Al ratios are elevated below SSWTP until the confluence with the Finley River, while P/clay ratios are elevated until the confluence with the James River. The differences between channel sediment longitudinal P/Al and P/clay trends suggest that aluminum normalization is not solely related to clay content in the sediment. This could suggest the role of Al-oxide coating adsorption in the James River is important between the confluence of Wilson's Creek and Finley River.

Phosphorus/Al/Fe. Normalization of P to Al and clay resulted in nearly consistent values for much of the JRA, with the exception of zone four, displaying increased variability in both P/Al and P/clay plots (Figure 37 and 38). In order to further understand sediment-P enrichment factors in this zone, additional normalization plots were developed. Normalizing P to Al and Fe resulted in minimal variability in zone four (Figure 39). The importance of Fe to sediment-P concentrations within this zone suggests the influence of Fe geochemically redistributing sediment-P in the JRA. This is likely due to seasonal anoxic release of sediment-P, followed by deposition during oxic conditions, concentrating P within this zone.

Multiple Regression Analysis of Geochemical Ratios. A Pearson correlation matrix shows the relationships between physical and geochemical sediment variables and the geochemical ratios used to describe P enrichment and variability in the JRA (Table 6). This matrix shows significant covariance between the majority of variables

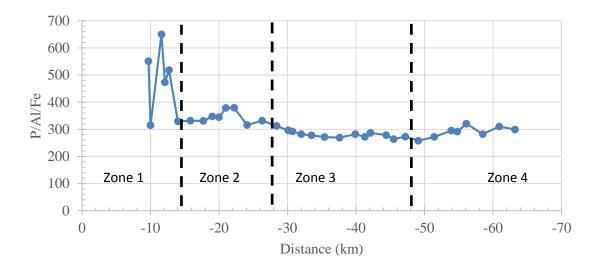


Figure 39. Longitudinal profile of P normalized to Al and Fe for the JRA.

investigated. This matrix was then used to develop stepwise linear regression models predicting geochemical ratios in the JRA. Three linear regression models were developed for each geochemical ratio (Tables 7, 8, and 9). Two one-parameter models were created, one with a spatial variable and the other with a geochemical variable. The final model uses the best two variables.

The one-parameter regression equations predicting P/Al values are relatively weak (Table 7). Depth explains 30% of the variability, while organic carbon concentration explains 35%. The best two-parameter model includes organic carbon and sand concentrations, explaining 50% of the P/Al variability.

Sediment P/clay values are largely unexplained by depth (Table 8). This is expected due to the strong covariance between depth and clay concentrations. The best one-parameter model uses Zn concentrations to predict P/clay values, with an R<sup>2</sup> value of 0.43. The best two-parameter model uses Zn and Pb concentrations, with an R<sup>2</sup> value of 0.48. The importance of Zn and Pb in predicting P/clay values is likely due to similar

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	(m)	(%)	(%) Al %	Ca %	Fe %	ppm	P ppm		e		$\neg$	%		%
Depth (m)	1	**008.	.836**	.141	.872**	.613**	.937**		620**	.473	412**	388**	**659	.902
OC (%)	**008.	1	.760	.115		.617**	.854**		485**	.034	448	519**	408**	.807
AI %	.836**	.760		.409	.947**	.724**		.212*	862**	.502**	635**	612**	490**	.958**
Ca %	.141	.115	.409			.081		212*	414**	.223*	396**	449**	.104	.311**
Fe %	.872**		.947	.301**	Π	.735**		.348**	857**	.545**	459**	413**	659**	.925**
Mn ppm	.613**		.724**		.735**			.324**	637**	.447	403**	438**		**889.
P ppm	.937**	.854**	.926		.933**	.734**	1	.548**	692**	.495			578**	.947**
P/Al	.557**	.565**	.212*		.348**	.324**	.548**	1	.133	.176			463**	.352**
P/Al/Fe	620**	485**	862**	414**		637**	692**	.133	1	452**	.575	.472		768**
P/OC	.473	.034	.502**	.223*		.447	.495**	.176	452**	1			502**	.479
P/Clay	412**	.448**	635**	396**	459**	403**	463***		.575	142	1	.784		668**
Sand %	388**	519**	612**	449**	413**	438**	515**		.472**	061	.784**	1		604**
Silt %	659**	408**		.104	659**	352**	578**		.411**	502**	034	337**	1	547**
Clay % .902** .807** .958**	.902	.807	.958	.311**	.925	.688	.947	.352**	768**		668**	604**	547**	1
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\*\*. Correlation is significant at the 0.01 level (2-tailed).

\*. Correlation is significant at the 0.05 level (2-tailed).

OC - Organic carbon content analysed using CNS method.

Table 7. Linear regression models for sediment-P/Al prediction

Model	$\mathbb{R}^2$	SE	Sig.	$\mathbf{b}_0$	$\mathbf{b_1}$	$\mathbf{b}_2$
1 Parameter Depth	0.30	61	0.00	513.489	Depth(m) 3.11	
1 Parameter Geochemical	0.35	61	0.00	-396.81	OC (%) 69.94	
2 Parameter Geochemical	0.50		0.00	328.95	OC (%) 91.51	Sand (%) 2.90

OC - Organic carbon content analysed using CNS method

Table 8. Linear regression models for sediment-P/Clay prediction

Model	$\mathbb{R}^2$	SE	Sig.	b <sub>0</sub>	<b>b</b> 1	<b>b</b> <sub>2</sub>
1 Parameter Depth	0.16	4.78	0.00	28.92	Depth(m) -0.16	
1 Parameter Geochemical	0.43	3.93	0.00	41.15	Zn (ppm) -0.16	
2 Parameter Geochemical	0.48	3.77	0.00	38.82	Zn (ppm) -0.27	Pb (ppm) 0.50

Table 9. Linear regression models for sediment-P/Al/Fe prediction

Model	$\mathbb{R}^2$	SE	Sig.	$\mathbf{b}_0$	<b>b</b> 1	<b>b</b> 2
1 Parameter Depth	0.38	82	0.00	433.7	Depth(m) -4.95	
1 Parameter Geochemical	0.70	55	0.00	-741.112	Zn (ppm) -4.19	
2 Parameter Geochemical	0.77	50	0.00	592.27	Zn (%) -3.82	Silt (%) 1.90

characteristics between Zn, Pb, and P. These three elements are generally in a particulate phase, associating with fine-grained sediment through sorption processes.

Sediment P/Al/Fe variability is not well explained by depth, with an R<sup>2</sup> value of 0.38. This is likely due to the covariance between depth, Al, and Fe (Table 6). The best one-parameter model uses Zn to explain 70% of the variability in P/Al/Fe. By adding silt concentration the model explains 77% of the variability. Zinc is likely a key variable due to its similarities with P, associating with fine-grained sediment, both as adsorbed constituents as well as part of Fe and Al oxide coatings on sediment grains.

## **Sediment-Phosphorus Response to SSWTP Upgrades**

The temporal changes in sedimentation trends and patterns will be evaluated from two periods of time based on the available datasets. The pre-upgrade to present period (2001-2013) will be quantified using the work by Frederick (2001) and Owen (2003) as the pre upgrade dataset. The 2003/4 to present period changes will be quantified using the work by Rodgers (2005) as the 2003/4 dataset. Sediment geochemistry changes from 2001 to 2013 are summarized in Table 10, while changes from 2003/4 to 2013 are summarized in Tables 11 and 12. Percent change from 2001 to 2013 was calculated as the median percent difference to account for unpaired sample sites. Percent change from 2003/4 to 2013 was calculated as mean percent difference because all sample sites are paired. These summarized results will be discussed throughout this section.

**Sediment-Phosphorus Response.** Sediment-P response to SSWTP upgrades will be quantified in this section, developing the longitudinal and then the lateral response trends. In order to fully describe the sediment-P response, both sediment-P concentration

Table 10. Sediment geochemistry change from 2001 to 2013 by zone

			%	Chan	ge			
Zone	Fe/Al	P/Al	Al	Cu	Fe	P	Pb	Zn
Upper James	71	37	-9	53	22	53	38	30
Upper Wilson's Creek	21	168	-37	211	-25	62	73	86
Lower Wilson's Creek	123	21	-70	-69	-29	-58	-52	-43
Middle James	369	121	-58	-62	37	-24	-35	-14
Lower James	-2	4	-18	0	-15	-14	-29	-17
Zone 1	-1	-40	9	93	11	-32	14	-3
Zone 2	-8	-46	17	113	8	-33	10	1
Zone 3	-8	-50	29	260	16	-36	17	32
Zone 4	-14	-50	34	-7	15	-31	12	24

<sup>%</sup> change calculated as (2013-2001)/2001\*100

Table 11. Sediment geochemistry change from 2003/4 to 2013 in Wilson's Creek by zone

				%	Cha	nge			
Zone	Site Pairs	Fe/Al	P/Al	Al	Cu	Fe	P	Pb	Zn
Upper Wilson's Creek	4	-10	10	9	21	-3	15	24	31
Lower Wilson's Creek	6	-5	10	-3	-38	9	-31	-27	-10

<sup>%</sup> change calculated as (2013-2003/4)/2003/4\*100

Table 12. Sediment geochemistry change from 2003/4 to 2013 in Wilson's Creek by zone and depositional surface

				9/	6 Cha	nge			
Zone	Site Pairs	Fe/Al	P/Al	Al	Cu	Fe	P	Pb	Zn
Upper Wilson's Creek									
Channel	2	-10	24	1	58	-11	23	47	72
Upper Wilson's Creek									
Floodplain	2	-9	-4	17	-17	6	7	2	-10
Lower Wilson's Creek									
Channel	3	4	39	-24	-48	11	-35	-43	-14
Lower Wilson's Creek									
Floodplain	3	-3	-6	18	-27	7	-26	-11	-6

<sup>%</sup> change calculated as (2013-2003/4)/2003/4\*100

and P/Al value changes will be quantified.

Longitudinal Response. Sediment-P reductions have occurred in all zones below SSWTP between 2001 and 2013 (Figure 40). The largest reductions have occurred immediately below SSWTP and in the middle zones of the JRA. Increased sediment-P concentrations are seen in the Upper James River and Upper Wilson's Creek zones. Increases in the upper portions of the watershed are likely due to land-use source changes, with agriculture influencing the Upper James River and urbanization influencing Upper Wilson's Creek. Sediment-P concentrations responded to nutrient reduction at SSWTP quickly, with over half of the total sediment-P reduction (2001-2013) occurring in the first two to three years (Figure 41).

Sediment P/Al reductions have occurred throughout the JRA, while increases are observed throughout the stream zones (Figure 42). Reduced P/Al values in the JRA are expected, as sediment-P concentrations decrease in response to nutrient load reductions, the P/Al should decrease. The increased P/Al ratios in the stream portions of the watershed warrant further investigation. As mentioned, sediment-P concentrations decreased below SSWTP in Wilson's Creek and the James River, suggesting increased P:Al values are due to changes in Al concentrations.

Concentrations of Al have increased in the JRA and decreased in the stream zones (Table 10, Figure 43). The large Al concentration changes, 70% in Lower Wilson's Creek, may complicate the use of Al as a conservative sediment tracer. The limitations, potential error, and assumptions surrounding the treatment of Al as conservative will be discussed in the next section.

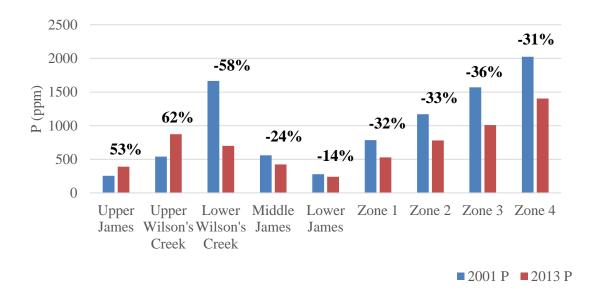


Figure 40. Median sediment-P concentration change between 2001 and 2013.

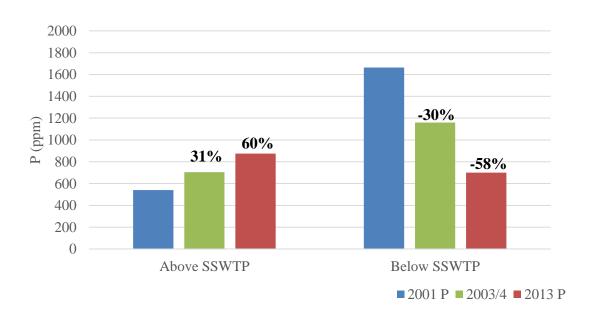


Figure 41. Average channel-sediment-P concentration change in Wilson's Creek.

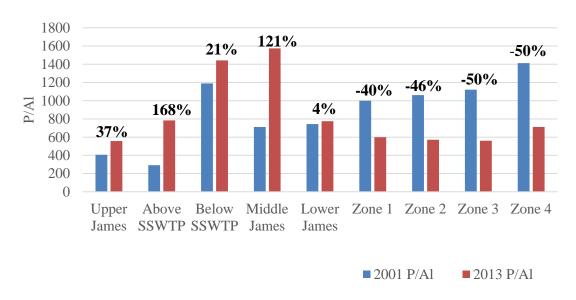


Figure 42. Median P/Al ratio change from 2001 to 2013.

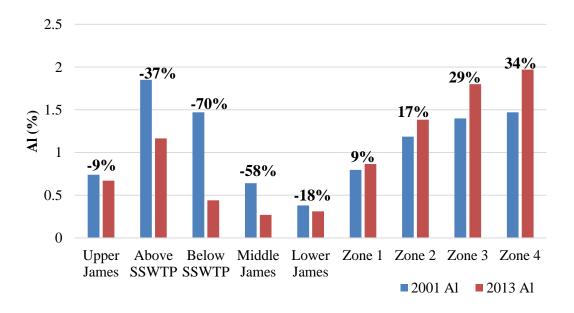


Figure 43. Median Al concentration change from 2001 to 2013.

Lateral Response. Lateral sediment-P response in the JRA is quantified by investigating P vs depth, P:Al vs depth, and Al vs depth relationships. The plots are separated by zone in order to investigate response trends based on source, as well as sedimentation, and geochemical processes. Sediment-P reduction within the JRA is increased in the deeper portions of the lake, with 2013 concentrations lower than 2001 (Figure 44). Zone one sediment-P concentrations are largest in the deepest part of the cross-section (Figure 45). Sediment-P concentrations are higher in shallow portions of zone two, and lower in deeper portions. Zone three sediment-P trends are similar between the two studies, with many of the data overlapping. Sediment-P concentrations in zone four are generally lower in the 2013 study.

Lateral P:Al trends are similar to sediment-P trends, with increased reduction in the deeper portions of the lake (Figure 46). The P:Al in the 2001 study is increasing throughout the JRA, while in 2013 it remains fairly constant. P:Al relationships are much weaker in the 2013 compared to 2001, with very low R<sup>2</sup> values in zones one and three (Figure 47).

Lateral Al concentrations increase with depth, with similarly sloped trendlines for 2001 and 2013 (Figure 48). Al concentrations increase in the 2013 study, again suggesting that the conservative nature of Al within the system should be investigated. The parallel nature of the regression trendlines can also be seen within each zone (Figure 49).

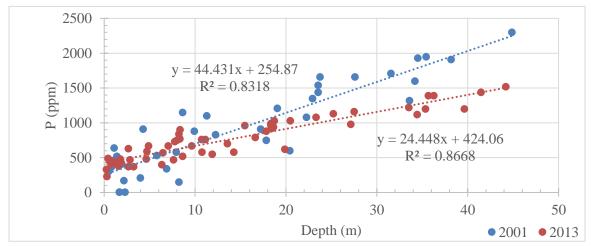


Figure 44. 2001 and 2013 lateral sediment-P concentrations by depth for the JRA.

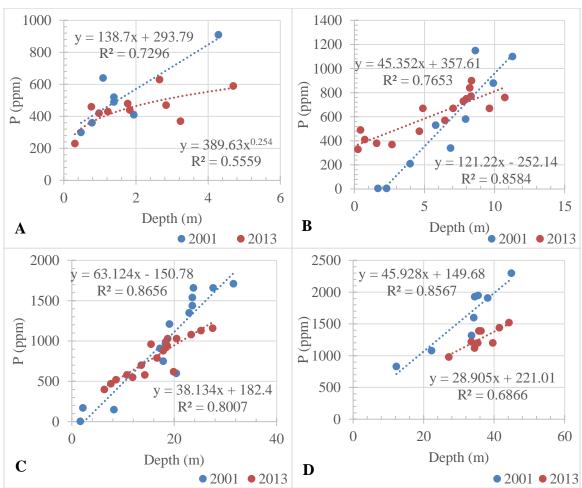


Figure 45. 2001 and 2013 lateral sediment-P concentrations by depth and zone for the JRA. A. Zone one; B. Zone two; C. Zone three; D. Zone four.

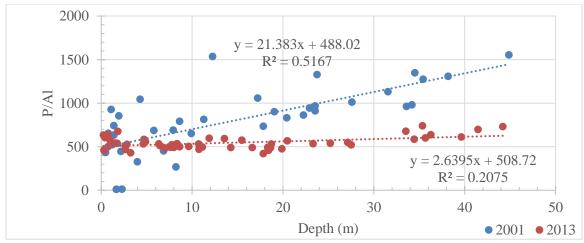


Figure 46. 2001 and 2013 lateral sediment P:Al values by depth for the JRA.

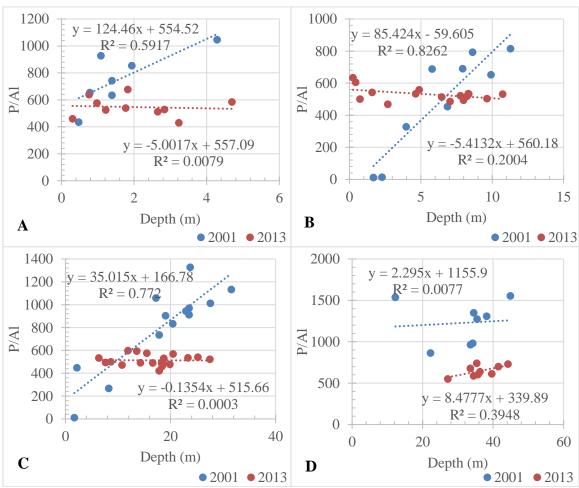


Figure 47. 2001 and 2013 lateral sediment P:Al values by depth and zone for the JRA. A. Zone one; B. Zone two; C. Zone three; D. Zone four.

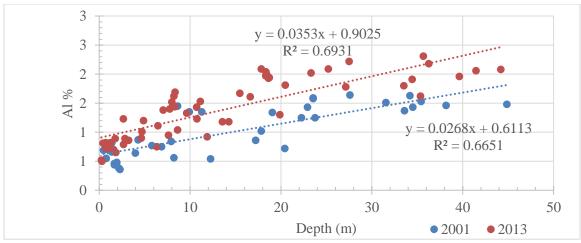


Figure 48. 2001 and 2013 lateral sediment-Al concentrations by depth for the JRA.

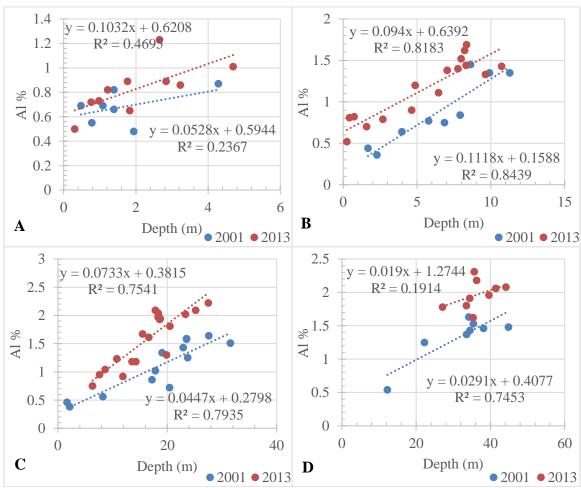


Figure 49. 2001 and 2013 lateral sediment-Al concentrations by depth and zone for the JRA. A. Zone one; B. Zone two; C. Zone three; D. Zone four.

Lateral sediment P, P:Al, and Al changes were estimated using regression equations using on depth values at 5, 25, 50, 75, and 100% of the maximum depth (Tables 13, 14, and 15). This was done to identify lateral sediment change thresholds within the JRA. Sediment-P reduction occurs throughout the JRA below the 50% total depth (Table 13). Reduction in the shallower portions of the lake occurs in zone one. This is most likely due to sedimentation processes and the relatively minor amount of total depth variation within this zone. Sediment within the riverine zone should mixed upon deposition and also has a greater chance of physical resuspension. Zones two and three are similar in sediment-P reduction trends, with a clear threshold at 50% maximum depth (Table 13). This threshold could be due to lake sedimentation processes or geochemical resuspension processes. Fine-grain sedimentation should maximize in the deepest parts of the cross-section suggesting that sedimentation rates are slow in the shallow portions. The lake is deep enough within these two zones to experience seasonal anoxic conditions below 50% of the maximum depth. Sediment-P reduction occurs below 25% of the maximum depth in zone four. The 25% depth of 11 meters is within the thermocline depth range of 7-12 meters, suggesting that geochemical redistribution processes associated with seasonal anoxic conditions influence sediment-P reduction within this zone.

Sediment P:Al values are reduced throughout the JRA below 50% of the maximum depth (Table 14). Zones one, three, and four are reduced below 25% of the maximum depth, and zones one and four are reduced below 10% of the maximum depth. The increased reduction below the 25-50% maximum depth range suggests sediment-P source changes between 2001 and 2013, presumably the reductions at SSWTP.

Table 13. Sediment phosphorus change by depth percentage from 2001 to 2013

	1	1	Max	Sed	iment-P	change	by dept	h percer	ntage
Zone	2001	2013	Depth (m)	<b>5%</b>	10%	25%	50%	<b>75%</b>	100%
1	7	10	4.7	-17	-10	-11	-22	-31	-39
2	9	16	22.2	-447*	2563*	45	-21	-37	-44
3	13	20	40.6	-1248*	220*	16	-15	-24	-28
4	8	9	44.9	13	-1	-18	-26	-30	-31
All	37	56	44.9	35	17	-7	-22	-29	-32

<sup>\*</sup>Influenced by potentially anomalous sediment-P concentrations from 2001 study

Table 14. Sediment P/Al change by depth percentage from 2001 to 2013

	]	n	Max		P/Al ch	ange by	depth p	ercentag	ge
Zone	2001	2013	Depth (m)	5%	10%	25%	50%	<b>75%</b>	100%
1	7	10	4.7	-5	-9	-21	-36	-46	-53
2	9	16	22.2	1470*	321*	28	-44	-66	-76
3	13	20	40.6	117*	67	-2	-42	-59	-68
4	8	9	44.9	-69	-68	-63	-56	-49	-43
All	37	56	44.9	-4	-11	-26	-41	-51	-57

<sup>\*</sup>Influenced by potentially anomalous sediment-P concentrations from 2001 study

Table 15. Sediment Al change by depth percentage from 2001 to 2013

	n		Max Depth	Al change by depth percentage					
Zone	2001	2013	(m)	<b>5%</b>	10%	25%	50%	<b>75%</b>	100%
1	7	10	4.7	6	8	13	20	26	31
2	9	16	22.2	163*	108*	49	20	9	3
3	13	20	40.6	43	47	53	57	59	60
4	8	9	44.9	178	153	103	60	38	24
All	37	56	44.9	46	45	42	40	38	37

<sup>\*</sup>Influenced by potentially anomalous sediment-P concentrations from 2001 study

Sediment-Al concentrations increase throughout the JRA (Figure 49). Several anomalously low sediment-P values influence the zonal predictions of Al, however the whole lake trends show about a 40% increase in Al concentrations from 2001 to 2013 (Table 15). The lateral sediment Al concentration increase is on the same order as the longitudinal increase, showing consistently higher Al concentrations in the JRA.

Potential Variations in Sediment Source. Several potential factors influencing sediment-Al concentrations were investigated in order to identify limitations associated with using Al as a conservative tracer. The possibility of alum being released from SSWTP as part of their tertiary treatment procedures was investigated. Sediment source changes associated with increased flood frequency and intensity, as well as land-use change was also investigated. Finally, potential error associated with the sampling method was investigated.

Alum Inputs from SSWTP. Al released from SSWTP would have the potential to increase sediment-Al concentrations downstream, possibly explaining the increased concentrations of Al in water or sediment in 2013. Recently, studies have implied increased Al concentrations in watersheds using alum to treat water (Driscoll, Lee, Montesdeoca, Matthews, and Effler, 2014; Harper, 2007). Alum can be used in a variety of nutrient load treatments including STP, stormwater, and drinking water (Driscoll et al., 2014). Driscoll et al. (2014) investigated Al mobilization potential in a New York reservoir, analyzing lake bottom sediment as well as water chemistry for Al concentrations. The addition of alum directly to the lake reduces treatment cost for the municipal drinking water. Although total Al concentrations in the sediment are not quantified, the study suggests a substantial increase in Al concentrations within the lake

bottom sediments. Harper (2007) describes the influence of treating stormwater with alum to reduce turbidity and remove contaminants. Aluminum flocs and their constituents are quite stable over large pH and eH ranges.

Potential Al release from SSWTP was investigated using baseflow water chemistry data from the USGS gage on the James River at Galena, Missouri. If SSWTP treatment processes are releasing Al into Wilson's Creek, it would be in dissolved form, however it would quickly bind to sediment in the stream channel. A time series of total Al concentrations shows no statistically significant change in total Al concentrations through the sampling period (Figure 50). Percent suspended Al is lower during the preupgrade period, opposite what we would expect if SSWTP were the source of Al to the JRA (Figure 51). These data suggest increased Al concentrations in the JRA are not related to alum treatments at SSWTP.

Dissolved Al concentrations were also investigated, with concentrations abruptly decreasing by nearly 80% in 2001, with consistently high values pre-2001, and low values post-2001. The 2001 transition between high and low dissolved Al concentrations is suspicious due to the timing, however no link between dissolved Al and SSWTP could be found. Also, the reduced dissolved Al concentrations do not explain increased Al concentrations in JRA sediment.

Flood Frequency and Intensity. Changes in flood frequency and intensity could change the sediment source characteristics, potentially altering Al concentrations in the watershed. More frequent or more intense storms could increase erosion rates of bank and upland material. Increased erosion rates of bank and upland material could provide more fine-grained sediment to the stream, increasing the Al concentration of the sediment.

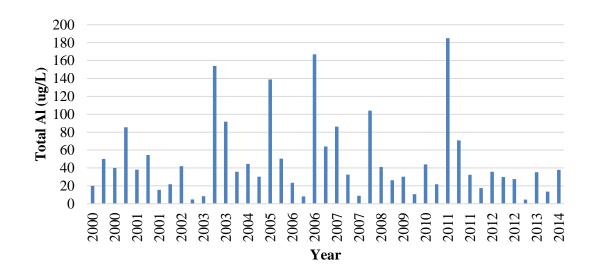


Figure 50. Baseflow total Al concentrations in the James River from 2000 to present.

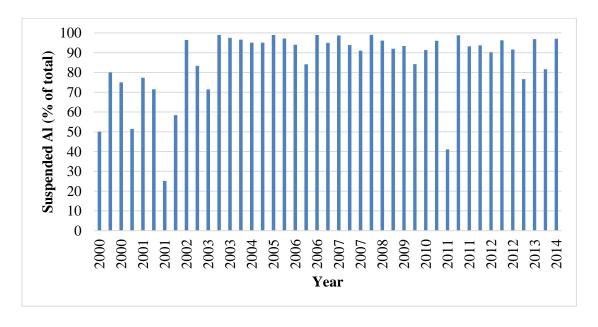


Figure 51. Baseflow percent suspended Al in the James River from 2000 to present.

Foreman (2014) investigated climate driven changes in flood frequency. In the James River Basin, discharge increased over the past 30 years for the 1.5, 2, 2.33, 10, 25, 50, and 100 year floods. Foreman (2014) suggests a combination of land-use, rainfall intensity, and total annual rainfall are causing increased flood magnitudes over the past 30 years. Although increased flood frequency and magnitude could explain the Al concentration change from 2001 to 2013, there is not enough evidence to suggest it is so.

Land-Use Change. Changing land-use within the watershed could influence sediment sources and therefore Al concentrations. Increased urbanization and agriculture within the watershed could result in increased erosion of sediment, altering the sediment-source characteristics. Sediment-P concentrations from the Upper James River and Upper Wilson's Creek have increased from 2001 to 2013, possibly related to urban and/or agriculture land-use changes. The observed change of sediment-P concentrations in the upper parts of the watershed allows for the possibility of Al concentration change associated with land-use change.

Sampling Error. Sampling error associated with the Ekman grab sampler is primarily related to sample depth variability. The sample depth is influenced by sediment properties and the operator, including parameters such as sediment cohesion, texture, water content, and the impact velocity of the sampler (Blomqvist, 1985). Variable sample depth can result in sediment samples that don't represent the same sedimentation period. In this study, collecting too much sediment, from greater sampler penetration into the bed, would likely result in higher sediment-P values associated with older enriched sediment. The same concept would apply to Al concentrations, however sampling older sediment would result in lower Al concentrations in the current study.

Sediment-Phosphorus Response to SSWTP Upgrades. Sediment-P reductions in the James River occurred in both zones below SSWTP, although diluted by Finley River. Sediment-P reductions in the JRA average 33%. Reductions at SSWTP reduced nutrient loading to the JRA by about 24%. This suggests the observed sediment-P reductions are not solely due to upgrades at SSWTP.

As discussed in Chapter 3, SSWTP P load contributions to the JRA were 27% of the total, the largest point source, but not the only one to upgrade treatment processes (U.S. EPA, 2001). Upgrades at STPs within the watershed occurred at 12 facilities besides SSWTP from 2001 to 2008. The combined treatment capacity of all other STPs in the watershed (3,847,250 GPD) is less than 10% of the capacity at SSWTP (42,500,000 GPD) (U.S. EPA, 2001). The sediment-P reduction observed in the JRA not attributed to SSWTP upgrades could be related to upgrades at these other facilities.

## **Summary**

This section will review the major findings of this study, focusing on key observations and expanding the discussion on their implications. This section will focus on comparing the current study to other studies, identifying areas where the James River basin is unique and similar to other places.

Sedimentation Zones of the James River Arm. Sedimentation zones of the JRA were identified based on physical and geochemical properties of sediment, as well as lake morphometry. Zone one corresponds with the riverine zone (Morris and Fan, 1998). This zone is characterized by sand content, indicating a diverse sediment load deposited by reduced flow velocities. Zone two is the transition zone, characterized by increased

concentrations of clay, Al, and Fe, while inorganic carbon and Ca decrease. Zones three and four are within the lacustrine zone, with similar down-lake trends of Al, Fe, and clay. Zone four was identified based on sharply decreasing concentrations of Ca and inorganic carbon, as well as increasing concentrations of Mn. Zone four could be influenced by sediment from the White River portion of the lake. Knowlton and Jones (1989) hypothesize water from the White River Arm flows into the JRA through the thermocline during summer stratification. This water could provide sediment from a different source, explaining the geochemical trends in zone four.

Understanding the location of these zones, as well as their geochemistry allows insight into potential geochemical and physical redistribution processes within the JRA. Within the riverine zone, changing lake levels can alter sedimentation patterns, building the delta during high water periods and redistributing sediment during low water periods (Morris and Fan, 1998). This is important because physical redistribution of sediment during low lake level conditions could mobilize P, loading the water column with P. The concentrations of P within the riverine zone are low compared to the rest of the lake, suggesting physical redistribution of sediment from this zone would be providing lower concentration P sediment to the transition and lacustrine zones.

Spatial Trends of Sediment Phosphorus. Sediment-P concentrations in the James River Basin are highest in Wilson's Creek and the JRA, close to the P source and in the sediment sink respectively. Sediment-P concentrations increase with depth, both laterally and longitudinally. Regression analysis suggests that 88 % of the sediment-P variance can be explained by one variable, depth. The simplicity of this relationship makes it an easy tool to predict sediment-P concentrations.

Channel and floodplain sediment is enriched in P below SSWTP based on normalization plots using Al and clay. The floodplain is enriched in P immediately downstream of SSWTP within Wilson's Creek. Channel sediment is enriched from SSWTP to the James River using P/clay and to the Finley River using P/Al. Within the JRA, P/Al linearizes the down-lake trends, with minor variability in zone four. The P/Al in the JRA is nearly equal to the P/Al recorded in floodplain sediments, suggesting the JRA is primarily responding to a mixture of point and nonpoint source P entering during storm flow conditions. Owen (2003) used P/Al to investigate enrichement in lake sediments. The results show P/Al steadily increasing down-lake, with increased variability in zone four. The difference between the down-lake 2001 P/Al (increasing) and the 2013 P/Al (constant), suggests that P concentrations in the JRA were responding to both baseflow and storm flow conditions during the 2001 period. The reduction in P/Al slope in the 2013 study suggests baseflow P inputs are not a significant part of the total load.

Several studies have quantified longitudinal geochemical gradients in the JRA, including Owen (2003) investigating sediment quality and Knowlton and Jones (1989) and Obrecht et al. (2005) investigating water quality. Water column P reductions in response to upgrades at SSWTP were quantified by Obrecht et al. (2005), showing an 80% decrease in the range of P concentrations in the water column from 1996 to 2003. The sediment P response to SSWTP upgrades shows the same trend, however the magnitude change is not as large, with a 45% reduction in the sediment-P range from 2,220 ppm in 2001 to 1,210 ppm in 2013.

Owen (2003) used stepwise regression analysis to predict sediment-P concentrations in the JRA. The regression equations are similar between 2013 and 2001. The one parameter depth model has a higher R<sup>2</sup> value in the 2013 study, 0.88 compared to 0.74. The depth coefficient has decreased by nearly 40% from 2001 to 2013, further quantifying the sediment-P gradient change between 2001 and 2013. Iron is the best geochemical predictor in the 2013 study, while Al is the best in the 2001 study. The two parameter geochemical models use the same variables, Mn and clay, in both studies. The relationship is stronger in the 2013 study, with R<sup>2</sup> values of 0.91 compared to 0.84. Clay content was analyzed using different methods between the two studies, however hydrometer and laser particle sizer method comparisons suggest clay content values are similar between the two methods. Finally, the two parameter, depth and geochemical, models use the same variables between the two studies. The relationship is stronger in the 2013 study, with R<sup>2</sup> values of 0.92 compared to 0.89.

Sediment-P Change from 2001 to 2013. Sediment-P reductions have occurred in every zone downstream of SSWTP from 2001 to 2013. The largest reductions (58%) have occurred immediately below SSWTP in Wilson's Creek, while sediment P concentrations have decreased by an average of 33% in the JRA. Sediment-P reductions occurred quickly, with more than 50% of the total 2001-2013 reduction occurring in the first 2-3 years. Lateral sediment-P reductions are highest below 50% of the maximum depth.

The sediment-P response time observed in this study is similar to predicted response times summarized by Meals et al. (2010) and Carpenter et al. (1998). Sediment-P response to SSWTP upgrades is likely complete, with P/Al values quite constant

throughout the JRA suggesting baseflow P inputs from point sources are low. This suggests that the observed 33% reduction in sediment P is likely due to SSWTP upgrades and that recovery due to these upgrades has occurred over the past 12 years. Sediment-P response was fast in Wilson's Creek, close to source, and it is inferred to have happened relatively quickly in the JRA based on the results of Obrecht et al., (2005) showing significant reduction in water column P concentrations during the first two-three years after the upgrades.

Sediment-Al concentrations within the James River Basin have not remained constant throughout the study period, from 2001 to 2013. Increased Al concentrations are found in the JRA, while decreased concentrations are found in Wilson's Creek and the James River. This suggests sediment sources have changed over this time period. Several factors could cause this observation, including drivers from climate and land-use variables. Increased rainfall amounts and intensity associated with climate change could alter the relative abundance of sediment entering streams from upland erosion and channel banks; however investigating this further is outside the scope of this study. Land-use changes in the urban core, Springfield, Missouri, or the agricultural region, the Upper James River, could also influence sediment source characteristics entering the streams. The changed sediment-Al concentrations observed in this study should be investigated further in order to understand sediment source characteristics of the James River Basin.

#### **CHAPTER 6**

#### CONCLUSIONS

This study focused on quantifying the spatial and temporal changes of sediment characteristics and sediment-P in response to point-source reductions in the James River Basin. This was accomplished by quantifying the present sediment-P concentrations in sediment from Wilson's Creek, James River, and JRA, evaluating sedimentation variations longitudinally and laterally in the JRA. Finally determining the effect of STP upgrades on sediment concentration and distribution in the James River Basin. Two additional datasets were used to quantify sediment-P reduction, one from 2001 and one from 2003/4. The 2001 data are from work completed by Frederick (2001) and Owen (2003), while the 2003/4 data are from Rodgers (2005).

Major findings of this study include:

1. Lake morphometry, physical sediment properties, and chemical sediment properties were used to identify four longitudinal sedimentation zones in the JRA. The riverine zone (0-14 km) contains the majority of the bed load, with a diverse sediment load characterized by the presence of sand. The transition zone (14-27 km) is characterized by fine-grained sedimentation, increasing concentrations of Al and Fe, and decreasing concentrations of inorganic carbon and Ca. The lacustrine zone was divided into two sections (27-48 km and 48-63 km) based on sediment geochemistry and carbon content analyses. The upper zone is characterized by increasing concentrations of Al, Fe, Ca, carbon, and clay, while the lower zone is characterized by decreasing inorganic

carbon and Ca and increasing Mn. Lateral sedimentation trends show increasing P and clay with depth. These lake zones are an important step in understanding sedimentation processes and patterns within the JRA. The next step would be to quantify sedimentation rates and temporal sediment geochemistry by collecting sediment cores from the lake.

- 2. Sediment-P concentrations are highest in Wilson's Creek and the JRA.

  Sediment-P concentrations are strongly tied to depth, both laterally and longitudinally.

  Longitudinal sediment-P trends show two locations of decreased concentrations, probably due to dilution and mixing with cleaner sediment at the confluence of Wilson's Creek and the James River and again at the confluence of the James River and Finley River.

  Sediment-P concentrations are generally higher in floodplain and bench surface deposits, likely due to a combination of grain size and sediment source control. Floodplain sediments tend to be finer grained and record both nonpoint and point source P. They also tend to contain a larger clay-silt sediment fraction, increasing their association with P.

  Regression analysis showed a simple one-parameter model using depth can explain 88% of the sediment-P variance. The strongest model included depth, Mn, and Ca, predicting 93% of the sediment-P variance. The strength of the one-variable model, along with the simplicity, make it an easy tool to accurately predict sediment-P concentrations in the JRA.
- 4. Sediment-P reductions from 2001 to 2013 are observed in all zones downstream of SSWTP, with the largest average reductions occurring in Lower Wilson's Creek bed sediment and in the JRA, 58% and 33% respectively. Sediment-P reductions in Wilson's Creek occurred quickly, with nearly half of the total observed reduction recorded 2-3 years after SSWTP upgrades.

5. Sediment-P concentrations have increased in the Upper James River and Upper Wilson's Creek zones. These increases warrant future investigation into potential nonpoint P sources and management strategies. Likely these increases are related to landuse change within the agriculture and urban areas of the watershed, Upper James and Upper Wilson's Creek respectively; however, it is unclear how subtle changes in sampling and analysis procedures may have influenced 2013 results.

These findings provide a reference for evaluating the effects of STP upgrades on sediment quality. In the Ozarks region, evaluation of point source nutrient load reductions due to wastewater treatment has primarily been based on water quality measurements. This study uses sediment quality to evaluate the response of the watershed to reduced nutrient loading. The interactions between sediment and water quality, particularly between dissolved and sediment-P, warrants investigations into sediment-P concentration response to point source reduction to quantify both the response and response time to nutrient loading reductions of this nature. This study is an additional tool to evaluate STP upgrades on achieving the TMDL goals. Sediment quality response to point source P reductions in the watershed have not been used to assess whether or not TMDL goals have been reached in the James River Basin. This study provides a first step in assessing nutrient load reduction effectiveness within the watershed.

Future steps include collecting cores from the JRA to further quantify the temporal variation of sediment-P and other geochemical variables at a specific location in the JRA. Sediment cores could also provide sedimentation rates, allowing calculation of sediment-P accumulation and rates of accumulation in the JRA. Understanding the amount of P stored in JRA sediments, as well as their rate of accumulation, could help

further quantify nonpoint source P loads (Juracek, 1998). Sediment cores could also be used for a paleolimnological study to investigate biological response to nutrient load reduction in the JRA of Table Rock Lake. Paleolimnology studies have been used to identify food web structure changes associated with both eutrophication and reoligotrophication (Batarbee et al., 2005; Manca et al., 2007), providing another tool for assessing the effectiveness of TMDL guidelines.

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APPENDICES

Appendix A. Spatial Characteristics of Sample Locations

G.	- ·	Y 41	<b></b>		<b>D</b> (1) ( )		Sample Mass <2mm
Site	Easting	Northing	Type	Location	Depth (m)	Distance (km)	(g)
1	453965.2	4072106.9	Lake	Long.	3.7	11.60	179
2	454106.0	4071531.2	Lake	Long.	4.3	12.10	261
3	454343.3	4070794.0	Lake	Long.	5.5	12.70	296
4	454284.0	4069751.5	Lake	Long.	8.6	14.00	253
5	456052.3	4069349.0	Lake	Long.	8.2	15.80	245
6	455820.8	4067826.6	Lake	Long.	8.8	17.70	195
7	454728.3	4067391.7	Lake	Long.	9.4	19.00	271
8	454910.6	4066416.5	Lake	Long.	9.9	20.00	228
9	455732.1	4066224.0	Lake	Long.	10.8	21.00	276
10A	455264.9	4065078.1	Lake	Long.	11.5	22.20	287
10B	455539.7	4063590.0	Lake	Long.	11.5	22.20	285
11	455539.7	4063590.0	Lake	Long.	14.0	24.10	237
12	454748.9	4062002.3	Lake	Long.	17.0	26.30	255
13	454106.0	4063434.8	Lake	Long.	17.1	28.40	273
14	452588.3	4063234.8	Lake	Long.	19.6	30.10	272
15	452088.2	4063758.5	Lake	Long.	19.6	30.70	259
16	451421.1	4063806.4	Lake	Long.	20.7	32.00	211
17	452218.1	4062528.2	Lake	Long.	22.1	33.50	190
18	452155.4	4060672.6	Lake	Long.	23.2	35.40	238
19	453646.7	4059772.9	Lake	Long.	25.6	37.60	195
20A	451842.2	4058956.8	Lake	Long.	27.7	39.90	190
20B	451842.2	4058956.8	Lake	Long.	27.7	39.90	214
21	451492.6	4057962.0	Lake	Long.	27.9	41.30	208
22	450927.4	4057160.7	Lake	Long.	28.6	42.10	209
23	452416.3	4056174.4	Lake	Long.	31.1	44.40	195
24	453725.3	4056144.9	Lake	Long.	31.4	45.50	230
25	455201.2	4056274.3	Lake	Long.	33.5	47.20	199
26	455169.1	4057536.9	Lake	Long.	34.7	49.10	212
27	455316.5	4058445.6	Lake	Long.	36.0	51.40	195
28	455717.5	4059365.0	Lake	Long.	38.7	53.90	191
29	456272.4	4058563.5	Lake	Long.	39.0	54.80	165
30A	457451.2	4058178.1	Lake	Long.	41.5	56.10	190
30B	457451.2	4058178.1	Lake	Long.	41.5	56.10	143
31	458491.5	4053939.0	Lake	Long.	46.6	63.20	180
32	457205.5	4054947.5	Lake	Long.	44.5	60.90	150

Site	Easting	Northing	Туре	Location	Depth (m)	Distance (km)	Sample Mass <2mm (g)
33	456878.9	4056010.5	Lake	Long.	42.4	58.50	156
34	454639.6	4071138.4	Lake	Long.	4.4	8.40	-
35	454612.4	4071619.0	Lake	Long.	3.6	9.00	_
36	454588.1	4072358.9	Lake	Long.	6.2	9.70	297
37	454791.5	4072637.3	Lake	Long.	6.7	10.00	166
38	454551.1	4072935.6	Lake	Long.	6.2	10.50	-
39	454281.6	4072931.4	Lake	Long.	5.9	10.70	-
40	454053.9	4072607.6	Lake	Long.	6.0	11.10	-
41	470538.4	4115645.1	Stream	Bar	N/A	21.8	101
42	470515.8	4115654.6	Stream	FP	N/A	21.8	594
43	467131.8	4113625.8	Stream	Bar	N/A	15.1	158
44	467134.2	4113634.8	Stream	FP	N/A	15.1	399
45A	466623.9	4111240.0	Stream	Bar	N/A	11.7	490
45B	466623.9	4111240.0	Stream	Bar	N/A	11.7	417
46A	466818.2	4111260.9	Stream	FP	N/A	11.9	671
46B	466818.2	4111260.9	Stream	FP	N/A	11.9	591
47	464125.1	4108048.1	Stream	Bar	N/A	6.9	294
48	464118.5	4108051.4	Stream	FP	N/A	6.9	752
49	464410.5	4103852.6	Stream	Bar	N/A	1.5	511
50	464411.2	4103865.3	Stream	Bench	N/A	1.5	494
51A	510672.8	4122229.4	Stream	Bar	N/A	136.3	487
51B	510672.8	4122229.4	Stream	Bar	N/A	136.3	246
52A	510696.8	4122210.9	Stream	Bench	N/A	136.3	462
52B	510696.8	4122210.9	Stream	Bench	N/A	136.3	609
53	499784.7	4124012.5	Stream	Bar	N/A	122.2	376
54	499784.7	4124012.5	Stream	Bench	N/A	122.2	388
55	470605.7	4106618.3	Stream	Bar	N/A	74.2	817
56	470524.0	4106611.3	Stream	Bench	N/A	74.1	241
57	470587.1	4106623.6	Stream	Bar	N/A	74.2	325
58	481999.5	4111595.1	Stream	Bar	N/A	93.6	211
59	482351.9	4112135.8	Stream	Bench	N/A	94.3	249
60	473591.7	4105065.7	Stream	Bar	N/A	79.6	470
61	473607.5	4105068.9	Stream	Bench	N/A	79.6	461
62	466898.6	4103366.6	Stream	Bar	N/A	67.6	573
63	466898.6	4103366.6	Stream	Bench	N/A	67.6	235

Site	Easting	Northing	Туре	Location	Depth (m)	Distance (km)	Sample Mass <2mm (g)
64	467245.9	4094183.8	Stream	Bar	N/A	51.4	780
65	467236.8	4094133.4	Stream	Bench	N/A	51.4	342
66	467182.7	4094357.2	Stream	FP	N/A	51.6	366
67A	465107.2	4100722.3	Stream	Bar	N/A	61.3	714
67B	465107.2	4100722.3	Stream	Bar	N/A	61.3	640
68A	465136.2	4100617.1	Stream	Bench	N/A	61.2	185
68B	465136.2	4100617.1	Stream	Bench	N/A	61.2	265
69	465658.1	4088124.8	Stream	Bar	N/A	41.9	534
70	465658.1	4088124.8	Stream	Bench	N/A	41.9	356
71	463909.4	4082646.1	Stream	Bar	N/A	31.8	650
72	463968.4	4082695.5	Stream	Bench	N/A	31.8	332
73	463891.4	4082675.1	Stream	FP	N/A	31.8	416
74	460000.3	4076265.2	Stream	Bar	N/A	15.6	657
75	459947.3	4076229.0	Stream	Bench	N/A	15.6	280
76	460147.4	4076352.6	Stream	FP	N/A	15.4	284
77	473621.0	4105051.4	Stream	Tops	N/A	79.6	185
78	466898.6	4103366.6	Stream	Tops	N/A	67.6	156
79	499769.2	4124033.8	Stream	Tops	N/A	122.2	134
80	454158.4	4072116.2	Lake	Lateral	0.3	11.6	761
81	454118.8	4072101.3	Lake	Lateral	1.2	11.6	372
82	454093.6	4072096.5	Lake	Lateral	0.8	11.6	418
83	454074.0	4072095.7	Lake	Lateral	2.7	11.6	288
84	454050.2	4072093.6	Lake	Lateral	4.7	11.6	319
85	454020.4	4072088.6	Lake	Lateral	3.5	11.6	-
86	454016.0	4072075.4	Lake	Lateral	3.1	11.6	-
87	453992.0	4072073.6	Lake	Lateral	2.5	11.6	-
88	453988.3	4072083.5	Lake	Lateral	2.5	11.6	-
89	453971.1	4072083.0	Lake	Lateral	3.2	11.6	286
90	453951.2	4072090.7	Lake	Lateral	1.4	11.6	-
91	453954.0	4072087.9	Lake	Lateral	1.9	11.6	-
92	454347.2	4071528.1	Lake	Lateral	1.5	12.60	-
93	454326.3	4071523.3	Lake	Lateral	1.8	12.60	368
94	454276.2	4071507.4	Lake	Lateral	1.0	12.60	423
95	454223.4	4071472.4	Lake	Lateral	1.8	12.60	342
96	454197.3	4071475.4	Lake	Lateral	2.8	12.60	445

Site	Easting	Northing	Туре	Location	Depth (m)	Distance (km)	Sample Mass <2mm (g)
97	455809.2	4067788.7	Lake	Lateral	2.1	17.70	<u> </u>
98	455802.8	4067793.6	Lake	Lateral	4.9	17.70	310
99	455793.2	4067810.1	Lake	Lateral	8.2	17.70	325
100	455781.3	4067831.5	Lake	Lateral	8.4	17.70	283
101	455761.9	4067861.2	Lake	Lateral	6.5	17.70	376
102	455738.4	4067883.6	Lake	Lateral	4.6	17.70	342
103	455688.8	4067898.9	Lake	Lateral	2.7	17.70	392
104	455678.3	4067925.0	Lake	Lateral	1.6	17.70	419
105A	455667.2	4067947.9	Lake	Lateral	0.7	17.70	260
105B	455680.4	4067951.4	Lake	Lateral	0.8	17.70	480
106	455662.9	4067974.7	Lake	Lateral	0.4	17.70	282
107	455659.8	4067991.9	Lake	Lateral	0.2	17.70	538
108	455628.2	4065130.6	Lake	Lateral	2.7	22.20	-
109	455616.5	4065121.4	Lake	Lateral	5.5	22.20	-
110A	455573.9	4065101.9	Lake	Lateral	7.0	22.20	312
110B	455580.1	4065092.6	Lake	Lateral	7.1	22.20	346
111	455522.6	4065077.1	Lake	Lateral	7.8	22.20	263
112	455501.3	4065064.4	Lake	Lateral	8.0	22.20	304
113	455452.6	4065069.0	Lake	Lateral	8.3	22.20	355
114	455403.7	4065039.3	Lake	Lateral	7.2	22.20	-
115	455380.3	4065044.0	Lake	Lateral	6.5	22.20	-
116	455355.1	4065032.0	Lake	Lateral	9.6	22.20	313
117	455321.9	4065041.1	Lake	Lateral	10.7	22.20	332
118	455284.9	4065034.1	Lake	Lateral	11.1	22.20	341
119	452057.8	4063767.8	Lake	Lateral	7.0	30.70	-
120	452061.3	4063768.4	Lake	Lateral	9.8	30.70	-
121	452070.0	4063769.3	Lake	Lateral	14.1	30.70	-
122	452073.8	4063775.6	Lake	Lateral	15.5	30.70	292
123	452094.2	4063783.2	Lake	Lateral	18.3	30.70	155
124	452112.5	4063799.8	Lake	Lateral	18.7	30.70	192
125	452158.0	4063814.4	Lake	Lateral	18.3	30.70	193
126	452179.8	4063815.7	Lake	Lateral	14.3	30.70	247
127	452212.4	4063823.9	Lake	Lateral	10.8	30.70	325
128	452239.7	4063829.0	Lake	Lateral	8.6	30.70	377
129	452268.4	4063833.0	Lake	Lateral	6.3	30.70	465

<b>5:4</b> 0	Facting	Nouthing	Turno	Lagation	Don'th (m)	Dictorios (lem)	Sample Mass <2mm
Site	Easting	Northing	Type	Location	Depth (m)	Distance (km)	(g)
130	452306.7	4063842.4 4063833.9	Lake	Lateral	2.9	30.70	-
131	452284.3 452273.4	4063836.8	Lake	Lateral	4.8 5.7	30.70	-
132			Lake	Lateral		30.70	200
133	452254.8	4063824.8	Lake	Lateral	7.6	30.70	388
134	452133.8	4063800.0	Lake	Lateral	17.8	30.70	216
135	452082.3	4058406.2	Lake	Lateral	2.8	40.60	-
136	452061.3	4058412.9	Lake	Lateral	7.0	40.60	-
137A	452032.8	4058426.0	Lake	Lateral	11.9	40.60	380
137B	452000.0	4058482.1	Lake	Lateral	14.0	40.60	64
138	451986.5	4058449.7	Lake	Lateral	13.6	40.60	119
139	451950.9	4058462.2	Lake	Lateral	16.6	40.60	200
140	451901.2	4058485.9	Lake	Lateral	18.4	40.60	226
141	451871.4	4058505.9	Lake	Lateral	18.6	40.60	199
142	451832.5	4058523.1	Lake	Lateral	19.9	40.60	156
143	451813.1	4058533.9	Lake	Lateral	25.2	40.60	189
144	451774.4	4058560.3	Lake	Lateral	27.5	40.60	165
145	451727.6	4058577.1	Lake	Lateral	23.3	40.60	158
146	451683.4	4058595.1	Lake	Lateral	14.3	40.60	-
147	451695.8	4058595.1	Lake	Lateral	20.5	40.60	165
148	452021.9	4058452.9	Lake	Lateral	11.6	40.60	-
149	452004.7	4058472.7	Lake	Lateral	13.0	40.60	-
150	457267.0	4055218.8	Lake	Lateral	9.8	60.90	-
151	457256.3	4055207.7	Lake	Lateral	17.9	60.90	-
152	457238.3	4055190.6	Lake	Lateral	28.3	60.90	-
153	457250.2	4055145.1	Lake	Lateral	36.3	60.90	137
154	457222.8	4055090.1	Lake	Lateral	35.7	60.90	139
155	457226.4	4055018.7	Lake	Lateral	35.4	60.90	146
156	457237.3	4054973.9	Lake	Lateral	41.5	60.90	149
157	457250.2	4054938.8	Lake	Lateral	44.2	60.90	162
158	457224.0	4054885.0	Lake	Lateral	39.6	60.90	148
159	457228.3	4054805.0	Lake	Lateral	34.4	60.90	149
160	457201.9	4054713.0	Lake	Lateral	33.5	60.90	189
161A	457204.2	4054650.4	Lake	Lateral	27.1	60.90	165
161B	457182.5	4054692.6	Lake	Lateral	32.9	60.90	150
162	457164.0	4054632.3	Lake	Lateral	18.5	60.90	-

Site	Easting	Northing	Туре	Location	Depth (m)	Distance (km)	Sample Mass <2mm (g)
163	457164.0	4054659.2	Lake	Lateral	27.5	60.90	-
164	457152.4	4054667.4	Lake	Lateral	27.5	60.90	-
165	454524.3	4067921.2	Lake	Flat	6.3	-	246
166	450698.4	4060324.0	Lake	Piney	14.6	-	165
167	458279.1	4057686.7	Lake	Aunt's	26.2	-	144

## Appendix B. Sediment Characteristics and Geochemistry

### APPENDIX C

## FREDERICK (2001) – SUMMARIZED SEDIMENT DATA

### APPENDIX D

## OWEN (2003) – SUMMARIZED SEDIMENT DATA

### APPENDIX E

# RODGERS (2005) – SUMMARIZED SEDIMENT CHARACTERISTICS AND GEOCHEMISTRY